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Silicon nitride – a promising candidate for the bioactive composite implants

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Keywords: biomaterial, bioinert, bioactive, silicon nitride

Silicon nitride-based ceramics are characterized especially by high chemical resistance, superior combination of fracture toughness, hardness, and thermal shock and wear resistance. Recently also silicon nitride attracts interest for bio-applications in the human body as bio inert material. Silicon nitride based biomaterials have a potential to be used as total hip-joint replacements, mini-osteofixation systems, multiwall drug-release devices, intervertebral spacers and spinal surgery or implantations in otorhinolaryngology and traumatology. However, the biological applications often require additional properties, e.g. bioactivity enabling stronger bonding to the host tissue and moreover ceramic bio-implants are of different size, shape or form with foreseen mechanical, physical or chemical properties. In this work porous or dense silicon nitride based substrate in the form of bulk or granules/microspheres were prepared and subsequently covered by the hydroxyapatite/calcium phosphate phase thin layer in order to change the substrate from bio-inert to bio-active. Four different silicon nitride based bio-active materials will be presented with the aim to show a potential of silicon nitride in bio applications:

1. Porous silicon nitride with bone-like pore structure prepared by replica method and
2. porous spheres of size about one millimeter (or more) on average prepared by water silicon nitride suspension by freeze drying. Silicon nitride–hydroxyapatite composites were prepared by infiltration of hydroxyapatite precursor sol into the silicon nitride based porous ceramics (porosity up 80%). Cytotoxicity and *in vitro* bioactivity of Si_3N_4–HA composites were tested in order to verify the effect of hydroxyapatite addition on the biological properties of composite. After immersion of porous composite into simulated body fluid (SBF) for 21 days, calcium phosphate (CP) layer was formed on the surface of silicon nitride–hydroxyapatite composites, indicating their bioactivity.
3. Surface modification of dense silicon nitride body using an oxyacetylene torch at high temperatures and the formation of a thin (2–5 µm) and porous bioactive layer based on the grain boundary composition with chemical adhesion to substrate.
4. Porous silicon nitride microspheres of size about 10–100 µm prepared by flame synthesis.

The formation of thin layer utilizing of high temperature oxidation of dense silicon nitride with different grain boundary phase (SiO_2 or $Ca_3(PO_4)_2$) by oxyacetylene torch was studied. After short dwell time (30–60 sec.) at high temperature (aprox. 1480–1500 °C) two processes were started – formation of a thin layer of glassy phase on the surface and decomposition of silicon nitride (acting as a pore forming agent). This method of surface modification seems to be a promising route for the bio-active layer formation. Finally, porous silicon nitride microspheres with different ratio of $S_3N_4/Ca_3(PO_4)_2$ within starting mixture were prepared by flame synthesis method. The influence of feed rate on the size distribution and porosity of microspheres were studied.

Multiscale integration challenges in alternative and renewable energy systems

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It is estimated that globally 10 terawatts of power will be needed (equivalent to an additional 150 million barrels of oil) per day by 2050. Future energy production and distribution must be sustainable, environmentally conscious, and less reliant on conventional fossil fuels that are associated with a massive carbon footprint. Advanced ceramic materials and multiscale ceramic integration technologies will dramatically impact the energy and environment landscape due to their wide scale applications in all aspects of alternative and renewable energy production, storage, distribution, conservation, and efficiency. Examples include fuel cells, thermoelectrics, gas turbine systems, distribution and transmission systems based on superconductors, nuclear power generation, NOx and COx reduction technologies, and a wide variety of green and energy efficient manufacturing processes and technologies. Affordable and reliable solar energy technologies could play key role in sustainable development around the globe without major impact on environment since solar power is a clean, renewable, and sustainable energy source. However, revolutionary approaches for thermal energy storage (TES) system at elevated temperatures (>700 °C) for concentrated solar power (CSP) are needed for reliable energy supply. Integration technologies are key to making these systems a reality. The development of robust and reliable integrated systems with optimum performance requires the understanding of many thermochemical and thermomechanical factors, particularly for high temperature applications. In this presentation, various challenges and opportunities in design, fabrication, and testing of integrated systems will be discussed. Specific examples will be given for integration of fuel cell systems, thermal management, and thermal energy storage devices. Potential opportunities and need for the development of innovative design philosophies, approaches, and integrated system testing under simulated conditions will also be discussed.

T01: New developments in processing and synthesis with a special focus on additive manufacturing

Invited lectures

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Development of ceramic parts for semiconductor manufacturing equipment using additive manufacturing

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Keywords: additive manufacturing, powder layer manufacturing, ceramics, reaction bonded SiC, semiconductor manufacturing equipment

TOTO has been producing a variety of ceramic parts for semiconductor manufacturing equipment such as stepper and plasma etcher, as well electrostatics chucks (ESC), plasma-resistance Y_2O_3 film by aerosol deposition method, slip-casted large size alumina parts, low thermal expansion ceramics (cordierite) and high rigidity ceramics (reaction bonded SiC). We are also investigating joining and additive manufacturing technologies of reaction bonded SiC to make complex shape and large size ceramic parts for semiconductor manufacturing equipment.

Particularly we have been developing the additive manufacturing technologies in "High-Value Added Ceramic Products Manufacturing Technologies" project[1], which has been conducted since 2014 as a part of Strategic Innovation Promotion Program under the sponsorship of the Japanese government. In this project, three kinds of additive manufacturing technologies, powder layer manufacturing (powder bed fusion, or indirect selective laser sintering), slurry layer manufacturing (stereolithography) and ceramic laser sintering (direct selective laser sintering), are investigated.

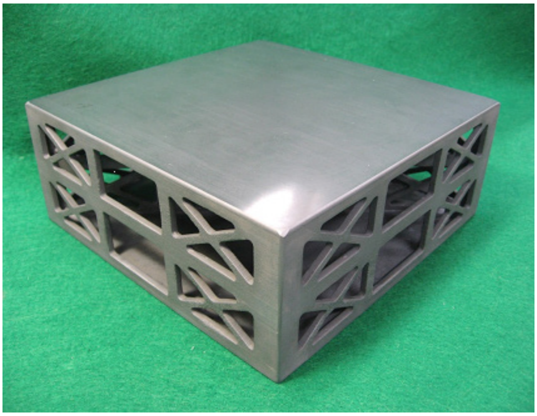

Fig. 1. Truss structure stage model

We have developed the powder layer manufacturing technology for producing a reaction bonded SiC parts which has excellent mechanical properties, furthermore having a complex shape and large size. The reaction bonded SiC parts produced by this technology show almost the same mechanical properties as conventional forming method such as slip-casting, having Young's modulus of 340 GPa and flexural strength of 290 MPa. Fig. 1 shows the truss structure stage model with the width of 20 cm, the length of 20 cm and the height of 8 cm, which has been made by this technology. This paper will introduce these latest research achievements.

Acknowledgement
This work was conducted as a part of "High-value added ceramic products manufacturing technologies project" supported by CSTI, SIP, "Innovative design/manufacturing technologies (managed by NEDO)".

Reference

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Anisotropic hierarchical porosity ceramic electrodes for high performance Li-ion batteries

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Porous electrodes are critically important for high performance Li-ion batteries. This application demands optimization of a multitude of properties, which have conflicting requirements on the microstructure. Using available models for the effect of the porous microstructure on the important battery performance characteristics, it will be shown the electrodes with designed anisotropic and hierarchical microstructures have the potential to optimally address the different performance requirements.

Results will be presented on two processing approaches to make these designed microstructures. Both tape cast and partially sintered bulk electrodes have been investigated. With the developed processing protocols, it will be shown that it is possible to independently control several relevant microstructural parameters. The 3D microstructure has been characterized at relevant length scales and these results will be presented. The electrochemical performance of the designed porous electrodes will be compared to that of the uniformly porous isotropic electrodes. It will be shown that, compared to uniform porosity electrodes, due to reduced tortuosity leading to deeper electrolyte access, thick electrodes can be made. These electrodes demonstrate high energy density and without significant capacity fade at higher charge/discharge rate.

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Additive Manufacturing with inorganic polymers: an alternative to the powder-binder approach

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Very few commercially available AM systems are suited for ceramic materials, and most of them use ceramic powders as feedstock; AM technologies employing polymers are at a much more advanced stage of development. We tried to exploit such advances and to provide alternatives to the ceramic powder-binder approach.

Preceramic polymers (e.g. silicones) convert into nanostructured Si-based ceramic materials by high temperature pyrolysis; we employed them as a non-sacrificial, reactive binder to develop inks for stereolithography and direct ink writing. We were able to fabricate porous structures of advanced silicate ceramic phases, including bioceramics, starting from preceramic polymers and (reactive) fillers. We also produced ceramic matrix composites (CMCs) embedding fibers in the preceramic polymer matrix.

Geopolymers are inorganic 3D networks usually obtained through reaction of aluminosilicate powders in a silicate alkaline solution. They consolidate at low or even room temperature, show intrinsic micro- and meso-porosity, good mechanical properties, chemical durability and high temperature stability.

We explored direct ink writing of highly porous lattices using a geopolymeric binder for different potential applications. As the material in the inks consolidates with time forming a continuous inorganic network, time becomes the 4th dimension in printing. It is therefore necessary to control the characteristics of the system to allow for a suitable time window for the process.

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Porous ceramic foams and nanofibers

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Creation of porous ceramics has been an objective of much research for decades. The pore architecture within the material is of key importance to specific applications such as catalysis, filtration, adsorption and thermal insulation. This talk will concentrate on the mechanism of pore formation driven by *in-situ* chemical transformations within two different systems.

On the one hand, the formation of ultralight bulk ceramics using a non-hydrolytic sol-gel foaming process will be described. The unique foaming mechanism involves simultaneous phase separation, gelation and drying, giving rise to ultralight foams with a porosity that can exceed 99%. The work has been demonstrated on alumina and alumino-silicate ceramics, and is currently used commercially in India.

On the other hand, sub-micron fibers are of great interest for heterogeneous catalysis, electrodes and adsorbents. The large pores between the fibers facilitates superior transport properties between the fiber surface and the bulk. Furthermore, the presence of open and accessible nano porosity within the nanofibers increase the active surface, potentially improving the material performance. In catalysis applications lower deactivation rates are expected due to confinement of the catalytic moieties. This part of the talk will focus the pore formation in Fe-Al-O ceramic nano fibers with core-shell architecture.

Both examples will demonstrate how internal chemical transformation can be harnessed to generate controlled porosity in functional ceramics.

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Processing of porous ceramic structures for efficient mass transport

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Ability to manufacture ceramic structures with efficient porosity and at the same time, sufficient mechanical robustness is important for a broad range of applications, such as; catalyst supports, filters, fuel cells, electrolysis electrodes, membrane reactors, CO_2 capture and flue gas purification.

The use of sacrificial pore formers, one of the most commonly used methods to generate porous ceramic structures, delivers structures with random and inefficient porosity. Therefore, alternative processing routes capable of delivering effective porosity are under high demand.

Three approaches capable of accomplishing high mass transport ceramic structures will be discussed: use of non-combustible pore formers, use of ice templating (freeze casting) and additive manufacturing. Non-combustible pore former route is based on porosity formation after final sintering step via reduction or mild leaching and results in a highly-interconnected porosity. Ice templating route is based on porosity creation through generation and sublimation of ice crystals and is capable of generating ceramic scaffolds with desired pore size and orientation. Additive manufacturing technique is based on generation of complex large scale ceramic bodies with programmed porosity channels. All these approaches proved to deliver so called efficient porosity at different scales. Both ice templating and additive manufacturing routes can be further tuned to generate structures with hierarchical porosity distribution.

The talk will be illustrated with some practical examples, where the challenges related to fabrication of desired microstructures via these approaches will be presented.

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Advanced manufacturing of porous ceramic structures for use in energy applications

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Keywords: porous ceramics, multilayer, membrane, gas separation

Tailored porous ceramic materials and structures are utilized in energy devices at DTU Energy, including electrochemical converters, membranes, adsorbents for gas separation and storage and catalyst supports. These materials can contain pore sizes from the nanometers to several millimeter, and can have oriented to random porosity or hierarchical porosity based on various pore architectures. Ceramic structures with tailored porosity can be processed by a variety of traditional or advanced shaping methods (phase inversion tape casting, templating, freeze casting, electrospinning, etc.).

Often, some additional challenges need to be addressed if porous support or catalysts layers with tailored porosity need to be integrated into asymmetric multilayer gas separation devices to achieve high performance.

For the fabrication of oxygen transport membranes (OTM)[1] or solid oxide fuel cells (SOFC), the shaping, multi-layering and co-firing of porous support structures in ceramic multilayer devices will be presented, which include the use of sacrificial templates (pore former) in extrusion[2,3] or phase inversion tape casting[4]. The correlation between the fabrication, the microstructure of the porous support structures and key performance parameters, such as gas transport, mechanical properties, thermal stability or electrical conductivity in the final ceramic multilayer structures and devices will be shown. Finally, a brief outlook on recently started R&D activities with highly porous ceramic structures will be presented, including novel concepts for the structuring of adsorbents in gas separation and storage.

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Suspension plasma spraying: the meeting point for ceramic processing and plasma spraying technique

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Keywords: suspension plasma spraying, suspensions stabilization, coatings characterisation

Plasma spraying represents a well-known deposition technique with numerous industrial applications in many diverse sectors such as aerospace, manufacturing, energy, biotechnology, etc. because of the flexibility of the technique in terms of the composition and nature of the feedstock used. Powders ready to be adequately sprayed have been traditionally employed in plasma spraying. However, in the last years the use of liquid feedstocks has started to gain the attention of scientific community owing to the simpler feedstock preparation as well as the possibility of obtaining enhanced properties in the final coatings. Thus, Suspension Plasma Spraying (SPS) or Solution Precursor Plasma Spraying (SPPS) have merged as alternative or complementary methods to the state-of-the-art technique known as Atmospheric Plasma Spaying (APS).

When a suspension instead of a powder is used as feedstock new challenges arise for the plasma spraying process. This is because the suspension has to be prepared, stored, pumped and finally, homogenously atomised into the plasma torch with the aim of producing coatings with the targeted microstructure and properties. Therefore, concepts such as colloidal stability, Z-potential, suspension stability, sedimentation, viscosity or suspension atomisation have necessarily to be taken into account when a SPS process is designed.

This work presents different examples of the whole suspension plasma spraying process, from suspension preparation to coating deposition, with the objective of showing the connection between the ceramic processing and the plasma spraying operation. SPS processes to obtain ceramic oxides coatings for wear-resistance applications (Al_2O_3-TiO_2), photocatalytic functionality (TiO_2) or thermal barriers (Y-TZP), and bioactive glasses for implants are described underlying the importance of the suspension preparation step on the performance of the process as well as on the microstructure and properties of the final coatings. The effect of the solid particle size (micro, submicro or nanometric size) and the solids content in the suspensions are also addressed. Finally, some insights on the new challenges and future possibilities of the SPS technique are given.

Acknowledgement
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New aluminosilicate nanoaggregates synthesis from low-temperature geopolymerization processes

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Nanoaggregates, such as carbon black and precipitated silica, have been one of the most important classes of nanofiller materials in modern technologies. We report development of new nanoaggregate materials with aluminosilicate compositions and their scalable high-yield production methodologies based on low-temperature geopolymerization process. Unlike the acid-base reaction process for known amorphous aluminosilicates, the geopolymerization process allows products that have tetrahedral aluminosilicate network structures with negative surface charges, and are highly stable in water and in alkaline conditions. By simply modifying the precursor compositions and reaction conditions, the new materials can be controlled to have high surface area, high porosity, high structure, high aspect ratio, different crystal structures, crystallinity, or microporosity. Usefulness of the new materials in large-scale applications is illustrated in rubber-composites, antimicrobials, catalysis and CO_2 separation.

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4D-printed hydrogel-based composite structures by additive processing

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Keywords: additive processes, 4D printing, hydrogels, bio-mimicking

Hydrogels are materials consisting of a permanent, three-dimensional network of hydrophilic polymers and water filling the space between the polymer chains with applications in diverse fields ranging from bio-medical applications and stimuli sensitive systems for agricultural, personal care, environmental, and industrial applications. We have used multidisciplinary approach and advances in programmable materials assembly to create transformable architectures. Using microscale 3D printing technology and fourth time dimensional parameter by environmental response, we have developed 4D-printed hydrogel composite structures. Although, the investigation is in its preliminary stages, we anticipate using meta-materials to detect and capture organic materials, volatile organic compounds and an extension of our work on capturing pharmaceuticals. Since, hydrogel composites contain cellulose fibrils derived from wood, response to environment is likely to produce bio-mimicking to external stimuli.

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Composite ceramic nanostructures for high-efficiency sunlight conversion

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In several types of excitonic solar cells, nanomaterials can play a critical role in boosting photoconversion efficiency by ameliorating the processes of charge photogeneration, exciton dissociation and charge transport. Several strategies can be pursued, including broadening of light absorbance to reduce solar light losses, fastening exciton dissociation and charge injection from the photoactive medium to the charge transporting materials, reducing charge recombination during charge transport and collection at the electrodes. In this lecture, a few examples of application of ceramic composites will be thoroughly discussed in two specific categories of excitonic solar cells, namely dye- and quantum dot-sensitized solar cells. Emphasis will be given to the investigation of both the photoactive medium (including composite and core-shell quantum dots) and the charge transporting scaffold (including metal oxide hierarchical structures, nanowires, nanorods and carbon-based hybrids) towards a materials-by-design approach.

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LSD-3D printing: a novel technology for the Additive Manufacturing of ceramics

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Keywords: 3D printing, Additive Manufacturing, layer-wise slurry deposition

The layer-wise slurry deposition (LSD) is an innovative process for the deposition of powder layers with a high packing density for Additive Manufacturing (AM). A slurry with small organic content is repetitively spread as thin layers on top of each other by means of a doctor blade. During the deposition, the ceramic particles settle to form thin layers with a high packing density (55%–60%). Each layer is then dried, resulting in the stacking of a dry powder bed with high powder packing. When coupled with a printing head or with a laser source, the LSD enables novel AM technologies inspired to the 3D printing or selective laser sintering, but taking advantage of having a highly dense powder bed.

The LSD-3D printing, in particular, offers the potential of producing large (>100 mm) and high quality ceramic parts, with microstructure and properties similar to traditional processing.

This presentation will give an overview of the milestones in the development of this technology, with focus on the latest results applied both to silicate and to technical ceramics.

Oral presentations

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Light weight metallic additive effect on ballistic performance of spark plasma sintered B_4C

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Keywords: boron carbide, ballistic performance, spark plasma sintering, fracture toughness

Boron carbide powders with different amounts of light weight metallic (Al and Si) additives are spark plasma sintered in order to examine the ballistic effects of these additives on boron carbide. As widely known, boron is a good candidate for body armours. Without increasing the weight, the mentioned additions were made to improve main drawback of boron carbide which is low fracture toughness. The final products having 61 mm diagonal, 10 mm height, and 31 mm length have been produced by spark plasma sintering in the temperature range between 1400–1550 °C for 4 minutes, under an applied pressure of 40 MPa. After spark plasma sintering procedure, the densification of composites were measured by Archimedes method whereas the hardness and fracture toughness of boron carbide composites were measured by Vickers indentation technique. The crack propagation behaviour of ceramics were observed by using Scanning Electron Microscopy.

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Additive manufacturing of Ti-B_4C composites by 4M technology

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Keywords: additive manufacturing, boron carbide, titanium, composites

Titanium Matrix Composites (TMCs) containing various volume fractions of boron carbide particles have been deposited onto Ti Gd2.0 substrates from powder feedstock mixtures using a Machine for Multi-Material-Manufacturing (“4M-System”) developed by RHP-Technology GmbH. In this process plasma transfer arc (PTA) is used as a heat source for *in-situ* reaction between Ti and B_4C particles, which allows the formation of TiB and TiC phases during the deposition. Additive layer manufacturing by using the “4M” system offers the production of large and complex 3D components on one side and gradient structures or multi-material concepts on the other side.

Various processing parameters such as deposition rate, travel speed of the torch as well as plasma parameters (power/current/gas flow) have been investigated in order to obtain pore- and crack-free B_4C reinforced titanium composites.

As deposited specimens were cut and the cross sections were analysed by optical- and scanning electron microscopy. Mechanical properties of such as hardness, tensile strength and Young's modulus were assessed.

Fully dense and crack free Ti specimens with 10 vol. % of B_4C were obtained by additive manufacturing with the optimized deposition parameters. In comparison to the pure titanium grade 1.0 the Ti with 10 vol.% B_4C test samples show higher Young's modulus (150 GPa against 103 GPa of the pure Ti[1]) as well as higher hardness values (374 ± 28 HV) and tensile strength (572 ± 49 MPa). However, the total strain at break is very low showing ceramic like behaviour. Further increase of the B_4C content up to 30 vol. % led to the cracking of manufactured specimens.

Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No [673817].

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Functional refractory molds for metal casting built by additive manufacturing

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Keywords: casting mold, additive manufacturing, alumina, selective laser melting (SLM), rapid prototyping

Additive manufacturing is more and more used in the field of industry. This technique is notably employed in investment casting process in order to build cores and models. Nevertheless investment casting remains not cost effective in case of prototypes and very small series due to the quite large amount time needed to build and dry the molds.

Additive manufacturing may also be used to directly shape metal parts but several problems are still linked to this technique as the presence of local defects in parts and the limitation of the number of metal or alloy available for this technique on the market.

We propose an intermediate method that permits to build directly molds and cores by additive manufacturing using equipment initially dedicated to build metal parts. This method presents the main advantage to cast with a large variety of metals or alloys using a single ceramic material and only one set of building conditions. The properties of the casted parts are very similar with those produced by investment casting.

This technique also permits the unique advantage to control the design of the shell thickness and structure in order to have a better control of the thermal fluxes during metal cooling. This would potentially ensure a better control of some casting defects.

The use of alumina processed by selective laser melting (SLM) is shown and its outstanding resistance to temperature differential is demonstrated through casting trials with two different representative alloys. Casting trials in industrial conditions will be illustrated.

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Flame spray synthesis of YAG:Ce nanoparticles

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Keywords: YAG, Ce, flame spray synthesis, photoluminescence, quantum yield

Yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) doped with cerium is a material widely applied as a phosphor for blue-to-white light conversion. Over the last decade, various methods for the synthesis of nanometric phosphor powders have been intensively studied because their small particle size and weak scattering of light are very attractive for applications in imaging and lighting. In this context, the preparation of submicrometric YAG:Ce particles with high quantum yield (QY) is the main focus of this work. Nanoparticles with different concentrations of cerium were prepared by Liquid-Feed Flame Spray Synthesis. Evolution of the crystalline phase, particle size and specific surface area (SSA) with increasing the thermal post-treatment temperature were investigated by X-ray diffraction, Transmission Electron Microscopy and N_2 sorption-desorption, respectively. At $T \geq 900$ °C, cubic-YAG phase is obtained together with an increase of the particle size and a decrease of the SSA. The maximal QY of 72% was obtained for particles containing 0.1 mol% cerium calcined at 1100 °C/1 h resulting in the average particle size of 01–02 µm.

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Synthesis of Ce-TZP – Al_2O_3 for dental applications – shaping by stereolithography

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Keywords: composite, stereolithography, stabilized zirconia

Often opposing to the subtractive manufacturing, additive manufacturing (AM) technologies, such as stereolithography (SLA), have the potential to produce, within a short time, unique, accurate and dense objects, while limiting the loss of matter. SLA is a layered manufacturing process based on the polymerization of an UV photocurable system (PS) composed of an UV sensitive resin highly loaded with ceramic particles (>45%vol). This process is based on the focussing of an UV light by digital projector screen on the system to cross-link the complex shape components layer by layer. After manufacturing, components are cleaned to remove the uncured PS, then debinded and sintered to obtain dense parts by a heat treatment. The parameters for manufacturing (cross-link time, layer thickness) and related to the thermal process are highly dependent on the PS.

The SLA known to enable the development of near-net shape components is well suitable for dental field. In this technical area, Yttria-doped tetragonal zirconia polycrystal (Y-TZP) is one of the most used material, and has been chosen as reference material. But, due to a poor behaviour to hydrothermal degradation (HD) other materials have been considered such as Ceria-doped tetragonal zirconia polycrystal (Ce-TZP). However, Ce-TZP shows lowest flexural strength values.[1] To obtain a material with high mechanical properties such as Y-TZP and with excellent durability to HD, alumina is added to Ce-TZP to create Ce-TZP – Al_2O_3 composites. Such composites, according to their properties, seem to be better candidates in the dental field.[2,3] Investigations related to composite synthesis routes, phase distributions and thermal treatments have been completed before adding this new ceramic system in the photosensitive resin.

Parts manufactured by SLA performed from a Y-TZP based UV sensitive resin and mechanical characterisations will be presented as well as the Pechini and sol-gel routes to synthesis Ce-TZP-Al_2O_3 powder, new filler in a PS.

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Synthesis, characterisation and properties of perovskite ceramics prepared by electric discharge assisted mechanical milling

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Keywords: Perovskite ceramics, electro-mechano-chemistry

Many functional materials are traditionally synthesized by slow reaction processes that are energy and time consuming. In the present world there is strong demand on development of modern materials and materials processing methods that could offer rapid reaction rates, energy efficiency and be environmentally safe.

Perovskite oxide ceramics have found wide applications in energy storage capacitors, electromechanical transducers and piezoelectric, and ferroelectric devices.

The conventional method to prepare Perovskite oxide ceramics is ceramic-powder-based processing, i.e., through solid-state reaction at high temperatures. This process has several disadvantages, such as high-temperature reaction, limited degree of chemical homogeneity, and low sintering ability. Therefore, during past years, several chemical-based processing routes, including freeze-drying, spray-pyrolysis, sol–gel, spray-drying, and pyrolysis of complex compounds, have been developed to prepare powders with more homogeneous composition, improved reactivity, and sintering ability at low temperatures. Recently, non-conventional processing methods such as mechanical alloying and mechano-chemical approaches have been used to create reactions between species. However in this method the reaction kinetics is very slow and processing time long.

The objective of the present study is to investigate the application of an Electric Discharge Assisted Mechanical Milling (EDAMM)[1] technique to synthesize various Perovskite oxide ceramics, in particular formation of nano-phases and characterize the structural, physical, and optical properties.

By using EDAMM, high purity single phase multi-element oxides can be formed in as little as 0.1% of the processing time required in conventional solid-state techniques. An even more important feature of EDAMM is that the crystallite size of the synthesized compound is able to be reduced to nanometer size, by careful selection of electrical (voltage, current, total power) and mechanical (vibration frequency and amplitude) experimental parameters.

We use EDAMM for (i) synthesis of oxides from elemental powders by oxidation in oxygen plasma and for (ii) synthesis of single phase multi element oxides from pre-mixed oxides as starting materials.

This presentation provides an overview of recent development of EDAMM method and its application in rapid synthesis of Perovskite ABO3 type oxide ceramics such as BaHfO3, BaTiO3, MnTiO3, PbZrO3 and others.

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Hydration layer: a potential key to manage colloidal processing of oxide nanopowder suspensions

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Keywords: hydration of oxides, colloidal processing of oxide nanopowders, rheology

The majority of ceramic processing techniques relies on the successful slurry preparation that ensures homogeneous distribution of powders in a highly loaded slurry with manageable flow characteristics. Only with effective slurry formulation, crack- and pore- free structures can ultimately be manufactured. However, this still remain a challenging issue for advancing technology of additive manufacturing. The available models to predict the colloidal properties of nanopowder slurries therefore require improvements. This presentation will show the presence and importance of hydration layer around oxide nanopowders that has been overlooked till very recently. Then, the influence of the hydration layer on the colloidal properties of oxide nanopowder slurries has been discussed. When the Krieger-Dougherty relation is modified according to the presence of hydration layer, the viscosity of suspensions can be successfully estimated. The resultant improvement in green body quality achieved is also demonstrated.

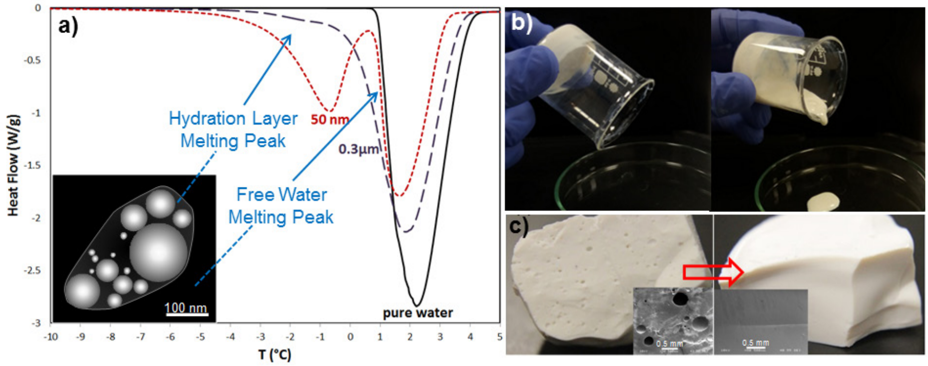

Fig. 1. DSC thermogram of water exhibits a secondary melting peak in the presence of oxide nanopowders (a).[1,2] Direct imaging of alumina nanopowders in an aqueous environment using fluid cell STEM proved the presence of hydration layer around powders (a-inset).[3] Control over the hydration and electrical double layers of oxide powders enabled to reduce the viscosity of suspension (b), and lead to the pore-free green bodies with finer surface finish (c).[4] Figure a, a-inset and c are adapted from references 1, 3 and 4, respectively

Acknowledgment

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Highly porous B-doped hardystonite bioceramics from preceramic polymers and engineered fillers: from foams to 3D-printed scaffolds

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Keywords: hardystonite bioceramics, polymer-derivedsilicates, scaffolds, direct ink writing

Highly porous hardystonite-based bioceramics, in the form of foams and 3D scaffolds, were obtained by thermal treatment in air (at 950 °C) of silicone resins and micro-sized oxide fillers. Besides CaO and ZnO precursors ($CaCO_3$ and ZnO powders), calcium borate, in both hydrated and anhydrous form ($Ca_2B_6O_{11}\cdot 5H_2O$ and $Ca_2B_6O_{11}$, respectively) was added to commercially available silicone resins. This latter addition had a significant impact on the microstructural evolution of the bioceramics. In its hydrated form, calcium borate led to a substantial foaming of silicone-based mixtures at low temperature (420 °C); after dehydration, upon firing, the salt provided a liquid phase, favouring the development of novel B-contaning hardystonite-based solid solutions ($Ca_2Zn_{1-x}B_{2x}Si_{2-x}O_7$). This role in the phase evolution upon firing was also maintained by the filler in anhydrous form, employed in formulations used for direct ink writing of scaffolds. The bioceramic foams and scaffolds exhibited remarkable mechanical properties (compressive strength exceeding 4 MPa, with a total porosity above 67%). Preliminary investigations concerning ceramics based on even more complex solid solutions ($(Ca,Sr)_2(Mg,Zn)_{1-x}B_{2x}Si_{2-x}O_7$), embedding also SrO and MgO, will be presented as well.

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Rheological properties of alumina formulations based on biosourced additives for micro-extrusion application

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Keywords: alumina paste, rheology, micro-extrusion, green chemistry, mechanical properties

Paste extrusion has been widely used in many forming processes of ceramics for different applications (biomedical, catalysts, electronic devices). However, the rheological behavior of these pastes remains largely unexplored. Most rheological properties of high concentrated paste extrusion are well described using typical empirical frameworks[1,2] and then needs further investigations to understand the impact of rheological properties on the green body obtained by extrusion process.

This study is part of a process of sustainable development of resources and is based on the respect of the principles of green chemistry. More particularly, the aim here is to quantify the impact of the amount of constituents of alumina pastes based on bio-sourced organic materials on their rheological behavior. Successful extrudability requires having rheological properties suited to the micro-extrusion process and conferring sufficient cohesion on the green bodies. Rheological characterization is necessary to get clearer understanding of the paste when the solid fraction is increased[3]. The nature of additives and their order of introduction into the mixture is also a major factor influencing the rheological behavior and consequently the paste extrudability. A feasibility study using an oscillatory experimental protocol was carried out and yielded promising results which allowed to link the nature of polymers, the amount of the constituents of the pastes with rheological properties. In addition, the effect of alumina paste's aging on the rheological properties was evaluated and discussed. It would seem that rheological behavior evolution is a major factor for prediction of the extrudability of the formulated pastes.

Finally, the mechanical properties of our pastes have been investigated to evaluate the hardness and estimate the mechanical resistance of the extruded material after consolidation with heat treatment.

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Osteoconductive ceramics of complex geometry fabricated by stereolithography

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Keywords: stereolithography, bioceramics, Kelvin structure, gyroid, permeability, calcium phosphates

The work tackles the issue of bioceramics with interconnected macropores with special architecture of pores space. Kelvin structure and gyroid, as a member of triply-periodic minimal surfaces family, were chosen to reach desirable permeability (up to 1000 Darcy) in order to reveal osteoconductivity. FEM-analysis of loading and simulation of fluid flow through the structure (SolidWorks 2013) facilitated making a choice. The above complex shapes were reproduced as phosphate ceramics scaffolds via DLP-stereolithography of light-curable slurries based on $Ca_3(PO_4)_2$ and $Ca_{3-x}M_{2x}(PO_4)_2$ ($x = 0 – 1$, M = Na, K) ceramic powders. Optimization of the process parameters as well as reaching high lateral resolution of printing (up to 30 μm) were underlined with the study of photosensitivity of the slurries and light scattering in them. To convert the as-printed scaffolds into the ceramics one, preserving their geometry, a special regime of thermal treatment allowing release of polymer with the rate lower than 0.1 wt.%/min was elaborated. Time-temperature profile of the regime was stated through the inspection of kinetics of polymer pyrolysis. Detailed study of densification and grain growth in the course of sintering of ceramic scaffolds made us possible to fabricate prototypes of bone implants (for small laboratory animals, cylinders with o.d. = 2–3 mm and height up to 6 mm) with overall porosity up to 80%, demonstrating compressive strength up to 12 MPa and fracture toughness up to 0.7 $MPa \cdot m^{1/2}$.

Acknowledgement

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Porous and dense materials using bioplastics as structurers in colloidal processing

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Keywords: hydroxyapatite, magnesium, nickel oxide, tape casting, electrospining, 3D printing, PLA

The aim of this work is to develop dense and porous films through the use of colloidal techniques, such as tape casting and electrospinning, for health and energy applications. These processing techniques required the use of a polymer as processing structurer or matrix. PLA (Poly-L-lactic acid or Poly-L, D-lactic acid) is the front runner in the emerging bioresources and bioplastics market with the best availability and the most attractive cost structure. The production of the aliphatic polyester from lactic acid, a naturally occurring acid and bulk produced food additive, is relatively straightforward. PLA base materials were developed with different inorganic loads which present diverse particles sizes such as $Ni(OH)_2$ (200 nm), Hydroxyapatite (3 µm) and Magnesium (30 µm). Differences on morphology and characteristics of those powders have a strong influence on the limit of the inorganic load, properties and applications of the processed materials.

PLA/Inorganic materials processing route is based on the homogeneous mixture of a suspension of inorganic particles with a solution of PLA, where aqueous suspensions of inorganic particles were prepared preserving the colloidal and chemical stability in terms of zeta potential and packing density, varying the pH and the concentration of a stabilizer agent. On the other hand, solution of PLA was optimized, and THF (tetrahydrofuran) resulted to be the best solvent to prepare a homogeneous solution. The final suspension of PLA and Inorganic particles served to obtain a feedstock to 3D printing, electrospinning and tape casting processes. Those techniques allow us to obtain different inorganic and hybrid films and pieces, as well as study the effect of the inorganic particle size in the processes. Finally, materials were thermal treated if needed, and characterized focus on their applications, implants and/or supercapacitors.

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Truly comprehensive solutions to produce ceramic parts with 3D printing

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3D printing lets users push back production limits. Ceramics are no exception to the rule, but until now, the use of this material was reserved to ceramics experts. To open up this technology to a wider spread of professionals 3DCeram is sharing its maker experience to propose truly comprehensive solutions, depending both on users' expertise and the type of production they need.

Thanks to its large platform and high resolution, CERAMAKER 3D printer is particularly suited to series production. High quality parts, made of 3DMix ceramic pastes developed by 3DCeram, get the same properties as those produced via traditional processes.

The company also offers a cleaning booth and furnaces to deliver a turnkey production line to its customers. Assistance and support service will ensure they acquire the necessary know-how to produce parts independently.

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Additive manufacturing of monolithic catalysts

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Keywords: additive manufacturing, catalysts, cordierite, silicon nitride, magnesia

Current manufacturing methods for catalysts are still in general 2D-based processes such as extrusion with limited design freedom which do not allow the implementation of existing considerations for the improvement of catalyst designs and performance. Due to recent developments in the area of additive manufacturing (AM), it is now possible to allow 3D design freedom and therefore enables the implementation of new design features to improve performance as well as lifetimes of catalysts.

This contribution discusses the manufacturing of 3D-printed catalysts using the lithography-based ceramic manufacturing (LCM) process to produce monolithic structures based on various ceramic materials such as alumina, cordierite, magnesia and silicon nitride. Using this lithographic printing process allows the fabrication of highly detailed structures with defined feature sizes down to 150 µm. Such catalysts provide a high surface to volume area and significantly reduce the pressure drop standard pellet type catalysts suffer from. Moreover, it was shown, that the mechanical properties of the printed ceramic materials are similar to/same as conventionally processed ceramics. First results indicate that the implementation of advanced monolith designs enable the increase of the performance of the catalyst while reducing the geometrical surface area of the construct, which means that the monoliths can be miniaturized and there is less active phase is required. Thus, it would be possible to decrease weight, size, and costs of the final catalyst. These findings underline the potential for a future use of 3D printed catalysts, especially in the field of launcher and satellite propulsion where a significant need for capable catalytic solutions exists.

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Manufacturing of cemented tungsten carbide by hybrid machining in green state

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Keywords: green machining, hybrid machining, hard material

Manufacturing of complex shapes of hard material/ceramics from dense bulk is carried out mainly by two process routes:

- hard machining through Computer Numerical Control (CNC) equipments; large areas can be machined with a high removal rate. Despite technological advances since recent years, this process remains considerably energy and time consuming. Beside, due to mechanical properties of hard materials/ceramics the wear of tools is very high.
- physico-chemical processes such as electro-erosion or laser beam machining; such processes are very selective, as a consequence these shaping routes are efficient to perform high resolution details but not for large areas.

Green machining of hard material/ceramics through CNC is an alternative to manufacture complex shape. However, the low mechanical properties of the green parts are not suitable with high aspect ratio details realised by CNC machining. The use of a laser beam to perform high resolution details is relevant in this case.

A combination of these two approaches in a hybrid process in green state: roughing by machining then finishing by laser beam erosion, in the subtractive multi-scale approach was recently carried out at BCRC.

Green machining WC-Co12% is performed by the hybrid approach from powder to dense complex 3D parts. A suitable additive was mixed with the ceramic powder to be machined by conventional milling tools and laser beam. With the processing route reported here, complex ceramic parts have been manufactured having a relative density up to 99%. The use of such manufactured parts is relevant for drill bit application.

Some examples will be detailed in a case study.

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Porous ceramic by crystallization of combustible additive method

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Keywords: porous ceramic, carbamide, zirconium oxide

Requirements for new materials with unique properties are increased with the introduction of new manufactures. Zirconium dioxide can be used such as material due to high physic-chemistry properties. Porous ceramics (including at the base of zirconium dioxide) are widely used in different fields to develop filters, bioimplants, catalysts and etc.[1,2] There are a lot of methods to investigate porous ceramics[2]. One of perspective method is the combustible additive crystallization method. This method alloys to control size and direction pores, porosity and to develop geometrically complicated parts. Carbamide is a very acceptable material for this method. Carbamide dissolves in water very easily, solidifies in the form of thin needles at the change of solution temperature and burns at the sintering. Micron and nanopowders of zirconium dioxide (amount of nanopowders from 10 to 50 vol%) were used to develop porous ceramics. Two forms with different thermal conductivity were used to form porous samples with unidirectional pores: polyurethane (0.315 Wm/°C) and metal (197 Wm/°C) forms. What is more composite form on the base of polyurethane and metal was discovered to investigate thin needles of carbamide. Porous samples were formed by freeze-casting method. Different temperature conditions were used for freezing samples. The crystals of carbamide grew unidirectional as the result of the gradient of temperature. The temperature of samples sintering was 1580 °C. Porosity of development samples varies from 28% to 62%. Pores have sizes from 0.2 to 200 μm. The samples strength is up to 82 MPa. Samples of porous ceramics with thin permeable pores can be used as filters to clean air. The crystallization of combustible additive method can be applied for different powders to develop porous samples.

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Micro- and mesopore structure control in silicon carbonitride-based ceramics using molecular porogens

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Keywords: polymer-derived ceramics, microporosity, pore generation, polysilazane, membrane

Micro- and mesoporous ceramics have gained increasing attention for prospective uses in the fields of energy production and conversion, in particular for applications in the field of separation of liquids or gases. Here, the high thermal and chemical stability of ceramic materials is a decisive advantage over state-of-the-art polymer materials; however, the generation of well-defined pore structures in the desired size range remains a major challenge.

In this contribution, we report on the generation and tailoring of micro- and mesoporosity in polysilazane-derived silicon carbonitride. While microporosity is primarily created during the polymer-to-ceramic conversion step, the addition of molecular porogens, including conventional polymers, organometallic compounds, and solvents, was shown to further affect both the micro- and the mesopore structure. Through a systematic investigation of various candidate materials, polystyrene was found to have the most profound impact on the resulting pore structure, which was characterized in detail using gas physisorption techniques. Finally, selective layers of the polysilazane/polystyrene material were successfully deposited onto oxide ceramic membrane supports. Single-gas permeance tests up to 300 °C demonstrated the general suitability of this material combination for prospective gas separation applications.

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Tribological behavior of HiTUS W-doped hydrogenated carbon based coatings

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Friction behavior of carbon based coatings may be strongly affected by the presence of hydrogen used for the stabilization of the carbon structure. The aim of the work is to investigate the influence of the addition of hydrogen into W-doped carbon based coatings prepared by reactive High Target Utilization Sputtering (HiTUS) from the viewpoint of the control of its tribological behavior under different conditions. The investigations of the influence of deposition conditions on the other properties including roughness, wear resistance, hardness and elastic modulus are included and the results are compared with the properties of the conventionally deposited W-C coatings.

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Additive manufacturing of silicon nitride with Laser Induced Slip Casting (LIS)

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Keywords: additive manufacturing, silicon nitride, LIS

Additive manufacturing opens the opportunity for new application of ceramic materials, but until now there is a lack of methods for the additive manufacturing of large monolithic ceramic parts which are dense and therefore have sufficient mechanical properties. Until now voluminous additive manufactured ceramic parts are produced by powder bed based processes. We have developed a new additive manufacturing method, the Laser Induced Slip casting (LIS), based on the layerwise deposition of slurries and their sequent local drying by intense laser radiation. Laser Induced Slip casting generates ceramic green bodies which can be afterwards sintered like traditional produced ceramic parts. Green bodies and sintered parts are presented and their microstructure and mechanical properties are discussed.

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Ecofriendly alumina suspensions for tape casting process

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Keywords: alumina, tape casting, green chemistry, aqueous suspensions

Tape casting process is widely used in the ceramic industry in order to produce thin and flat ceramic tapes for microelectronics[1] or membranes for gas separation[2]. The suspensions used in the tape casting process are basically composed of a ceramic powder, a solvent, a dispersant, a binder and a plasticizer. The binder and plasticizer are usually polymers coming from

the petrochemical sector and they may present risks for the operator health or the environment (in particular with organic solvents).

Due to the REACH regulation in Europe (Registration, Evaluation, Authorisation & restriction of Chemicals) and with respect to the "Green Chemistry" principles, the use of some of these products could be forbidden in the near future.

The aim of this study is focused on the elaboration of new alumina suspensions with biopolymer additives and rheological properties adapted to the tape casting process. Natural polymers extracted from plants were identified as promising candidates in order to substitute the classical organic additives. The interactions between different organic additives with alumina were studied. The influence of the incorporation order of the different organic additives on the viscosity of the suspension were evaluated. Then, mechanical properties of the green and sintered tapes were determined in relation with the nature of bio-polymer additives.

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Influence of different external lubricants and their deposition mode on nuclear fuel green pellets during cold compaction

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Keywords: lubrication, friction index, ejection force, pellets, compaction, nuclear fuel, zinc stearate

In the framework of the fabrication of future nuclear fuels, some solutions are attempted to optimize the compaction process of the nuclear powder. In fact, lubrication is used for the fabrication process in order to decrease the friction between actinide oxide grains and press tools. A higher plutonium content and an isotopic composition including more ^{238}Pu because of plutonium multi-recycling would increase radioactivity and temperatures in future UO_2 + PuO_2 powder mixtures. This temperature could be detrimental to maintaining lubricant properties within the mixture.

A solution could be the replacement of the internal lubricant[1] by a lubricant deposit on the die wall (external lubrication)[2] during compaction process. This lubrication technic, when combined with the internal lubrication, is known to enhance mechanical strength and density of the pellets resulting from the powder compaction[3].

This paper investigates the influence of this kind of lubricant deposition on the die wall for UO_2 powder pelletization. Different lubricants and various ways of lubricant deposition on the die wall were investigated through sliding coefficient determination during powder compaction and pellets characterization. For example, depositing zinc stearate solid by lubricant pelletization and spraying are compared. Results show that tensile strength of green pellets is enhanced when lubricant is sprayed. Furthermore, the application of viscous oils on the die wall does not allow the production of UO_2 pellets probably due to the tribological inefficiency of this form of lubricant in our conditions. The lubrication mechanism changes from a lubricant to another and acts on the friction index, the slide friction and the characteristics of the final green pellets.

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Synthesis and characterization of nanometric gadolinia powders by low temperature solid-state displacement reaction

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Nanometric-sized gadolinia (Gd_2O_3) powders as well as Eu:Gd_2O_3 red phosphor were obtained by applying solid-state displacement reaction at room temperature and low temperature calcination. The structural properties have been carried out using X-ray diffraction, Thermal analysis (DSC-TG), Field emission scanning electron microscopy (FE-SEM) and Raman spectroscopy. The luminescence measurements were performed at room temperature on the spectrofluorometric system, utilizing 500 W Xenon lamp as excitation source. Photoluminescence emission spectra were measured within the spectral region from 350 to 600 nm and excitation from 250 to 400 nm.

The XRD analysis revealed that the room temperature product was gadolinium hydroxide, $Gd(OH)_3$ that upon calcining transforms to cubic Gd_2O_3 phase at 600 °C. The subsequent calcination at 600~1200 °C of the room temperature reaction products was studied. Cubic Gd_2O_3 phase is converted to monoclinic Gd_2O_3 phase between 1400 °C and 1600 °C.

High-density (96% of theoretical density) ceramic pellet free of any additives was obtained after pressureless sintering at 1600 °C for 4 h in air. The red phosphor emits a strong visible light, implying its potential application in the field of luminescence devices.

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Direct Ink Writing of boehmite gels: rheological understanding of printability

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Keywords: Direct Ink Writing, additive manufacturing, boehmite

Direct Ink Writing (DIW) is an additive manufacturing technique based on continuous layer-by-layer filament deposition[1]. Suspensions must be tailored with specific rheological properties to ensure shape retention after printing. Among the required properties, suspensions should be viscoelastic, shear-thinning, and have a sufficient yield stress to support stacking. These behaviours are often intrinsically linked in complex fluids, such as controlling them independently is impossible. Therefore, suspensions must be optimized to allow extrusion through fine nozzles, but also layer stacking without deformation. The proper flow behaviour for DIW suspensions has been thoroughly investigated to obtain porous spanning structures[2]. However, literature lacks a clearer criterion to obtain ceramic objects that are free of printing defects. In this work, we used boehmite as model suspensions to assess the rheological properties required to print perfectly filled objects.

Boehmite gels undergo complex sol-gel reactions over time, considerably changing their flow behaviour from Newtonian liquids, to solid-like yield stress fluids. This evolution is an asset since it allows studying a broad range of rheological properties with a single suspension, only by changing the solids loading. As gelation occurs, we tracked well-established rheological landmarks, like gelation point and the appearance of a measurable yield stress, and show that they are strongly dependant of boehmite solids loadings, drastically changing over time. By combining a clear objective definition of deformation to image analysis of printed objects at different aging stages, we show that boehmite suspensions become printable when dynamic yield stress is able to overcome gravitational slumping, but also capillary forces. Our work introduces a dimensionless number that provides a clear definition of printability. We show that boehmite suspensions produce objects with shape fidelity greater than 90% when this number is higher than unity. Even though the required shape fidelity may be subject to the operator's discretion, this number establishes a universal and direct link between the rheological properties of a DIW suspension and the printed object shape fidelity.

We believe that this dimensionless number is a first step towards objects with potentially enhanced properties, as it is the next challenge for DIW.

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Fabrication of transparent $MgAl_2O_4$ spinel using spark-plasma-sintering (SPS) technique by suppressing discoloration

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Keywords: spark-plasma-sintering, transparent, spinel, discoloration

Spark-plasma-sintering (SPS) technique has widely been utilized to consolidate various types of materials. It is reported, however, that the SPS processed oxides such as Al_2O_3, ZrO_2 and spinel exhibit discoloration. Such a discoloration is known to be remarkable than the HIP/HP processed oxides and affect the optical properties.

The discoloration in spinel can be explained by the combination of carbon contaminations and lattice defects, which are introduced in the spinel matrix depending on the SPS conditions. Although the carbon contamination and defects formations can be reduced with decreasing the heating rate to some extent, those still remain in the oxide matrix. The lattice defects can be removed by post-annealing in air. However, since the carbon phases transform to CO/CO_2 babbles within the materials by the post-annealing in air due to the reacting with oxygen, it is very difficult to remove the carbon from the sintered bulk materials. Therefore, the carbon contamination during the SPS processing should be suppressed, especially for attaining transparent ceramics.

In the presentation, we will mainly discuss the carbon contamination mechanism and discuss a possible SPS processing to suppress the carbon contamination.

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Role of the interfaces in metal-ceramic nanocomposites processed by novel routes in air

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Metal-ceramic composites in which a ceramic matrix is reinforced by a metal comprise a wide range of compositions and applications in the field of construction, machining or biomedicine, among others. A major difficulty for this type of material relates to its processing. High temperatures and reducing or inert atmospheres to avoid the metal oxidation are needed. When nanostructuring is needed, this make the problem even more complicated. In this work, we present a novel and successful processing route that combines high energetic milling in air and Spark Plasma Sintering to have metal-ceramic nanocomposites with particular properties. We recently reported[1] that metal-oxide functional interfaces developed *in-situ* during the processing give new and enhance properties in thermoelectric materials. This opens new application possibilities beyond the traditional ones. In these sense, the mechanical and magnetic properties of alloys/oxides nanocomposites obtained by the mentioned route are shown in this work.

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LSD-based Selective Laser Sintering starts up to new quality of silicate ceramic bodies

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Selective Laser Sintering of ceramic powders is a promising technique for additive manufacturing (AM) of complex- and delicate-shaped parts. Most AM techniques have in common that material is spread out as thin layers of a dried powder/granulate by a roller or a shaker system. These layers are mostly characterized by a low packing rate. On the other hand, appreciable densities can be reached by the use of ceramic slurries. Therefore, the layer-wise slurry deposition (LSD) has been developed. Powder beds built up by employing the LSD technology exhibit a density comparable to ceramic compacts by means of conventional forming technologies. By the right choice of laser parameters for creating a homogenous energy distribution across the entire cross section of the sliced object, parts could be manufactured which can be post sintered to dense ceramics.

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Ceramic powder synthesis by spray pyrolysis: aerosol formation and evolution

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Keywords: aerosol generation, droplet size distribution, non-oxide ceramics, spray pyrolysis

Spray pyrolysis is a process developed for the synthesis of ceramic powders from liquid precursors which allows composition and size modulation of the particles. This technique, based on the ultrasonic generation of a hexamethyldisilazane (HMDS) liquid precursor aerosol that is heat-treated in a furnace, has been used to obtain Si/C/N sub-micron powder ceramics with a high thermal stability[1].

The process is based on *one droplet one particle* (ODOP) mechanism corresponding to the formation of one particle from one aerosol drop[2]. The final aim of this work is to model the process, improving its comprehension, from the liquid precursor to the formed aerosol characterization, its transport and the chemical-physical phenomena involved in this stage. At first, to understand the relation between the precursor physical properties and the synthesized particles size, aerosol characterization is an important aspect to obtain information about the influence of droplet size on final particle size. However, modelling the aerosol formation was not considered due to the complexity of two involved interdependent mechanisms, the liquid surface wave instability development and the cavitation phenomena. Thus, the choice was made to experimentally determine the spray's droplet size distribution using the shadowgraphy technique in similar conditions to synthesis ones. Different natures of fluids close to HMDS one were used, and the evolution of the spray size distribution was evaluated at three positions of the aerosol generating device. The results show a bimodal distribution of drop size for the three positions, precursors and operating parameters of the nebulization device.

In order to predict the aerosol mean droplet size according to liquid properties and nebulizer operating conditions, measured droplet diameters were compared with values issued from correlations laws proposed in the literature. Furthermore, these correlations developed for a slightly different generating system but nevertheless involving the same aerosol formation mechanisms were adapted and used to estimate the mean droplet diameter generated by our system. Droplet size distribution represents the input information for decomposition and recombination phenomena, next stage of the process. To clarify the mechanisms responsible of particle formation, the precursor behavior at high temperature is being studied. These experimental results will complete the numerical model of the process leading to its entire comprehension.

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Influence of specific interactions between processing additives and the surface of oxide particles on Epoxy Gel Casting

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Keywords: Epoxy Gel Casting, surface interaction, epoxy cure reaction, ceramic oxides, MEMS

Epoxy Gel Casting (EGC) revealed to be a suitable direct consolidation technique to fabricate high green strength micro-components for advanced applications such as in microelectromechanical systems (MEMS) and biomedical devices (Bio-MEMS). The process involves casting well dispersed high solid loading suspensions with added epoxy resin and hardener into silicon rubber moulds.[1,2] Very high green strength values were achieved, enabling overcoming the elevated shear stresses upon un-moulding micro-components with high aspect and surface to volume ratios. This is an essential and unique feature of EGC conferred by the *in situ* polymerization of epoxy resins in the presence of suitable amine-based crosslinking agents. The specific interactions between the surface of the powder particles and the processing additives are likely to determine different partitions of the crosslinking species, dissolved in the bulk solution, or adsorbed at the surface of the particles, and affect the EGC process.

The present work aims at evaluating the influence of surface chemistry on the extent of the specific interactions at the solid/liquid interface and how it affects the polymerization kinetics and the properties of ceramic green bodies consolidated by EGC. Different ceramic oxides (alumina, zirconia and fused silica) having similar particle size distributions were used. Stable colloidal suspensions with 45 vol.% solids were prepared by dispersing the powders in aqueous solutions containing a fixed amount of a common dispersant and various dissolved amounts of an epoxy resin. Zeta potential, rheological measurements and calorimetry were used to assess the specific interactions and their effects on the consolidation kinetics upon adding a polyamine hardener, and on the final properties of consolidated parts. With the isoelectric point of the naked particle surface decreasing, there were noticeable decreases in gelation time, shrinkage, green density, and flexural strength of the green ceramic body's properties. An interaction model is proposed to explain the observed differences.

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Additive manufacturing of ceramics from preceramic polymers: from nanometers to centimeters

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Keywords: Additive Manufacturing, Digital Light Processing, 2-Photon-Polymerization, preceramic polymer, macrofabrication, microfabrication

Ceramic structures across different length scales were fabricated by additive manufacturing using stereolithography of preceramic polymer solutions. Commercially available polysiloxanes were selected, physically combined and photocrosslinked using the visible light range of the Digital Light Processing (DLP) printer for macrofabrication and the IR-wavelength of the 2-Photon-Polymerization (TPP) printer for microfabrication.

Compatible polysiloxanes were combined with one material possessing the necessary photocrosslinkable groups for fabrication and the other a high ceramic yield. The printing process and solutions were optimised regarding printing parameters and additives like solvent, photoinitiator and photoabsorber to print 3D structures with accurate geometry in an appropriate time frame as well as preserve the shape after pyrolysis.

We present the DLP and TPP fabrication of SiOC ceramic macro- (heights up to several cm) and micro-fabricated parts (features down to a few hundreds of nm) starting from commercially available preceramic polysiloxanes. Complex ceramic structures, with a chemical composition which is not realizable other than from the preceramic polymer route, were manufactured with ceramic yields up to 60.2 wt%. In comparison to other additive manufacturing techniques, DLP offers higher resolution and the possibility of achieving dense ceramic parts, while sub-micron resolution can be achieved with TPP.

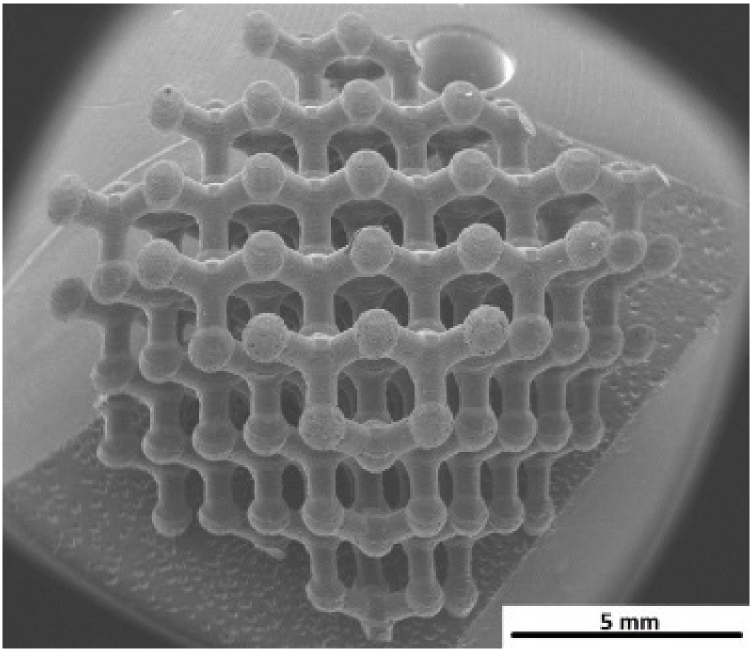

Fig. 1. PSA/Pol2 = 1/1 (not pyrolysed produced by DLP)

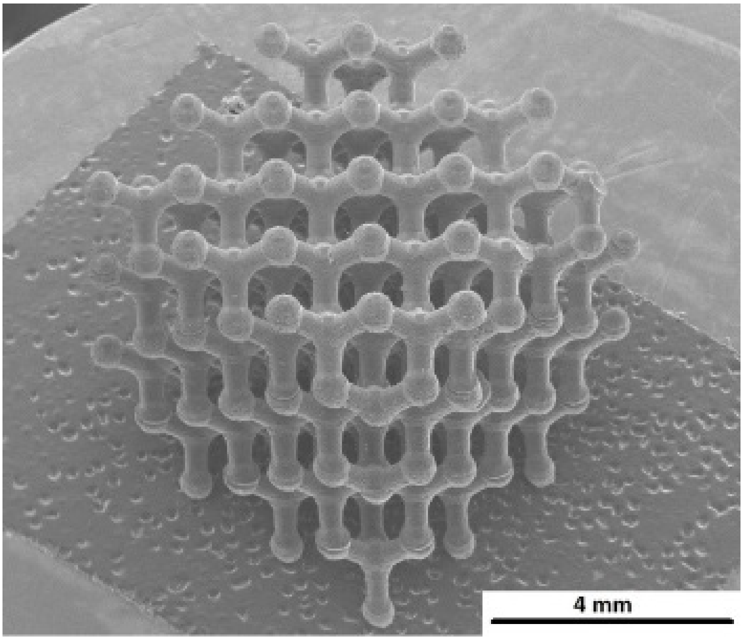

Fig. 2. PSA/Pol2 = 1/1 (pyrolysed produced by DLP)

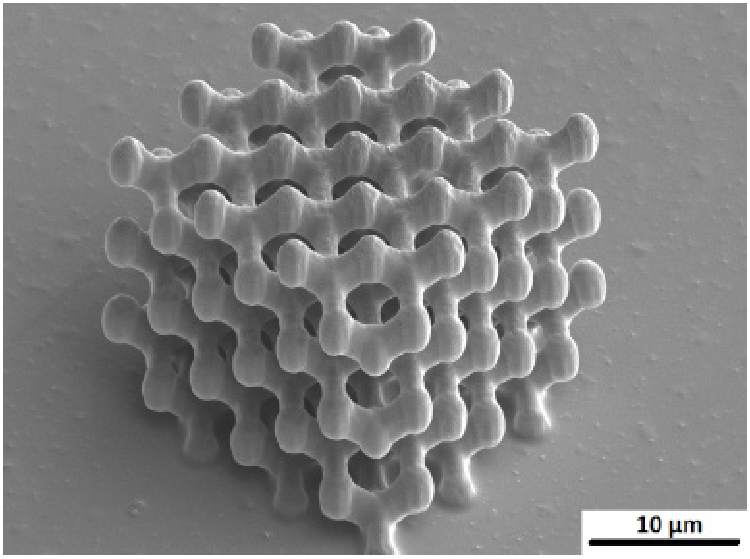

Fig. 3. PSA (not pyrolysed produced by TPP)

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Laser melting initiated deeper structural heterogeneity in oxide ceramics

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Keywords: laser melting, nonstoichiometric oxides, nonequilibrium, physical properties, structure-performance relationship

Selective laser melting, as a kind of additive manufacturing process, has proven itself a powerful method in manufacturing of customized parts, made especially of metals and alloys. Besides the success in 3D net-shape forming, this process has been recognized by its dynamic and non-equilibrium characteristics, which has enabled the formation of amorphous metals and high-entropy alloys. In ceramics, this process introduces deeper structural heterogeneity that would alter their properties. In our work the selective laser melting process was used to treat oxide ceramics. Here we demonstrate that complicated multi-scale structures and rich defects can be implanted. Thus, nano-crystallites, with size much smaller than that of the precursor particles, were found to form in laser melted oxide ceramics, which assembled together to form larger grains with identical crystallographic orientation as the constitutional nano-crystallites. Such deeper structural heterogeneity further results in significant changes in the electric, magnetic and optical properties of these functional oxides. The process thus is proven to be an efficient way for synthesis and modification of oxide ceramics with novel properties that would add more benefits to the additively manufactured ceramic parts, enabling the manufacture of customized ceramic parts with customized performances.

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$MgTi_2O_5$ and related pseudobrookite-type ceramics

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Keywords: pseudobrookite, low bulk thermal expansion, anisotropic structure, spherical porous granules

Magnesium dititanate ($MgTi_2O_5$, MT2[1]) has the pseudobrookite structure (general formula Me_3O_5), corresponding to Mg-enriched artificial endmember of Fe_2TiO_5–$FeTi_2O_5$–$Mg_{0.5}Fe_{0.5}Ti_2O_5$ (pseudobrookite–ferropseudobrookite–armalcolite) solid solution found in

natural igneous rocks. $MgTi_2O_5$ was named 'karrooite,' but it is not an official mineral name. Apollo 11 mission in 1969 found a new mineral, $Mg_{0.5}Fe_{0.5}Ti_2O_5$ in lunar rocks collected by the astronauts Armstrong, Aldrin and Collins; it was termed armalcolite after them. The discovery of $Mg_{0.5}Fe_{0.5}Ti_2O_5$ stimulated renovated interests on $MgTi_2O_5$. To date, studies on $MgTi_2O_5$ mainly focus on basic properties such as cation order–disorder and anisotropic thermal expansion. Also, $MgTi_2O_5$ is used as a 'pseudobrookite-phase stabilizer' for Al_2TiO_5, which is widely known as a low-thermal-expansion ceramic.

Recently, our group have developed a variety of $MgTi_2O_5$ and related pseudobrookite-type porous and dense ceramics for energy and environmental applications[2–8]. In this presentation, we introduce various functional applications of these pseudobrookite-type ceramics.

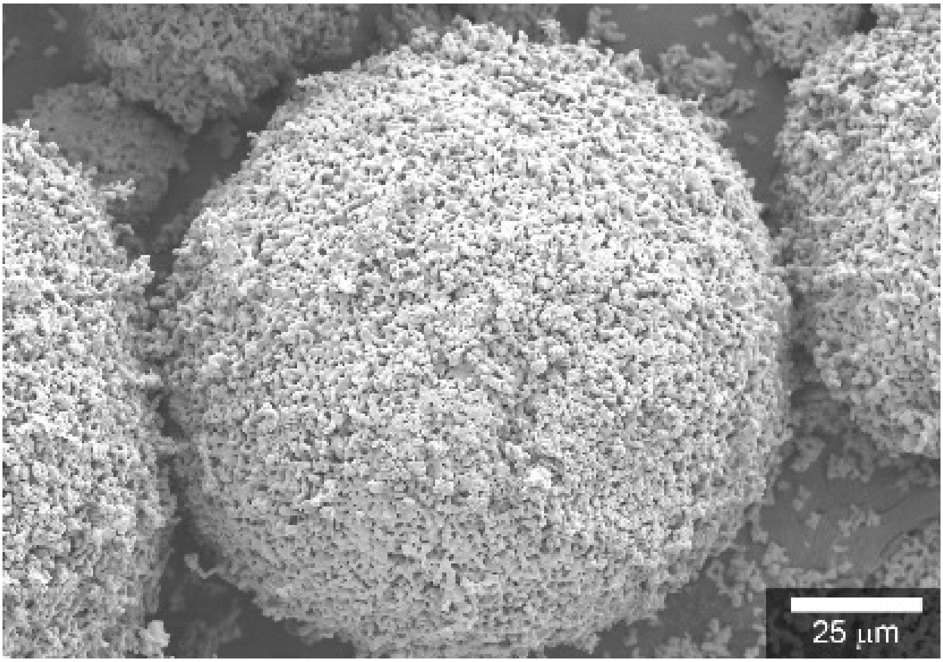

Fig. 1. Pseudobrookite-type spherical porous granules by one-step reactive sintering[8]

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From primary particle coating to sintered ceramics – an alternative method to create homogenous ZTA ceramics

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Keywords: ZTA, core-shell, coating, sintering

Zirconia toughened alumina (ZTA) ceramics exhibit many favorable properties. They are less inclined towards low temperature degradation and therefore suitable for medical applications. Furthermore ZTA exhibits higher toughness and strength than alumina with reduced costs compared to pure zirconia ceramics, which allows a mass market usage e.g. as pump components, sensors. As for all composite ceramics, the phase distribution as well as grain size and density are main features of the ceramic mechanical properties. It stands to reason that a more homogenous phase distribution at comparable grain size and density leads to increased toughness and strength values. The aim of this project was to investigate whether significant differences in the phase distribution can be observed when either ball-milled powder mixtures or coated primary particles are used as ZTA raw material.

The coating of primary particles can be achieved by various technologies e.g. by fluidized bed drying or flame spraying technology. In this project a wet chemical synthesis – a modified Pechini process[1,2] – was established. Zirconyl nitrate was dissolved in an ethylene glycol, citric acid and water mixture and afterwards mixed with an alumina-water suspension (particle size of alumina in the range of 200 nm). After rotary evaporation and calcination for removing the volatile parts, the generated powder was grounded, pressed and sintered. At every step of the process several characterization methods were carried out. The primary and coated particles were analyzed by SEM, XRD, DTA and TG. The sintered ceramics were characterized by microstructure, XRD and density measurements were carried out.

Results of the powder coating showed a disturbed layer of ZrO_2 on the alumina core. Nevertheless, first SEM images of the sintered ceramic show a locally very homogenous distribution of the zirconia phase. The zirconia grains are uniformly located at the interparticle grain boundary.

Due to the high additive content an insufficient densification occured during sintering and no defect free sampled could be produced so far. Modification of the drying process could be the main challenge for the production of these kinds of ceramics and the main focus for further research.

Acknowledgment

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Sol–gel routes in different media to obtain nanostructured, superhydrophobic coatings on copper surfaces

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Keywords: copper, nanostructured coatings, superhydrophobic surfaces, sol-gel

Due to peculiar properties like thermal and electrical conductivity, alloyability, malleability and so on, copper is widely used as reference material for a great number of industrial components, such as heating/cooling devices and electronics. When copper is in contact with a water flow, it could become crucial to control its surface wetting properties to enhance efficiency in such devices. With this aim, copper surfaces were functionalized by deposition of hybrid, nanostructured layers to achieve advanced water repellence, e.g. superhydrophobicity. First, alumina nanoparticles obtained by sol-gel routes were deposited to form a thin gel layer, which, after treatment in boiling water, turned into a nanostructured boehmite coating with a peculiar *flower-like* morphology. Two sol-gel syntheses of Al_2O_3 nanoparticles were attempted, namely in water and in isopropyl alcohol. This latter revealed to be able to provide a better organized nanostructured coating with higher superhydrophobicity after chemical grafting of a fluoroalkylsilane moieties with respect to the water-based one. The further analyses of XPS spectra confirmed these circumstances.

Moreover, the effect of thermal treatment temperature on surface morphology were also evaluated. After formation of the gel film, the surfaces were heat-treated at either 200, 300 or 400 °C. SEM investigations showed that *flower-like* boehmite prevailed when $T \leq 300$ °C, while at $T = 400$ °C CuO microwires grew, displacing boehmite itself. Even though all coated samples displayed superhydrophobic behavior, the 400 °C-treated surface was extremely brittle, while the 200 °C-treated sample could perfectly withstand ultrasonic treatment with no loss in superhydrophobicity. These results suggest that it is necessary to strictly control both the synthesis of coatings precursors and the processing variables when copper surfaces modifications leading to advanced water repellence have to be designed.

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Fabrication of silica glass from mesoporous powder by SPS

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Silica glasses containing noble metal nanoparticles are of great interest due to the surface plasmon resonances of these nanoparticles which behave as optically functional phases. These composite materials are expected to be exploited in photonic devices. Despite the prospects of application, the traditional fabrication methods impair homogenously nucleation of nanoparticales resulting in an obstacle to control the size and dispersion of nanoparticles dopnant. Here, a new versatile processing strategy based on solid-state sintering is reported for preparation such bulk transparent glass composite. Mesoporous silica SBA-15 powders encapsulating Au, Ag and Pt nanoparticles are prepared via host-guest synthesis method and then dynamically consolidated to form a bulk transparent specimen by Spark Plasma Sintering(SPS). The whole sintering process takes place under much lower temperature (1020 °C) and within very short times (10 min) than traditional melting-quenching method. The obtained composite glasses show different colors due to the surface plasmon resonance differences from Au, Ag, Pt nanoparticles and exhibit large nonlinear optical susceptibilities (ranging in 10^{-12}~10^{-11} esu) regarding with the extreme low dopnant (ca. 0.05 wt%). This approach should be applicable to the synthesis of silica glasses embedded with a wide variety of nobel metal and semiconductor nanoparticles.

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Freeze-cast cylindrical silicon oxycarbide shells fabricated by cryo thiol-ene photopolymerization

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Keywords: freeze casting, ice templating, polymer derived ceramic, cryo photopolymerization, thiol-ene click chemistry, graphene oxide, ceramic shell

Porous ceramics are of interest for various applications including filtration, separation and catalysis. They demand extensive research towards new processing routes. Among them, freeze casting technique (also called ice templating) attracted a considerable attention in the recent years.

Herein, we report the first example of low temperature thiol-ene click photopolymerization combined with ice templating that allows for fabrication of macroporous ceramics from liquid preceramic precursor. We show that this technique is highly suitable for directional freeze casting of the UV active polymers, which cannot be produced by conventional freeze casting method. Furthermore, we observe that a hollow monolith with a cylindrical shape and radial density gradient is produced when introducing the graphene oxide (GO) suspension into the preceramic polymer. The whole reaction, especially the UV light absorption rate and the degree of polymerization, are strongly affected even by adding only one weight percent of GO. GO sheets define the material's architecture by limiting the depth of the penetrating UV light as well as the volume which is cross-linked by UV light. As a result the size of the void inside the ceramic monolith can be easily controlled by adjusting the GO concentration.

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Porous γ-$(Y_{1-x}Ho_x)_2Si_2O_7$ thermal insulator with excellent strength retention at high temperature

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Keywords: porous γ-$(Y_{1-x}Ho_x)_2Si_2O_7$ solid solution, high temperature thermal insulator, *in situ* reaction foam-gelcasting method, strength retention, low thermal conductivity

High temperature thermal insulation materials challenge extensive candidates with good mechanical, thermal and chemical reliability at high temperature. Recently, porous γ-$Y_2Si_2O_7$ was shown a promising thermal insulator in harsh environment; however its strength at 1300 °C degraded to 38% of the magnitude at room temperature. In this work, we significantly improved its high temperature strength by doping Ho. Highly porous γ-$(Y_{1-x}Ho_x)_2Si_2O_7$ solid solution was fabricated by *in situ* foam-gelcasting method and has low thermal conductivity (~0.19 W/(m·K)) and high compressive strength (~12 MPa) with the porosity of 80%. SEM and X-ray tomography observations showed interesting multiple pore structures, including large pores (30–230 μm) and small pores (0.1–2 μm), in the as-prepared porous samples. Porous γ-$(Y_{2/3}Ho_{1/3})_2Si_2O_7$ demonstrated the best optimization on strength, 65% retention at 1300 °C. Porous solid solution samples also displayed obviously lower thermal conductivity than the two end pure-phase porous materials. Porous γ-$(Y_{1-x}Ho_x)_2Si_2O_7$ ceramic is highlighted as a promising high-temperature thermal protection material with optimal low thermal conductivity and excellent strength retention.

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Borothermal reduction of group IV and V metal oxide with $NaBH_4$: synthesis and characterization of metal diboride nanocrystals

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Group IV and V metal diboride (MB_2) have very high melting point (>3000 °C), high hardness, good solid-state phase stability, high thermal and electrical conductivity. Metal diboride-based ceramics are expected to be potential candidate materials for ultra-high-temperature applications in the aerospace industry[1]. Availability of submicrometric/nanometric boride particles has indeed the potential to improve several stages of ceramic processing[2], or for instance to facilitate the sintering of bulk ceramics[3], due to enhanced particle reactivity. Meta diboride nanocrystals can be synthesized by various methods: chemical route from inorganic precursors such as metal halides and $NaBH_4$, mechanical alloying and self-propagating high-temperature synthesis[4–6]. However these processes often require expensive facilities or raw materials and are carried out under extreme conditions.

In this work group IV and V metal diboride ($MB_{2,}$ M = Ti, Zr, Hf, Nb, Ta) nanocrystals were successfully synthesized by a thermal treatment of metal oxide and sodium borohydride ($NaBH_4$) at 700 °C under atmospheric pressure[7]. The reaction occurs first via decomposition of $NaBH_4$, followed by the formation of amorphous boron and crystalline ternary species with general formula $Na_xM_yO_z$ and $Na_xB_yO_z$. Finally all of the intermediary species yield metal diboride (MB_2) and sodium meta-borate ($NaBO_2$).

Synthesized TiB_2 nanocrystals have an average size of 11 nm and the powder has a specific surface area (s.s.a) of 33.45 m^2/g. ZrB_2 has grains have a platelet morphology with aspect ratio of 10, with average size of 22.5 nm and s.s.a of 24.97 m^2/g; HfB_2 has a similar morphology with a crystals size of 28 nm, while the s.s.a is even higher, 36.36 m^2/g. As far as we know, the latter is the finest powder obtained via borothermal reduction of metal oxides ever reported. Synthesized NbB_2 powder consists of crystallites around 12 nm and has an s.s.a of 21.09 m^2/g. TaB_2 powder has an s.s.a of 11.38 m^2/g and consists of 200 nm agglomerates of spherical and needle-shaped nanocrystals with average size of 11 nm.

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Poster presentations

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Fabrication of Cu-Mo composites combining SHS and SLS technologies

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Cu-Mo alloys have been attracted tremendous interest in the recent past due to excellent combination of high thermal conductivity of copper and low thermal expansion coefficient of molybdenum. Primary applications of these materials are high power electronic devices and electrical contacts especially at high voltage, welding electrodes, electric discharge machine, and heat sinks.[1] Because of the mutual insolubility of molybdenum and copper the main densification mechanism is considered to be the particle rearrangement associated with the movement of the liquid phase. However, Cu-Mo compacts show very poor sinterability even above the melting point of copper. In this regard, a novel approach has been explored to enhance Cu-Mo composite densification by energy-saving combustion processes (SHS) combined with selective laser sintering (SLS).[2,3] As high-dense Cu-Mo materials with homogeneous microstructure are required for high performance, attempts were made to prepare ultra-fine and well-dispersed Cu-Mo powders. For this purpose the co-reduction of metal-constituents from oxygen containing compounds was performed using Mg+C mixture as combined reducers. It was demonstrated that at certain amount of reducers and slow propagation of combustion wave, the joint and complete reduction of both metals becomes possible. Cu-Mo alloys developed by SHS process and subjected to consolidation using SLS technology possess uniform distribution of consisting phases and high density. The combination of SHS and SLS undoubtedly is advantageous in comparison with the other technologies and may be considered as an alternative pathway to fabricate Cu-Mo alloys with enhanced properties.

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Solid state sintering and thermal expansion behavior of cordierite with CeO_2 and MgF_2 additions

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Keywords: cordierite, solid state sintering, quantitative X-ray diffraction analysis

Due to excellent thermal and electrical properties, cordierite ($2MgO.2Al_2O_3.5SiO_2$) ceramics have a wide range of industrial applications. Conventional solid state sintering of cordierite exhibits some limitations. Firstly, the cordierite formation process via solid state reaction is extremely slow. Since there is an interface area between reactants leading to cordierite formation, in order to proceed the reaction, the reactants should diffuse through the generated cordierite barrier. Therefore the interdiffusion of reactants through this barrier of product slows down the overall reaction rate. Particularly the determinative step of the overall reaction rate is the interface controlled diffusion of reactants. Another limitation is the narrow sintering range of cordierite due to the eutectic and peritectic points near incongruent melting point of cordierite as can be noticed from MgO-Al_2O_3-SiO_2 ternary phase diagram. The temperature range between these invariant points is around 100 °C. The slow reaction rates and the narrow sintering temperature range result in meeting some difficulties about cordierite formation via solid state sintering. Different researchers have tried to employ different sintering additives so far, to be able to withstand these sintering problems. However, the individual effects of additives on cordierite formation at constant temperature, pressing pressure has not been determined yet.

In this study, the specific effects of 2-5 wt.% CeO_2 and MgF_2 additives on the formation rate and thermal expansion behavior of cordierite were investigated. The stoichiometric amount of spinel ($MgO.Al_2O_3$) and quartz (SiO_2) powders were pressed and sintered at 1350 °C for 10 to 50 hours. Qualitative and quantitative X-ray diffraction phase analysis, dilatometric analysis and density measurements using Archimedes principle were carried out. Regarding with the overlapping problem in spinel-cordierite phases, two different quantitative XRD methods were applied and the results were compared according to accuracy.

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Manufacture of alkali activated polymers from clay with mechanochemical activation

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Keywords: alkali activated cements, mortars, grinding, compressive strength

Alkali activated cements play an increasing role as a successful substitute of ordinary Portland cements due to their superior durability and environment friendliness. Raw materials commonly used for alkali activated cement synthesis are those which are rich in alumino-silicates such as natural pozzolans, fly ashes, calcined kaolins and also calcined clay minerals.[1]

Present research focused on the manufacture of this novel binding material system based on two clay minerals with different composition. The raw materials were activated before setting with two different methods; one hand with thermal activation on two different temperatures (700 and 850 °C) and with two chosen heat treatment time (1 h, 3 h). The other hand a novel, possibly cost-effective method, mechanochemical activation, was applied, a short but intensive grinding. The grinding time was altered during the experiment, and the physical performance of the obtained mortars were compared.

The degree of amorphous phase of differently treated samples was determined using x-ray diffraction which may have a direct effect on reactivity. 28 days of compressive strength was also determined of the mortar samples. In summary, alkali activated cement samples (produced from clay minerals) activated with mechanochemical activation have better physical properties as the samples derived by thermal activation.

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Synthesis of mesoporous tin dioxide powder using polystyrene latex and CTAB

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Keywords: tin dioxide, mesoporous, polystyrene, CTAB

In recent years, semiconductor metal oxides have considered much attention due to their wide range of applications. Tin dioxide (SnO_2) is a functional wide band gap (3.6 eV at 300K) n-type semiconductor and possesses special properties which provide applications in gas sensors, Li-ion batteries, dye-synthesized solar cells and photocatalytic devices[1,2]. Mesoporous materials have attracted considerable interest because of having large surface areas which makes them suitable candidates for distinctive applications. Different hard and soft templates have been used to fabricate nanostructured tin dioxide so far[3]. Using hard and soft templates simultaneously have enabled the formation of porous structures with high surface area and special properties[4].

Here, a facile method for the synthesis of mesoporous SnO_2 powder is reported. Mesoporous SnO_2 nanoparticles were synthesized using $SnCl_2.2H_2O$ precursor and polystyrene (PS) latex and cetyltrimethylammonium bromide (CTAB) surfactant as hard and soft templates respectively. Polystyrene nanospheres were prepared using conventional emulsion polymerization and they were analysed using Dynamic Light Scattering (DLS), Field emission electron microscopy (FESEM), and Fourier transformed infrared analysis (FTIR). Results showed successful synthesis of Polystyrene latex with spherical morphology and the mean particle size of 78 nm. In the synthesis process, CTAB micelles covered the polystyrene surface and then the precursor precipitated on templates. After optimizing synthesis parameters, templates were removed via different calcination procedures in air to protect the mesostructure. The obtained mesoporous SnO_2 powder was characterized using X-Ray diffraction (XRD), FESEM, FTIR, and Nitrogen adsorption/desorption. The powder had nearly spherical morphology and the specific surface area and the pore size value of the synthesized SnO_2 powder were 177.67 m^2/g and 12.5 nm, respectively.

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Production of inorganic polymers with different raw material activating methods based on kaolin

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Keywords: calcination, milling, mechanical properties, geopolymer mortars

During the past decades, manufacturing of binders has increased rapidly, and concrete has become an essential structural material, but cement manufacture causes massive CO_2 emissions and landscape destruction. A new kind of inorganic binders, called alkali activated cements provide solution for the listed problems. Alkali activated cements can be synthesised from alumina-silicate rich materials, such as natural pozzolans, fly ashes and calcined kaolins.

The present study compares two different activating methods of kaolin for the purpose of manufacturing these binding materials. Thermal activation is a well-known procedure, but here, the investigation focused on the influence of heat-treatment temperature and time. In this case a new method, called mechanochemical activation, was applied in parallel using various grinding parameters (grinding time, the mass ratio of sample to grinding body, and rotation speed). The structural and morphological changes of thermally and mechanochemically activated kaolinite were followed by X-ray diffraction (XRD), scanning electronmicroscopy (SEM). The effectiveness of thermal and mechanochemical activation was characterised by compressive strength at 28 days and a calculated "degree of amorphisation". The results demonstrate that mechanochemical activation is an effective method for producing geopolymers, the maximum compressive strength (55.6 MPa) of mechanochemically activated samples surpassed the best thermally activated one (43.0 MPa).

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An innovative extrudable alumina paste containing bio-sourced organic binder

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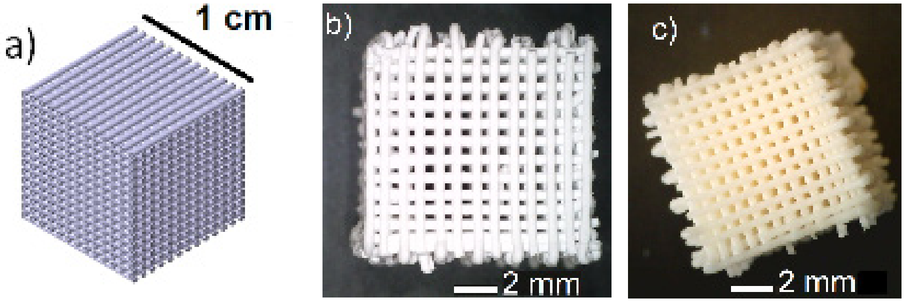
Keywords: micro-extrusion, natural additives, alumina, rheology, Young's modulus

Micro-extrusion is a shaping process which is used to make geometrically 3D complex ceramic green bodies from a paste on the micrometric scale[1]. This technique has a wide range of potential applications in various domains: health, energy, information and communication technologies. Moreover, it has great flexibility because parts can be made "on demand" from the modelling of the part in a CAD format without requiring machining or realization of tooling. However, its success depends strongly on the composition and consequently on the rheological behaviour of the used paste.

To obtain a ceramic paste which can be extruded correctly, its rheological behaviour must be controlled. For this, several additives are used (dispersant, plasticizer, binder). These additives come mainly from the petrochemical industry and could have a negative impact on the environment. In the context of developing low-cost and environmentally-friendly processes and in accordance with the development of the principles of green chemistry, a new formulation based on natural additives is studied. The challenge is to obtain a concentrated aqueous alumina ceramic particle systems based on bio-based polymers which is suitable for the micro-extrusion process and which ensures satisfactory structural and mechanical properties.

In this work, alumina pastes (widespread oxide ceramic material) are produced in an aqueous medium with a natural binder derived from plants and not chemically transformed (in comparison with cellulose derivatives). The amount of alumina in pastes is around $50\%_{vol}$.

The pastes are extruded with a digital controlled device consisting of an XYZ displacement platform and a home-made extrusion head. With this head, extrusion at pressures up to 600 bar is possible. The green parts are porous cubes made of 1 mm or 400 µm diameter alumina cords (Fig. 1).



a) CAD model of the part b) Green part c) Scaffold after heat treatment at 1600 °C

Fig. 1. Presentation of alumina parts made from a paste containing a natural binder

After having successfully produced parts from these pastes based on bio-sourced binder, their structural, micro-structural and mechanical characteristics are determined.

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Development of LTCC tapes for silicon-ceramics composites

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Keywords: tape casting, LTCC, Si-LTCC-composites

The LTCC technology (Low Temperature Cofired Ceramics) is a state-of-the-art technology that allows for miniaturization and integration of electronic circuits in a ceramic multilayer matrix. The processability of LTCC green tapes enables completely new interconnection and packaging solutions. The green sheets are mechanically structured, conduction lines are printed with thick film technique, and finally the multilayer stack is laminated and then sintered at about 900°C. In addition, there are favorable dielectric properties and the low resistance of internal conductor paths, which enable various HF applications. The result is a highly integrated three-dimensional cross-linked multilayer ceramic board.

Silicon and LTCC are used as semiconductor and ceramic packages for a variety of micro-sensors and microsystems technologies. Micro-technology methods, such as photolithography and micro-structuring, thick-film and thin-film techniques, as well as methods of assembly and packaging, are used for both materials. This allows efficient fabrication of microsystems in different product areas. By integrating both, silicon and LTCC, into one multi-material multilayer systems, microsystems with significantly greater complexity and application potential might be created. For the combination of silicon with LTCC two different methods can be used.

One method for the realization of silicon-ceramic composites is anodic bonding of silicon to an anodically bondable LTCC multilayer. The starting material consists of a powder mixture (particle size in the sub micrometer range) of alumina, cordierite or SiO2 and a sodium-containing glass as well as a polymer binder in the non-sintered state. The LTCC wafer is manufactured separately using standard LTCC technologies. After sintering, the LTCC wafer has a relatively high surface roughness (about 200 nm Ra). A lower roughness of Ra <50 nm is required for anodic bonding at the bonding surface, therefore the prefabricated LTCC wafer has to be lapped and polished in an elaborate manner. Silicon and LTCC wafers are then aligned with one another, heated to about 400 °C and subjected to a direct voltage of up to 600 V.

A second technology for bonding of silicon with LTCC ceramics is the newly developed SiCer process. For this purpose, a new ceramic LTCC material system was investigated which can be co-sintered with structured silicon leading to high-strength composite substrates. During the cofiring process, a solid bonding to the silicon is established. The formed SiCer substrate is a material composite, which is thermally completely adapted to silicon over a wide temperature range up to above 500 °C.

The poster presents the LTCC material classes developed for both connection technologies. Materials compositions, properties and some application examples will be discussed.

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Preparation of La_2NiO_4 powders using oxalic acid process

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Keywords: oxalic acid, dielectric constant, structure, XRD data

In this work, synthesis of La_2NiO_4 via a simple oxalic acid process, the nickel oxalate dissolved using ammonia as solvent then mixed with 0.1M of lanthanum nitrate and 0.1M of strontium nitrate as shown in Eqs. (1) to (4). The SEM image of La_2NiO_4 powders and XRD patterns of the different temperature calcined were shown in Fig. 1. The peaks as black spots at 2θ were corresponded to the La_2NiO_4 structure (JCPDS 34-0314) with the Ruddlesden-Popper structure and the white spots at 2θ were corresponded to the NiO structure (JCPDS 44-1159) in Fig. 1. However, the peaks of Sr compounds do not appear in XRD data although the process had been added 0.1M of strontium nitrate. This phenomenon has been described previously by Nie et al.[1], who stated that the formation of $A_{2-x}A'_xBO_4$ structure is partially related to the oxidation state of cation at B-site and that the valence of the B cation should be approximately $^{+2}$ for the K_2NiF_4 structure. This is an indication that Sr substitution on A sites helps stabilize the Ruddlesden-Popper structure.

1. $NiC_2O_4 \cdot 2H_2O + NH_4OH \rightarrow Ni^{+2} + C_2O_4^{-2} + NH_3 + 3H_2O$
2. $La(NO_3)_3 \cdot 6H_2O + H_2O \rightarrow La^{3+} + 3NO_3^{-} + 7H_2O$
3. $Sr(NO_3)_3 + H_2O \rightarrow Sr^{3+} + 3NO_3^{-} + H_2O$
4. $2Ni^{+2} + 2\,La^{3+} + Sr^{3+} + 5/2O_2 \rightarrow La_2NiO_4 + NiO$

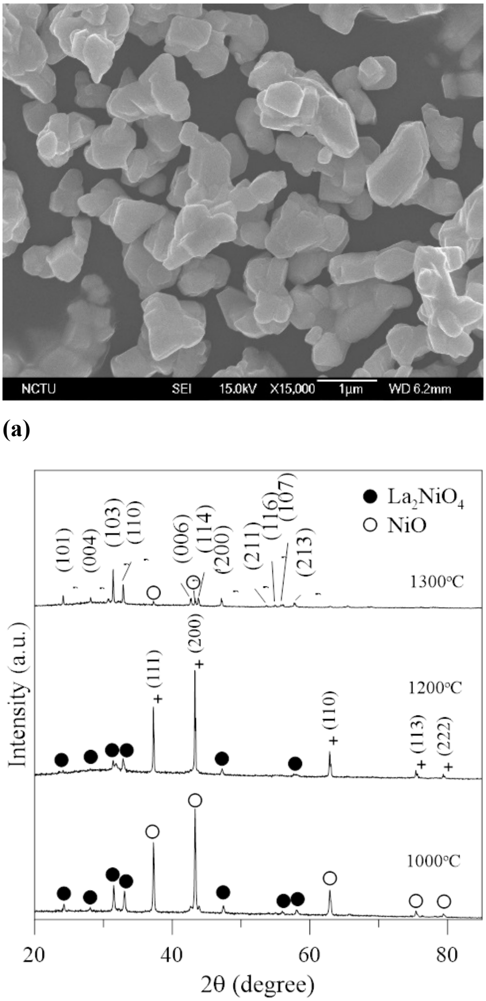

Fig. 1. (a) SEM image of La_2NiO_4 powders;
(b) XRD patterns of the different temperature calcined of La_2NiO_4 powders

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Growth of Si_3N_4 nanowires from amorphous Si_3N_4 powders synthesized by low-temperature vapor-phase reaction

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Keywords: silicon nitride, nanowire, amorphous

A novel synthesis method of Si_3N_4 nanowires from the amorphous silicon nitride (a-Si_3N_4) powder synthesized by low-temperature vapor-phase reaction method was investigated. Highly crystallized α-Si_3N_4 nanowires were synthesized from the heat-treatment of a-Si_3N_4 powder under ammonia atmosphere. The surface of the nanowires was smooth and clean without any attached particles. The thickness of the nanowires was in the range of 200 ~ 300 nm with lengths of tens of micrometers. The nucleation of nanowires from the reaction between SiO and N_2 occurs on the surface of a-Si_3N_4 powder which is covered by a thin layer of SiO_2, and the nanowires grow from the re-arrangement of Si and N atoms of the a-Si_3N_4 powder. The reduction of SiO_2 to SiO by ammonia was promoted by the presence of Ni catalyst, and so the growth was observed at lower temperature when Ni was added to the a-Si_3N_4 powder than when Fe was added. The growth of α-Si_3N_4 nanowires occurs along the [100] and [101] direction and follows Vapor-Solid-Solid mechanism.

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Wet chemistry routes for morphology-controlled actinide oxides powders

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Keywords: oxides, actinides, wet chemistry, synthesis, hydrothermal

The development of future generations of nuclear reactors led to consider wet chemistry routes for the fabrication of the fuel ceramics (e.g. UO_2 and $(U,Pu)O_2$ solid solutions) as they provide interesting powder properties (homogeneity, sintering capability) and enhance the resistance toward proliferation. Such processes are mainly based on the initial precipitation of low-temperature precursors (such as nitrates, carbonates or oxalates) which are further converted into the final compounds through a heat treatment step operated at high temperature. However, the resulting oxide powders can still incorporate some impurities[1] and frequently suffer from a poor flowability inherited from the morphology of the parent precursor.

In this context, we developed several wet chemistry routes aiming to precipitate directly hydrated actinides oxides in solution, with a particular attention paid to the control of their morphology. The first method retained is based on the formation of hydroxides colloids which rapidly aged in solution to yield nanocrystalline $AnO_2.nH_2O$[2]. Preliminary tests indicated that such powders can be directly sintered (i.e. without any prior heating step). They led to a significant decrease of the temperature required for a complete densification and allowed the preparation of a wide range of microstructures, particularly in term of final grain size.

On the other hand, the hydrolysis of actinides under mild hydrothermal conditions in presence of aspartic acid as a shaping agent[3], was investigated to prepare $UO_2.nH_2O$ microspheres. In this case, different operating parameters were studied (such as temperature, duration and aspartic acid concentration) and can be used to tailor the final grain size, typically between 100 and 500 nm. Both methods thus directly provided oxide powders with original microstructural features which can be of interest for future nuclear fuel cycles.

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Selective composite metal/ceramic coatings made by two-step laser cladding

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Keywords: composites, two-step cladding, coatings, selective, laser

The aim of this work is to develop a composite two-step laser coating process for metallic subtrates/parts with no need for post-machining. In the first step the coating is deposited via air spraying a slurry. The slurry contains the coating material as powder, some organic additives and a solvent. Drying is carried out either by an air stream at room temperature or laser radiation in case a higher temperature is required. In the second step the coating is remelted by laser radiation which densifies the layer, ensures a metallurgical bonding to the substrate by remelting a thin layer (only a few microns) of the substrate and produces a smooth (polished-like) surface finish. The overall innovation target is to develop a novel coating process which provides functional layers with a thickness between 20 and 300 µm and a smooth surface finish which spares post-machining. In detail the main innovations are slurries formulations adapted for spraying thin layers with high accuracy and minimum effort for drying, a spraying method adapted for high spray rates and high level of reproducibility, layers free of porosity and cracks after remelting, high area rates for laser remelting ($\AA \geq 0.5$ cm^2/s) and a smooth surface finish ($R_a \leq 0.5$ µm).

In the addressed thickness range (20–300 µm) no other technique providing both features is available. This technology allows depositing protective materials in a cost-effective and a sustainable process. The potential for exploitation is very high. The materials used and the applications considered are only a limited choice of potential applications. On the material side the process can be exploited towards corrosion protection of large areas, e.g. for marine applications. The process is also interesting for wear resistance applications by the reinforcement of superalloy metal matrix with carbide particles.

Acknowledgements

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Fabrication of Si_3N_4/SiCN layer structures with graded multiscalar porosity

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Keywords: polymer-derived ceramics, porosity, dip coating, polysilazane

Layered Si_3N_4/SiCN structures with multi-scale porosity were prepared with the future aim of using them as membrane materials. The focus was set on the deposition of continuous selective layers onto macroporous supports by dip coating with a preceramic polymer. The planar (disk shaped) supports were prepared in two different ways, via conventional slipcasting (resulting in Si_3N_4), and via the polymer precursor route (resulting in SiCN) including the use of polyethylene as a sacrificial filler. Before deposition of the top layers, it was necessary to generate an intermediate layer on top of the support, which was prepared by dip coating/slip casting with an Si_3N_4/preceramic polymer dispersion. The deposition of a continuous top layer was then tested on these two-layered structures using masking techniques.

Additional experiments were conducted to set up a model correlating the withdrawal speed and the resulting layer thickness applicable to the dipping solutions that were used to prepare the selective layer. These experiments were carried out on dense model substrates. Properties such as viscosity and surface tension of the dipping solutions were determined to see if the existing model by Landau-Levich fits the experimental data or has to be adapted.

On both support structures, the slip cast type and the polymer derived ceramic (PDC) type, an intermediate layer (with a thickness of around 30 µm) could be successfully deposited. A surface modification (silanisation) of the Si_3N_4 powder of the intermediate layer slip was necessary. Using polystyrene as sacrificial mask for the intermediate layer (and the support structure), a continuous top layer was successfully prepared in the crosslinked stage on both of the support types. The porosity of the underlying layers was preserved after pyrolysis. The Landau-Levich model could be easily adapted to the used polymer-solvent-systems.

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Fabrication of complex shaped boron carbide by robocasting and pressureless spark-plasma sintering

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Keywords: robocasting, B4C, spark-plasma sintering

Boron carbide (B_4C) is an interesting material for a wide variety of applications due to its low density, high melting point, low chemical reactivity, and high hardness. The main applications for B_4C include nuclear industry and armour applications.[1] However challenges associated with both shaping and sintering of morphologically complex components are the main hurdles for using B_4C.[2]

Robocating, as an additive manufacturing method (AMM), has opened new doors for fabricating green component ceramics with complex shapes. Robocasting is unique among the AMMs because it allows one to build 3Dstructures using water-based inks (highly concentrated suspension of desired materials for fabrication of the 3D structures) with minimal organic content capable of fully supporting their own weight during assembly. Colloidal gels are excellent candidate materials for direct ink writing of such complex 3D structures. The inks must fulfil two important requirements. First, they must exhibit a well-controlled viscoelastic response, so they flow through the deposition nozzle and then set immediately to facilitate shape retention of the deposited features even as they span gaps in the underlying layers. Second, they must contain a high colloid volume fraction to minimize drying-induced shrinkage after assembly is complete, so that the particle network is able to resist compressive stresses arising from capillary tension.[3]

The present work aims to fabricate complex-shaped B_4C by combining robocasting of highly loaded aqueous suspensions for the initial shaping stage with pressureless spark-plasma sintering (SPS) for the subsequent consolidation stage with shape retention. It will be shown that this combination allows the fast and energy-efficient manufacture of geometrically complex boron carbide components for a wide range of possible applications.

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Cold sintering process of magnetodielectrics for radio frequency (RF) applications

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Keywords: magnetodielectrics, cold sintering process, thermal stability, radio frequency

M-type hexaferrites, e.g. $BaFe_{12}O_{19}$, have attracted a lot of attention because of their excellent magnetic properties and potential application in various fields[1]. They are utilized throughout the electroceramic industry not only in magnetic storage systems[2,3,4] but also as RF substrates in the fabrication of filters and antennas.

The cold sintering processing (CSP) is a novel technique developed recently to achieve dense ceramics at extremely low temperatures (<180 °C) across a variety of ceramics, ceramic/ceramics and ceramic/metal and polymer/ceramic composites[5]. The process utilises a small volume fraction of aqueous-based solutions as transient solvents to aid densification by a nonequilibrium mediated dissolution–precipitation process[6].

Magnetodielectric composites have been fabricated using CSP at 120 °C from BaFe12O19 and Li2MoO4 end members. The microstructure, structure and properties of these composites have been studied with a view to developing substrates with bespoke permeability and permittivity for RF applications.

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Preparation of porous beta-alumina and application for water treatment filter

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Keywords: plate-like, β-alumina, porous ceramics, water treatment, reactive sintering

Introduction: For water treatment filters, rapid loss of filtration efficiency is one of the most serious problems. To solve this problem, anisotropic porous ceramics is focused. In this study, porous materials made of plate-like β-alumina were prepared by reactive sintering.

Experiment: α-alumina and sodium carbonate powders were ball-mixed by 5:1 molar ratio to obtain β''-alumina composition. Besides, 0.5 wt. % of LiF was added as a mineralizer. Each mixed powder was uniaxially pressed to obtain green pellets with the dimensions of ~2 mm in thickness and 30 mmφ in diameter. The green pellets were sintered at 1200 °C for 2 h to prepare disc-shape water filters. The obtained samples were characterized by XRD, SEM and filteration test via turbidity measurement.

Results: Plate-like porous structure of β-alumina was presented in Fig. 1. Turbidity was sharply decreased in non-doped β-alumina and clear water was obtained in Fig. 2.

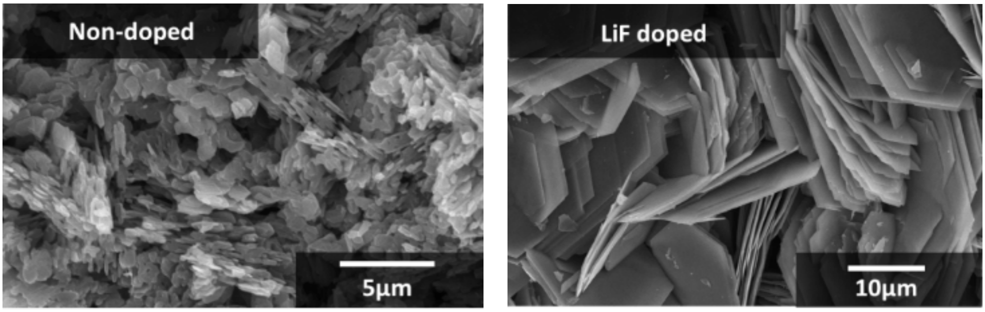

Fig. 1. SEM images of β-alumina plate-like porous structure

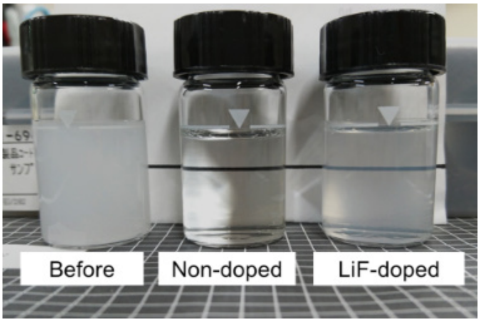

Fig. 2. Turbidity test for water treatment

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Influence of the starting conditions to tobermorite synthesis from CaO-SiO_2-H_2O system

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Keywords: C-S-H system, tobermorite, hydrothermal synthesis, XRD

Tobermorite is a mineral which crystalizes under hydrothermal conditions in system CaO-SiO_2-H_2O[1,2]. This system is very complicated and many variable factors have an influence on the creation of pure well crystalize tobermorite. Thanks to his microstructure, tobermorite is the key mineral in autoclaved aerated concrete[3]. From this point of view is very important to determine the real structure of the phase pure tobermorite. Up to this point of the research, the fully crystallised structure of the tobermorite was not synthetized yet, so the further study is required[1,2,4,5].

The main aim of this contribution is to study the influence of variable conditions and various starting materials of hydrothermal reaction to formation of tobermorite. As was mentioned before tobermorite crystallises from the CaO-SiO_2-H_2O system, so the sources of calcium and silicon oxides are very important. The cost effective Ca and Si sources was favoured. As the source of CaO a grounded calcinated limestone was used. As a source of SiO_2 two different sources differing in particle size were chosen, milled quartz sand (d_{50} = 28.33 μm) and silica sand Dorsilit (d_{50} = 3.53 μm). The C/S ratio was set to 0.83. Solubility of starting materials influences the hydrothermal reaction as well, so different water to solid ratios was used. All synthesis were performed at 180 °C in laboratory steel autoclaves. The prepared samples were characterized in order to determine the phase composition (by X-Ray diffractometery). Morphology and particle size of synthetized powdered products was studied by scanning electron microscopy. The influence of the procedure on the final particle size distribution was studied by laser diffraction.

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Application of solution combustion synthesis induced by microwave radiation for fabrication of yttria nanopowder

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Keywords: solution combustion synthesis, YAG nanopowder, microwave induced SCS

The work presents results of solution combustion method utilization for yttria (Y_2O_3) ceramic nanopowder fabrication. One of the most recent applications, in which yttria ceramics gains much interest, is for solid state lasers. Yttria ceramics sintered to near theoretical density shows transparency in broad spectrum of electromagnetic radiation. Thus it can serve as the matrix for laser active ions. It should be also noted that the radius of yttrium ion is very similar as the ion radius of neodymium, erbium and ytterbium ($r_{Y^{3+}}$ = 104 pm; $r_{Nd^{3+}}$ = 112.3 pm; $r_{Er^{3+}}$ = 103 pm; $r_{Yb^{3+}}$ = 100.8) so the dopant can be built in the yttria lattice.

The combustion method is based on the high energy reaction between the metal nitrates and reducing agent. In the researches the reaction was induced by microwave radiation, which makes the process much faster than one with conventional heating. In this study combustion synthesis was performed using urea and glycine in stoichiometric quantities. After synthesis the reaction products were analyzed in terms of phase composition, particle size and morphology.

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Additive manufacturing of functionalized LTCC ceramic material for electronic devices

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Keywords: additive manufacturing, DLP, inkjet, LTCC

The hybridization of Digital Light Processing (DLP) and two-dimensional (2D) Drop on Demand Inkjet technologies is presented in this work. This novel combination allows the fabrication of an electric circuit embedded within a three dimensional (3D) ceramic structure, that holds the promise of exploring new materials and designing with new levels of functionality.

The DLP technology, based on digital micromirror devices (DMDs), was used to build 3D geometries layer upon layer by polymerization of photosensitive resins, while the inkjet printing system accurately deposits droplets of conductive inks onto the generated substrate. Therefore, one of the main goals is the development of a slurry with appropriate features concerning the scattering phenomena and viscosity for DLP technology. In our approach the improvement and characterization of Low Temperature Co-firing Ceramic (LTCC) suspension was optimized considering the rheological behavior and its photopolymerization in the developed DLP machine.

The hybrid printed parts were characterized after the sintering process regarding their mechanical properties, density and electrical properties.

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Materials based on shaping of core-shell nanostructures prepared by chemical precipitation of hydroxides nanoparticles on the surface of particles in aqueous suspensions

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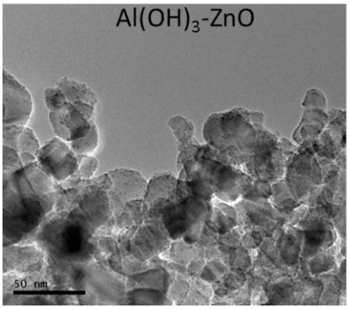
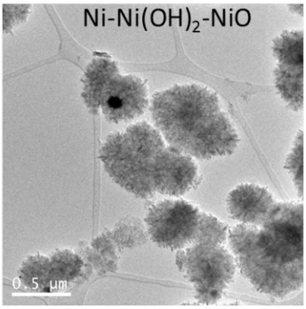
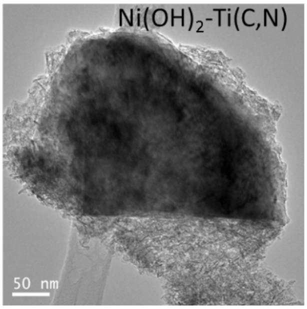
Keywords: core-shell, heterogeneous precipitation, pseudocapacitors, photoactive films, cermets

In the area of particle engineering, core-shell nanostructures with non-symmetrical shapes and compositions have been handled depending on the final application. Among all of them, inorganic/ inorganic core-shells have been proved to be extremely useful. In this work the chemical precipitation of hydroxides, under the influence of ultrasound, in the surface of particles in aqueous suspensions is proposed to produce inorganic/inorganic core-shell nanostructures to improve processing and properties of functional and structural materials. Three examples of the method efficiency are presented: the processing of photoactive TiO_2 and ZnO based films, supercapacitor electrodes and cermets.

The heterogeneous growth of $Al(OH)_3$ nanoparticles (2-5 nm in diameter) on semiconductor nanoparticles provides an effective doped nanostructure after sintering, which effectively modifies the photoactive response of the films in terms of degradation of organic molecules dissolved in liquid. Following a similar method, core-shell $Ni(OH)_2$-NiO flowerlike nanostructures were shaped by electrophoretic deposition (EPD) forming electroactive coatings leading to elevated capacity (around 1000 Fa/g at 2 mA) as a ceramic pseudocapacitor. Finally, $Ni(OH)_2$ nanoplatelets can be also precipitated on Ti(C,N) particles in suspension and, after the cermet shaping and sintering in vacuum, the ceramic particles appear imbibed in a Ni-based matrix. Those microstructures exhibit improved hardness and mechanical properties if compare with regular microstructures fabricated by conventional powder metallurgy techniques.







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Influence of printed layer's orientation on dental ceramics manufactured by stereolithography

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Keywords: stereolithography, alumina, orientation

Subtractive computer-aided design (CAD) and computer-aided manufacturing (CAM) technologies have led to major improvements in dentistry. They make it possible to produce reliable restorations with accurate dimensions and to reduce manufacturing time. However, these processes are limited by the waste of raw material (loss of unused portions of blocks and difficulty in recycling excess material) and heavy wear of milling tools. Microscopic cracks, which can weaken restorations, can also appear in objects due to the milling process. Additive manufacturing processes avoid these limitations by building objects layer-by-layer. Several researchers investigated the impact of slurry composition on mechanical properties. However, no data is available with regard to the impact of layer orientation manufacturing. The aim of this study was to compare mechanical properties of alumina and zirconia toughened alumina manufactured by stereolithography with different layer orientations.

Samples for this study were designed by CAD software (Catia, Dassault Systèmes) and were fabricated within 3 orientations (XY, ZX and ZY). Samples were sliced by Creation Workshop software (Envisionlabs) and transferred to the stereolithography software and equipment (CryoCeram Printer, CryoBeryl Software) for manufacturing. After sintering, sample size was 1.3 × 4 × 22 mm (ISO 6872:2008).

The physical and mechanical properties of stereolithographied ceramics prepared from alumina slurries (mean particle size = 1.56 ± 0.04 µm, dry matter content = 80%) were evaluated by microstructural analysis, hydrostatic weighing, fracture toughness, three-point flexural strength measurements with Weibull analysis.

No difference of density was found regarding the orientation of printed layers. The fracture toughness of XY was significantly higher than that found in the ZX group. All samples had large grains whose major axis was parallel to the layer orientation. The fracture surfaces of XY and ZY manufactured samples were trans-granular and inter-granular for ZX manufactured samples. These results were sixmilar to those exposed by Suzuki[1]who showed that samples produced by electrophoretic deposition with grains perpendicular to the load had trans-granular fracture surfaces and higher mechanical strength than when the load was parallel to the grain axis.

To conclude, the microstructural texture of alumina stereolithographied ceramics influenced the flexural strength, the crack propagation and the fracture mode.

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Influences of organic agents on the aluminium nitride tape casting process

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Keywords: tape casting, aluminium nitride, polyvinyl butyral, viscosity

Aluminium nitride (AlN) substrate has high thermal conductivity, high electric insulation, low dielectric constant, and high mechanical strength, which can be implemented to high power electronic packaging and modulus. Tape casting process is one of the efficient process to fabricate AlN substrates. In the tape casting process, AlN slurry is poured into a reservoir and casted onto a mylar carrier surface through the gap between blade and carrier.[1] In this study, the AlN slurry is prepared by mixing aluminium nitride powder with different ratios of Polyvinyl butyral (PVB) series binders, plasticizer and organic solvent to prepare appropriate viscosity slurry, and the slurry was coated uniformly on PET films via the tape casting process. The AlN raw materials are very sensitive to the humidity in the forming process[2], it easily reacted with vapor to form amorphous as well as porous AlOOH (boehmite) and $Al(OH)_3$ (bayerite). Since ethyl alcohol had hydrogen bond with deliquescence and absorb vapor in air, different ethyl alcohol/toluene solutions were selected as solvent in order to investigate a stable AlN slurry. Blown Menhanden Fish Oil, polyoxyalkylene, and Triton X100 were used as dispersing agents. A low volatilisity and non-phthalic acid derivative plasticizer was applied to develop plasticizing characteristics of the green tape. Types and ratios of mixed adhesive/plasticizer determined the viscosities of the slurries and tensile strength of the aluminium nitride green films. Green tapes with smooth surfaces were prepared by the slurries with viscosities in the range between 2000–4000 mPa·s. The highest yielding strength of green films was 0.159 kg/mm^2, the tapes had good machinability and laminating property. The green tapes were laminated and de-bindered at 450 °C for 2 hours. The aluminium nitride substrates were obtained after sintering of de-bindered tapes at temperature of 1700 °C for 6 hours in the nitrogen atmosphere.

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Preparation and water-filter application of porous spinel ceramics

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Keywords: porous material, $MgAl_2O_4$, reactive sintering, alumina powder, grain growth

Introduction: Water is indispensable in our lives. To maintain our life, it is recommended to drink 2 to 2.5 L water a day. However, many people, especially in Africa or in Southeast Asia, suffer from polluted water or water shortage. Water purification using porous ceramics is a key technology to solve the problem. In this research, porous $MgAl_2O_4$ microfiltration filters (MF filter) from different starting materials have been developed.

Experimental: As an MgO source, hydromagneasite powder ($MgCO_3$ (basic)) was used, and as Al_2O_3 sources, α-Al_2O_3, γ-Al_2O_3 and AlOOH were used. Besides, α-Al_2O_3 mixed powders doped with LiF as mineralizer were prepared. These powders were mixed by wet ball-milling. They were dried and sieved to obtain mixed powders. The mixed powders were uniaxialy pressed to obtain green compacts. These green compacts were reactively sintered at 1200 ºC–1600 ºC for 2 h. The samples were characterized by XRD, SEM observation and density calculation. $MgAl_2O_4$ thin plate filters were evaluated by filtration test and turbidity measurement.

Result and discussion: Almost single phase $MgAl_2O_4$ was synthesized in all samples confirmed by XRD. Fig. 1 shows SEM micrographs of porous $MgAl_2O_4$ sintered at 1600 ºC by using α-Al_2O_3, γ-Al_2O_3 and AlOOH as starting materials. In the order of α-Al_2O_3, AlOOH, and γ-Al_2O_3, density became higher. This difference may be caused by grain and grain size distribution of raw material powders. For this reason the filters prepared by each mixed powder show different result of filtration efficiency. Also in the samples sintered at 1400 ºC with LiF, grain growth was observed in microstructure. At 1600 ºC, suppression of densification was observed with increasing amount of LiF.

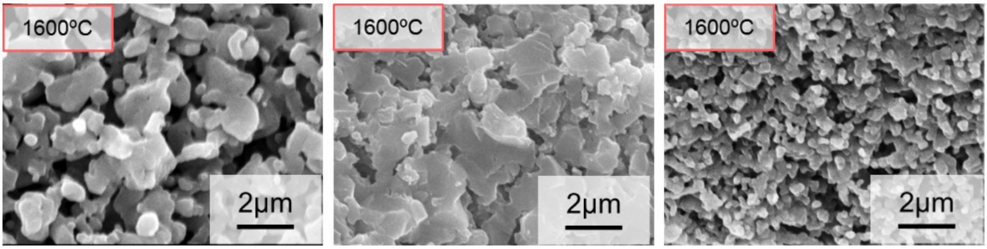

Fig. 1. SEM micrographs: (left) α-Al_2O_3, (middle) γ-Al_2O_3 and (right) AlOOH

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Compaction of high dense metal-ceramic composite using powerful ultrasound assistance

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Keywords: metal-ceramic composite, dry pressing, powerful ultrasound assistance, spark plasma sintering

The optimal content of the light metal-ceramic composite has been modeled by the discrete element method and experimentally verified: powder of Al/Mg matrix (74 wt.%) with inclusions of B_4C powder (6 wt.%), W nanopowder (20 wt.%). This content provides the maximum dense particle packing for all the components and strong alloy matrix with the coordination number greater than 4 and packing density of 0.67. Fully dense composite (density of 3.14 g/cm^3) has been consolidated by the spark plasma sintering at 490 °C, 39 MPa, 10 min while the known method of hot extrusion provides 95% relative density only[1].

Characterization of the compressibility of the dry powder mixture has been performed by plotting the compaction curves obtained for the conditions of uniaxial pressing with loading–reloading cycles and using an approximation by a logarithmic equation in a dimensionless form[2]. At pressure of 800 MPa the composite powder green compacts with a density of 92.6% were obtained by the conventional quasi-static pressing at room temperature. These samples were consolidated by free vacuum sintering at 590 °C up to density of 93.4%. However the uniaxial pressing of the composite powder at 800 MPa and using simultaneous non-cavitation powerful ultrasound assistance in the special mold – ultrasonic waveguide[2] allowed to reach the green density of 95.1% which is comparable with the density provided for the consolidated composite by the hot extrusion method. Following free vacuum sintering (590 °C) of the sonicated green compacts led to the density of 96.8%.

Thus the opportunity to press the dry composite powder mixture up to high density (95.1%) owing to application of the powerful ultrasound assistance has been shown. Free solid state sintering is not suitable for the complete consolidation of the composite. To achieve full density of the composite it is necessary to use spark plasma sintering (pulsed electric current sintering).

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Microwave-assisted one-step SCS synthesis of composite ceramic nanomaterials

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Keywords: microwave, solution combustion synthesis, composite ceramic nanomaterials

Composite cerametallic nanomaterials have attached great research and practical interest due to their unique properties that allow using them successfully for catalysis, microwave scattering, in microelectronics and etc. Nickel containing alumina based composite nanomaterials are one of the most broadly used. However, production of nickel nanoparticles in any form by solution combustion technique requires the usage of protective atmosphere or additional post reducing of metal oxides. To obtain cerametallic composite nanomaterial by one-step solution combustion method, where Al-containing phase acts a strong oxidizer, is even more complicated. In this case Ni and Al have a tendency to form a spinel phase, which is not so attractive.

In this work, we report a new modified solution combustion synthesis technique for one-step production of cerametallic alumina – nickel composite nanomaterials. The main unique feature of our approach is the use of microwave assisted foam preparation and ignition of combustion of precursors in combination with effective fuel. That allows us to obtain alumina-nickel composites under normal air atmosphere without any post reduction. Also, the effect of different components' concentration on the phase composition and grain size of resultant solid products were investigated. Moreover, nanomaterials prepared by the microwave-assisted and high-temperature radiation-convective ignitions of combustion were compared.

It was found that the microwave assistant accelerates water removal, decomposition of fuels, alumina and nickel oxide phases nucleation and then reduction of obtained NiO to Ni metal bonded nanoparticles during combustion process due to promotion of reducing species access to whole volume of reaction mixture. It was observed the formation of alumina nanoparticles on which Ni metal nanoparticles with the average grain size ~ 28 nm distributed.

The prepared materials are characterized by high coercivity (166 Oe and 64 Oe for microwave- and high-temperature-assisted method respectively). The formation of great amount of reduction gaseous mixture during fuel decomposition and rapid combustion reaction in metals nitrate – fuel systems promotes full Ni oxides reduction and prevents metallic Ni reoxidation. Moreover high velocity of reaction prevents spinel phase formation. In addition, our method allows to get nanoparticles with high degree of magnetostructural anisotropy, which strongly enhances magnetic properties of ferromagnetic nanoparticles.

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Complex shapes PLA/TCP constructions for bone regeneration obtained by 3D printing

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Keywords: polylactid, tricalcium phosphate, 3D printing, composite

Modern regenerative medicine has a great need in resorbable bioactive composite materials for bone implants. Biodegradable polymers, e.g. polylactide (PLA), filled with resorbable calcium phosphate (with the ratio $Ca/P \leq 1.5$, e.g. tricalcium phosphate) are good candidates. Specific macroporous architecture for osteoconductivity enhancing can be achieved by 3D-printing process. In the case of 3D thermal extrusion technique it is necessary to produce composite filament (PLA/TCP) with uniform distribution of the phosphate particles inside PLA prior to printing and to develop printing regimes[1].

The aim of this work is to create bioactive macroporous composites based on calcium phosphate and biopolymers, of predetermined complex shape for bone regeneration.

Composite filaments were fabricated with a different ratio β-TCP/biopolymer. 3D thermal extrusion technique was used for printing of 3D periodic structures with different mesh size and more complex shape implants. We have obtained macroporous bioactive PLA/TCP composites with computed complex architecture.

It was shown that osteoconductive composite implants made of degradable polymer and bioresorbable calcium phosphate with complex shapes can be fabricated by thermal extrusion 3D-printing technique.

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Solvothermal synthesis of kaolinite nanoscrolls

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Keywords: kaolinite, intercalation, nanoscroll, solvothermal

Kaolinite nanoscrolls are of interest in the research area of functional nanocomposites and nanohybrids. We present a simple, convenient and effective a solvothermal synthesis procedure for preparing kaolinite nanoscrolls. This solvothermal synthesis procedure produces high-quality kaolinite-cetyltrimethylammonium chloride complex from kaolinite-urea precursor. The desired kaolinite-cetyltrimethylammonium chloride complex is attained without prior (weeks-long, conventional stirring) treatments of the samples with methanol. We also investigate the factors that affect the efficiency of this solvothermal treatment using X-ray diffraction, thermal analysis, Fourier transform infrared spectroscopy, and electron microscopy. The eco-friend precursor proved to be suitable to directly intercalate cetyltrimethylammonium chloride using a short-term (16-h) solvothermal treatment at 100 °C. Our findings reveal that the formed kaolinite-cetyltrimethylammonium chloride complex can easily transform into kaolinite nanoscrolls. This conceptually new synthesis procedure using cheap urea and methanol as reagents is expected to be broadly applicable for a cost-efficient production of nanoscrolls-based functional materials.

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Direct Inkjet Printing of ceramic materials

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Keywords: additive manufacturing, Direct Inkjet Printing, ceramic materials

Direct Inkjet Printing (DIP) is a promising process for ceramic manufacturing. By applying aqueous suspensions with high solid contents (of up to 30 vol.-%) directly (through nozzles) onto a substrate, intricate and detailed structures can be fabricated. The ceramic inks have to be precisely conditioned in regard to their rheological properties (i.e. viscosity and surface tension) and particle size distribution in order to guarantee a steady flow of ink through the narrow channels of the printhead and thus minimize nozzle clogging. Consequently, any material that can be dispersed in water with the required rheological properties can be converted into printable suspensions. At the Institute of Mineral Engineering, RWTH Aachen, zirconi-

um oxide, aluminum oxide and silicon nitride have been successfully printed by DIP. Due to a low porosity and homogeneous micro structure, directly printed objects show a mechanical behavior comparable to slip casted or pressed specimens. The direct and droplet-wise deposition of material allows a simultaneous and spatially free combination of multiple materials in one manufactured part. Such functionally graded materials (FGM) enable a tailored adjustment of material properties by purposefully adding further materials whose properties suit the application and load of the part.

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Calcium phosphates powders synthesized in non-aqueous media to fabricate osteoconductive resorbable bioceramics

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Keywords: calcium phosphates, biomaterials, ionic liquids, non-aqueous synthesis

The topical issues of modern biomaterials science include the manufacture of nanosized bioceramics for bone tissue replacement. The latest developments are related to regenerative approach, which requires the investigation of calcium phosphate based materials with Ca/P ratio < 1.5. The usage of non-aqueous media is a promising way to eliminate water influence, avoid the impurities and gain strong control over the material. Another advantage of non-aqueous media is the ability to explore low-temperature synthesis and thus to liquidate calcination stage.

The key objects of the research were tricalcium orthophosphate (Ca3(PO4)2, TCP) and several condensed calcium phosphates (e.g. Ca2P2O7, CPP). The main requirement was the usage of liquids with high boiling point and fusible salts.

Ethylene glycol was chosen due to its solvent abilities and the fact that the only coproduct of the reaction should be the solvent itself. The precursors, such as calcium glycolate, crystal orthophosphoric acid, ammonium pyrophosphate were obtained previously. TCP was obtained by adding orthophosphoric acid or commercial ammonium hydrophosphate solutions in ethylene glycol to calcium glycolate solution. CPP was obtained in ethylene glycol using the same technique: ammonium pyrophosphate solution was added to calcium glycolate solution. The syntheses were carried out in the range from 30 to 150 °C.

The usage of ionic liquids is the key idea of the second approach. Temperature range from 150 to 350 °C was chosen for the calcium phosphates synthesis according to the KNO3-NaNO3 phase diagram. Calcium phosphates were obtained by mixing Ca(NO3)2-NaNO3-KNO3 melt with suspension of corresponding sodium phosphate in molten KNO3-NaNO3. By-products were washed out with alcohol.

The main aspects of the samples sintering, as well as the microstructure and qualities, were analysed using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and dynamic light scattering (DLS).

We have developed a unique method of microcrystalline calcium ortho- and pyrophosphate powder synthesis in non-aqueous media. Also we have investigated low-temperature range for calcium phosphate synthesis.

Development of the novel phosphate synthesis method makes possible obtainment of pure calcium phosphate phases without impurities of hydrophosphates. XRD data have confirmed the obtainment of pure crystalline TCP and CPP phases. DLS, SEM and TEM have demonstrated that phosphate particle size from 100 to 200 nm can be obtained.

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Synthesis, characterization and applications of environmentally friendly water-soluble tantalum and niobium precursors

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Keywords: water-soluble precursor, polymerizable complex route, Ta or Nb-based oxide, photocatalyst, ferroelectrics

Owing to the remarkable potentials of tantalate and niobate materials in ferroelectric and photocatalytic fields, development of environmentally friendly tantalum or niobium precursors becomes urgent. During wet chemical synthesis of Ta- or Nb-based oxide such as sol-gel and metalorganic decomposition, alkoxides of tantalum and niobium are most frequently used as starting sources. Nevertheless, some inherent issues are associated with Ta or Nb alkoxides, such as great sensitivity to moisture and relatively high cost. Recently a simple polymerizable complex (PC) route, known originally as the Pechini method, has been developed to solve these problems. However, air-stable water-soluble tantalum and niobium precursors are not easily available yet. In this work, a simple flexible route to synthesize aqueous tantalum and niobium precursors has been developed using cheap and stable Nb_2O_5 or Ta_2O_5 as starting source, based on the basic flux technique. Various analytical techniques have been used to characterize the formation mechanism, purity, and thermal decomposition features of the precursors. The synthesis processing has been optimized. These Ta or Nb precursor solutions have higher Ta or Nb ion purity over 99% among detectable positive ions with the higher yield. IR analyses confirms that the element Ta or Nb exists in the precursor solution as the group of COO-Ta (Nb)-O. Using home-made Ta and Nb precursors, several

photocatalytic nanopowders such as Ta-doped ZnO and $BiNbO_4$, and ferroelectric ceramics such as $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.35PbTiO_3$ (PMN-PT), have been prepared by a modified PC method. Compared to conventional solid phase reaction, these powders have pure crystalline phases with uniform sizes of 20-100nm and larger specific surface area in the range of 9–30 m^2/g. The related ferroelectric and photocatalytical properties have also been examined, implying that this is an attractive and flexible approach for fabrication of tantalate and nibonate functional materials.

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Strength of alumina ceramic produced by the LCM additive manufacturing technology

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Keywords: additive manufacturing**,** bending strength, fractography, microstructure

The strength of ceramic components and specimens is governed by inhomogeneities (called defects) which are present in the bulk, on the surface or on edges of the part. These defects are introduced during processing. Type and size of these defects may be influenced by changing process parameters with the goal to increase the strength. This principle is also valid for additive manufactured components.

A specific aspect of the strength of additive manufactured components and specimens is the building direction. The interface between adjacent layers may have properties that deviate from the properties of the layers themselves[1]. In a prismatic bar as usually used for strength testing of ceramics the layers may be oriented parallel to each of the specimens faces. During flexural strength testing the applied stress then acts normal or parallel to the interfaces. This enables an investigation of properties in relation to the building direction.

In this contribution we present mechanical properties obtained on specimens from additive manufactured alumina components. Specimens tested in different orientations with respect to the building direction are investigated. The relation between applied stress direction, strength and building direction is presented. It is shown that specific defects resulting either from printing, cleaning or the thermal postprocessing are responsible for failure Depending on the testing direction and testing conditions these specific defects may be identified or remain hidden.

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Hydrothermal synthesis of ferrite nanocomposites with core/shell structure

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In this work, we have prepared different ferrite nanoparticles, such as nickel ferrite, zinc ferrite and iron oxides and combined them in different manner in order to investigate the possibility to obtain the core/shell structure. Nickel ferrite and iron oxide are mainly used as a core material, while zinc ferrite owing to its low toxicity was used as a shell. Simple preparation of the samples, high physical and chemical stability and magnetic properties which can be easily controlled with the size of the particles, make these materials a good starting point for obtaining multifunctional particles used in biomedicine. XRD, TEM, DLS, Raman and VSM methods were used in order to investigate their structural and magnetic properties. Spinel structure was confirmed by X-ray and Raman measurements. TEM analysis indicated that synthesized nanoparticles are agglomerated, with possibility to obtain the core/shell structure. Magnetic measurement have shown that magnetic properties are increased by addition of zinc ferrite layer on to the nickel ferrite core.

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Selective laser melting for manufacturing of $MoSi_2/Si_3N_4$ composites

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Selective laser melting (SLM) technique has a potential to revolutionize the global parts manufacturing and logistics landscape and has been recognized as a blasting technology to manufacture customize designed, geometrically and functionally complex structures with a good dimensional tolerance. Despite of many advantages of SLM over conventional methods, high heating and cooling rates of materials restrict its use for manufacturing ceramic components. Moreover, usually the ceramics have low laser absorptivity to be manufactured by SLM.

To address this issue, we proposed a new approach for preparation of $MoSi_2/Si_3N_4$ composite by SLM. Thus, newly designed powders ($MoSi_2/Si$) with unique structure were synthesized by self-propagating high temperature synthesis method. The as-synthesized powders were shaped by SLM and reactive sintered in nitrogen. As a result, $MoSi_2/Si_3N_4$ composite with designed complex shape was performed. Morphology of the synthesized Si_3N_4 powders could be regulated from spherical to fibrous shape using different catalysts. The suggested design of the powders and strategy of consolidation will expand the possibility and application of SLM technology, find scientific interest and huge industrial usage.

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Adsorptive removal of methylene blue by high surface area mesoporous tungsten oxide

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Keywords: mesoporous, tungsten oxide, soft-template, tungstic acid, methylene blue

Dyes are widely used in various industries. The inevitable released related wastewater and contaminating our nature are major concerns. Therefore, the removal of synthetic dyes is very important from the environmental viewpoint because most of them are toxic and carcinogenic[1]. Methylene blue is one of these dangerous dyes with chemical formula of $C_{16}H_{18}N_3SCl$[2]. Various techniques have been applied to eliminate this dye from wastewater, e.g. adsorption on the surface of metal oxide as adsorbents[3]. Increasing the specific surface area by providing a mesoporous structure can improve the interaction between adsorbate and adsorbent materials[4]. Among several synthetic methods for producing mesoporous materials, soft- templating approach is commonly used, in which self-assembly of organic molecules such as block-copolymers forms the pores[5].

In this study, mesoporous tungsten oxide powder was synthesized by soft-templating route as an adsorbent for the removal of methylene blue from an aqueous solution. Inexpensive peroxo tungstic acid precursor and P123 block-copolymer were selected as metal oxide precursor and organic template, respectively. The resulting gel was calcined at 500 °C. An appropriate heating program was adjusted to protect the mesopores from destruction during calcination process. The inorganic networks were formed around the template through a sol-gel process during the synthesis development. Fourier transformed infrared spectroscopy confirmed complete elimination of the organic template after calcination step. X-ray diffraction analysis demonstrated the formation of orthorhombic crystalline structure. In addition, the morphology of powder was studied using a field emission scanning electron microscopy. The specific surface area of the resulting product was found to be 67 m^2/g using nitrogen adsorption/desorption analysis. The methylene blue adsorption potential of the synthesized mesoporous tungsten oxide was investigated in various concentration of solutions. The dye removal sufficiency of the designed adsorbent was verified by maximum methylene blue adsorption capacity of 85% (43.6 mg/g) in a short time.

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Pozzolanic reactivity assessment of Turkish calcined clay as a cement substitution

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Keywords: calcined clay, cement substitute, pozzalanic activity, SEM, XRD, TGA, conductivity

Cement manufacturing is a major source of greenhouse gases and it causes more than 5 percent of CO_2 production. Few studies tried to solve the emission production by the cement industry concentrating on intervention of the other affordable and attainable materials such as clay. In fact, an ordinary way to reduce the CO_2 emission attributed to cement production is to substitute a large portion of Portland clinker in cement to create blended cements, or replace an OPC in concrete mixture with proper supplementary cementing materials (SCM). Recently, the usage of the industrial by-products such as fly-ash and blast-furnace slag as substitution was widespread, but the amount of these materials is significantly less than the cement production and industrial demands. So, alternative sources like calcined clay were considered by the manufactures. Clays are the widely available material on the earth crust and in some part of it, the specifications of clay or schist type materials are proper enough to evaluate them as cement substitute. In this study the pozzolanic activity of 3 common clay type raw materials (C_1, C_2, C_3) coming from mining quarries have been investigated. This interest is a part of widely spread attention directed towards the utilization of waste by-products in cement industry to minimize the OPC consumption. Also, the mortars and concrete which contain pozzolanic materials exhibit tangible enhancement in durability properties. To evaluate the raw materials, several types of analyses have been performed. First, the potential reactivity of normal clays is analyzed by the thermo-gravimetry method to identify the optimum dehydroxylation temperature. Then, the phase analysis has done by means of X-ray diffractmeter (XRD) while the scanning electron microscopy (SEM) photos elaborate phases present in the raw material. Another method which is used to evaluate the pozzolanic activity is based on the measurement of compensated electrical conductivity of calcium hydroxide saturated solution, to which the material is added over time. The same characterization methods are used for Kaolin to compare the potential of calcined C_1 to C_3 with meta-kaolin. Results represent that the all samples could be feasible candidate as cement substitute while there is an assumption that C_1 could have the chance for more than 30% of replacement.

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Preparation and characterization of carbon nano/microfiber membranes for ceramic matrix composite applications

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Keywords: electrospinning, fiber, carbon, membrane

The needle-less electrospinning was employed for a preparation of two types of carbon nano/microfiber membranes with extraordinary high specific surface area. The prepared fiber membranes were produced in a large scale as potential heat-management materials, for reinforcement, high-temperature catalysis, membrane-based separation, and as components for nanoelectronics and photonics[1,2]. The polyacrylonitrile (PAN) and polyvinyl alcohol (PVA) were used as base polymers for preparation of electrospinning solution and subsequent precursor fiber membranes formation by needle-less electrospinning on device called "Nanospider". The exactly defined temperature schedules and atmosphere were suggested according to the results obtained from differential scanning calorimetry/thermogravimetric (TG/DSC) analyses for all heat treatments. The final heat treatments consisted of preoxidation process in air and carbonization in the pure Ar atmosphere[3]. The preoxidation process is responsible for the final geometry, strength and defectless structure of the individual nanofibers and the carbonization in Ar provides amorphous carbon character of final flexible membranes. The structural characterization of the precursor and final carbon membranes was visualized and evaluated by X-ray diffraction (XRD), scanning and transmission electron (SEM and TEM) microscopy and average diameter of PAN-based fibers was 450 nm and PVA-based fibers 220 nm. The roughness of fiber surfaces was measured by the atomic-force microscopy (AFM) and the values of specific surface area S_{BET} of the studied material were processed by the Brunauer, Emmett, Teller (BET) isotherms. The higher roughness was observed on the PVA-based fibers membranes what is in accordance with the higher specific surface area and porosity. These cost-effective electrospun membranes have obvious importance as reinforcement of ceramic matrix composites, especially multilayer systems.

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Very fine AlN powder production from $Al(OH)_3$ using dynamic carbothermal reduction and nitridation

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Keywords: aluminium nitride, dynamic carbothermal reduction, powder production

Carbothermal reduction and nitridation (CRN) method used in nitride-based ceramic powder production is an effective and economic technique that has been studied extensively. In this study, CRN process was carried out in an atmosphere controlled modified tube furnace. Unlike conventional CRN method, this novel approach in producing ceramic powders called the dynamic CRN method (designated as DCRN for the nitride powder production) where granulated reactants in a cylindrical reactor are rolled continuously rotary-type tube furnace during the process by means of using a servo motor[1]. It is believed that the diffusivity within the reactants increases with the dynamic motion of the particles in the system during reactor`s rotation. Thanks to this dynamic movement, quality of final products/powders improved significantly after the DCRN process. The resulting product of narrow size distribution of very fine (below 300nm) equiaxed aluminium nitride (AlN) powders were produced in a relative short period of time and lower reaction temperature compared to conventional static system of CRN method[2]. New technique is also suitable for the industrial scale production of the high quality and economic nitride based ceramic powder production. Results of this study shows that high yield, high quality, uniax homogeneous powders of very fine size aluminium nitride (AlN) could be produced using DCRN method from $Al(OH)_3$+carbon granules. Based on the new powder production technique, the conditions of the manufacturing process and new design parameters for AlN powder production have been determined and demonstrated. High conversation ratio with single-phase of submicron AlN powders were synthesised at 1450 °C for 90 min from $Al(OH)_3$ using DCRN method.

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Solid oxide fuel cells electrolytes fabrication by stereolithography technologies

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Solid oxide fuel cells (SOFCs) are one of the more promising future power generation technologies due to their high efficiency and fuel flexibility[1,2]. Even though their reliability and their clear thermodynamic advantages compared to other technologies, the number of steps to build-up a stack of fuel cells and the complexity associated has made the technology not being completely mature[3].

Additive manufacturing technologies represents a breakthrough on ceramics processing which could make SOFCs widely industrial competitive and assure its fast market adoption[4–6]. Going through this idea, Cell3Ditor project is developing the fabrication of monolithic SOFC stacks which could reduce in a half the estimated cost of a stack.

In this work 8YSZ electrolytes fabricated by additive manufacturing at 3DCeram have been analyzed taking into account the sintering behavior, microstructural and mechanical properties.

These tests demonstrated that the technology is suitable to produce electrolytes for SOFCs.

Acknowledgments
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Magnetic exchange coupling in RSPS-consolidated hexaferrites

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Keywords: permanent magnets, spring magnet, spark plasma sintering, nano-structured ceramics

In spite of impressive progress in rare-earth permanent magnet (PM) technology, bulk hexaferrites $M^{2+}Fe_{12}O_{19}$ (M^{2+} is a divalent cation, typically Ba, Sr) still retain a dominant fraction of the world permanent market, due to their inexpensive primary sources and a well-known "mature" technology[1]. The recent developments on soft chemistry and sintering can give still a new place to nanostructured hexaferrites. In this work, we show that a combination of polyol synthesized precursors subsequently consolidated by Reactive Spark Plasma Sintering (RSPS) can lead to materials with a very high energy product, and hence a large variety of PM applications, Fig. 1. The experimental parameters can be tailored to produce the hexagonal phase with a small content of other iron oxides (hematite, magnetite), with fine interfaces between these components and therefore the onset of exchange coupling.

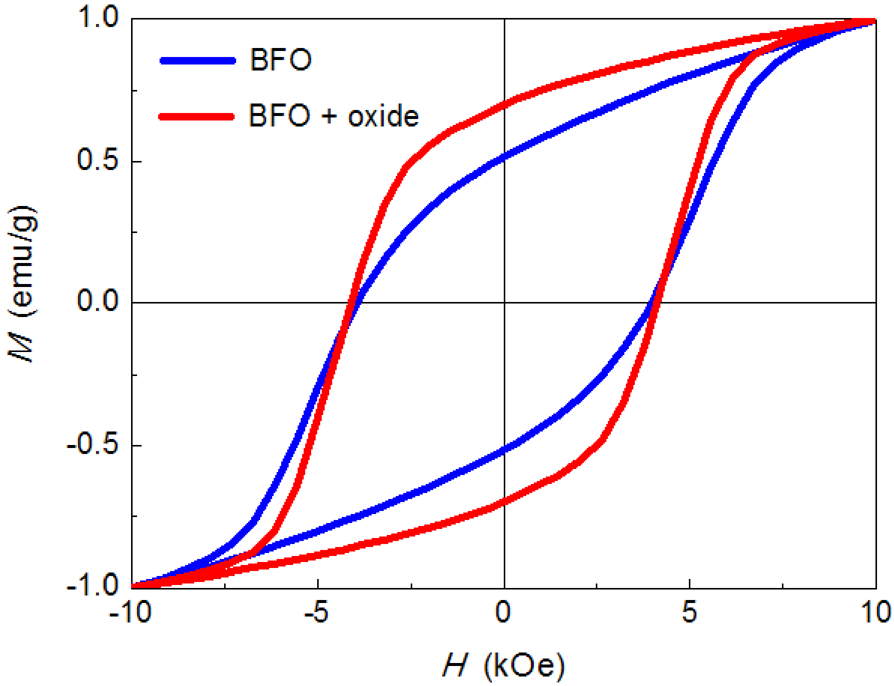

Fig. 1. Comparison of hysteresis loops (at RT) of pure $BaFe_{12}O_{19}$ (BFO) and BFO + iron oxide second phase. Saturation magnetization was normalized

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Sol-gel transparent nano-glass-ceramics base on SiO_2-GdF_3 matrix for optics applications

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Keywords: glass-ceramics, sol-gel, photonics applications

In recent years, Rare-earth (RE) doped transparent oxyfluoride nano-glass-ceramics (nGCs) materials obtained by sol-gel method at low-temperature processes have attracted much attention due to the possibility of use in a large variety of optic and photonic applications, such as infrared and tunable phosphors[1–3]. The inherent advantages of this method are the low sintering temperature, the versatility of the processing method (thin-films and bulk materials) and high purity and homogeneity of the materials obtained[4–6]. Moreover, this method also allows the incorporation of high quantities of fluoride precursors.

However, in the bibliography, oxyfluoride nGCs with composition up to 10 mol% of fluoride host without cracking has been only reported for its use in photonics applications. This fact was enough to carry out a study increasing the amount of fluoride. In the present work, undoped and RE^{3+}-doped transparent nGCs with composition of $(100\text{-}x)SiO_2\text{-}xGdF_3$, (x = 10 and 20 mol%), were prepared by a novel sol-gel route. Structural analyses have been realized by XRD, ATG/ATD, Raman, FTIR and HRTEM, revealing the GdF_3 nanocrystals precipitation. Photoluminescence studies confirm that RE^{3+} ions are located in the fluoride nanocrystals. As a result, adequate optical properties have been observed in these materials, showing up potential photonics applications.

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Analysis of melt pool characterization during selective laser melting by numerical simulation

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Keywords: selective laser melting, melt pool, numerical simulation, additive manufacturing

Selective laser melting (SLM) is one of the promising additive manufacturing processes and has been widely used for the fabrication of implants and aerospace components. However, many issues regarding process stability and the quality of the final parts arise during SLM manufacturing. One of the concern issues is the stability of melt pool, which may affect the formation of the so-called balling effect, pores, and other defects. This study adopted ANSYS-FLUENT software package based on the thermo-fluid dynamical multi-phase model to simulate the molten pool dynamics during SLM. In addition, the effects of various process parameters, such as laser power, scan speed, hatch spacing and layer thickness on velocity field, temperature gradient, cooling rate, melt pool sizes and surface morphology, and relative density were also investigated.

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Robocasting and co-sintering of a multimaterial device for radiofrequency applications

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Keywords: robocasting, co-sintering, mutimaterial, radiofrequency

Additive Manufacturing (AM) comprises a broad range of different techniques to build three dimensional objects layer-by-layer. It allows the design and rapid manufacturing of highly complex shapes with very few geometric limitations compared to traditional manufacturing processes. AM technologies enable the fabrication of complex and fully customizable parts made of functional or structural materials such as ceramic or metals. One of the main challenges in robocasting is the development of suitable paste formulations to print multimaterial devices with high resolution. Here we describe the printing of a copper/ceramic (low temperature co-fired ceramic) structure using robocasting with water-based inks. The solid content, the particle dispersion and the influence of the addition of Pluronic as rheology modifier are studied in order to achieve the optimal formulation. A co-sintering process has been developed to build an inductor for radiofrequency applications.

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Additive manufacturing of ceramics enabled by flash pyrolysis technique of polysilazane based polymers with nanoscale layers and oxidation resistance of final composites

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The key impediment to additive manufacturing of net shapes from Polymer derived ceramics (PDCs) has been the very slow heating rates with a process period of about 10 h, which are required to preempt fissures in the ceramic caused by shrinkage, and to allow hydrogen, as the polymer evolves into the ceramic phase, to escape.[1] For these reasons, the infiltration of fiber preforms from the polymer route, by the process known as PIP or polymer-infiltration-pyrolysis has been difficult. An additive manufacturing novel design has been developed at Colorado University to achieve CMC via preceramic route by reducing the time for pyrolysis to about few seconds (the so-called flash pyrolysis).[2] The goal of flash pyrolysis is to deposit preceramic polymer films around fibers having a thickness of few hundred nm; the pyrolysis of thin polymeric films leads to crack-free ceramic coating even when the heating treatment of curing and pyrolysis is carried out in few seconds. Full dense composites can be manufactured by repeating procedure of deposition and pyrolysis cycles. The wettability of fibers has been studied to permit a three-dimensional coating as well as the maximum thickness of the coating during infiltration to avoid cracks during shrinkage. Polysilazane polymer was used, pure or doped with [Hafnium(IV) tetra-isopropoxide], to achieve carbonitride (SiCN) and HfSiCN matrix respectively. The resulting CMCs were characterized by RAMAN spectroscopy to highlight the conversion of polymer into ceramic phase while microscopy analysis revealed the morphology of the coating from few deposition cycles to nearly-full infiltrated composite. Finally the oxidation resistance of coated single fibers and full infiltrated composites barriers has been investigated via TGA at increasing temperature and holding time.

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T02: High temperature processes and advanced sintering

Invited lectures

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Spark plasma sintering technique: a powerful research tool for developing new ceramic materials

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Keywords: SPS, ceramics, composites, graphene, carbon nanotubes

The search of new materials able to fulfil the increasing demanding operating conditions is frequently stopped by technological challenges. In this way, the spark plasma sintering (SPS), a pressure assisted pulsed direct current sintering technique, arises as a powerful research tool for developing bulk materials and ceramic composites with enhanced properties. As proof of concept, here we present few examples of new ceramics developed during the SPS process; in particular, a one-step approach for tailoring continuous *in-situ* functionally graded non-oxide ceramics from a sole homogenous powder composition, and the *in-situ* development of different multifunctional ceramic/carbon nanostructures (graphene or nanotubes) composites.

In the first example, continuous gradual mechanical properties (hardness and toughness) in the direction of the pressing axis for silicon nitride specimens were produced through the control of the temperature profile within the powder compact. This was achieved by both varying the SPS die-punches contact sections and introducing electrical insulators between the punch and the compact.[1] In the case of ceramic/carbon nanostructures composites with superior electrical and/or mechanical properties, different *in-situ* synthesis processes are presented: i) the growth of graphene sheets into a sole homogenous silicon carbide starting powder during the ceramics densification,[2] ii) the *in-situ* thermal reduction of graphene oxide films to graphene that takes place along with multilayered ceramics composite sintering,[3] iii) the carbothermal reduction of a 3D silica coated carbon nanotube network to *in-situ* develop silicon carbide/carbon nanotubes composites.[4]

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Sintering of ultra-fine nanocrystalline ceramics and how to avoid their growth

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Contradicting past reports, nanocrystalline dense ceramics have been recently shown to present mechanical properties that largely surpass those of the microcrystalline counterparts. The success in showing these properties relies on a highly controlled processing of nanoparticles followed by a densification process that minimizes grain growth and eliminates porosity. In this talk we discuss the novel Deformable Punch Spark Plasma Sintering method, in which a complaint tool is used to destabilize porosity at the final stage of densification of nanoparticles. The products are highly dense parts with grain sizes below 10 nm and unprecedented hardness. While these are interesting products by themselves, it is well known that coarsening can occur in such samples during operation conditions or further processing, limiting life time of the nanostructures at high temperatures due to the inherent excess energy coming from interfaces. Therefore, we further discuss in this talk how, by targeting a decrease in grain boundary energy, one can enable the creation of highly stable nanocrystalline ceramics, with virtually zero excess energy coming from interfaces.

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Reactive sintering activated by SPS

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The Spark plasma sintering gives new possibilities to sinter ceramics and composites which are traditionally very difficult to sinter. Together with the electric field, the rapid heating rate and short holding time give an additional driving force for the sintering making it possible to reach the eligible microstructure as well gives possibilities for the reactive sintering and synthesis. The reactions can be controlled during the sintering by changing the sintering profile giving possibilities to tailor the product and their microstructures simultaneously.[1,2]

Boride based materials are interesting for their good physical and chemical properties. They have high melting point and are chemically very stable against oxidation, thus can particularly be used in extreme environments at ultra-high temperatures. Due to the very high hardness but modest toughness and low self-diffusion coefficient their sintering is very difficult by conventional methods.

In order to improve the density of TiB_2, reactive sintering from the precursor powders was conducted. The reaction was aided by a small addition of conducting magnesium which increased the current flow inside the sample. This created many ignition points for the reaction between Ti and B which continued then in a self-propagating manner.[3] The rapid reaction and sintering improved the microstructure compared to the mixture without magnesium. When similar test to react TiB from precursor powder was tried in SPS it was obvious that the fast process could not finish to equilibrium during the short sintering times in SPS but reaction products were mixtures of different borides. When zirconium diboride based composites was sintered by reactive spark plasma sintering (RSPS) a significant grain refinement was observed increasing the grain size control and improvements of the properties. Also, by intentionally choosing a mixture of coarse and fine powders as the reactants, dual microstructure ceramics with simultaneously improved toughness and strength could be obtained.[4]

It is also possible to improve sintering and plastic deformation of sialon while adding a $LiCO_3$ in order it to react during the sintering with the glassy phase and in that way decrease the viscosity of the liquid phase and improve the non-equilibrium sintering and deformation of the sialon.

The SPS in argon atmosphere will open the possibility to sinter reaction-sensitive materials. Lithium hydride compounds has been tried to synthesize in SPS in protective atmosphere. The evaporation of lithium and its intercalation with graphite during the synthesis was avoided by inserting a closed crucible inside the graphite die. The protective atmosphere has also been shown to be beneficial to avoid the formation of ZnO in ZnSb compounds. The formation of ZnO was decreased to undetectable by X-ray.

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Segregation and surface excess during ceramic process and sintering

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Keywords: segregation, surface excess, sintering, surface energy, nanoparticle

Segregation is the process that differentiates the composition at an interface or surface from the average or bulk composition, and it is well-known in the metallurgical processes. However, it can often be mistaken as a process that occurs out of equilibrium due to the rapid cooling. Surface excess is a more generally term used in the thermodynamic of equilibrium for adsorption processes. In ceramic, the interface excess has been observed as a common phenomenon due to gas adsorption in surface and additive segregation in surface and grain boundaries and, consequently, changing the chemical compositions of the interfaces. That has a significant influence in the colloidal process, nanoparticle size stability, phase stability and sintering as well as in the ceramic application due to the reduction in the interface energy. The aim of this work is to point out the main mechanisms of interface segregation in ceramic materials and to present some consequences in the colloidal process, nanoparticle size stability, phase stability and sintering.

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Fundamentals of sintering and their future research directions

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Sintering, the oldest human technology with the firing of pottery, is an essential technique for fabricating ceramic materials and components. Although the technique has been used for over several thousand years, its scientific studies began only in the middle of the 20th century. During the past 70 years, sintering models and theories have been developed under the assumption that only the atom transport governs the sintering kinetics, and the results of sintering studies have been interpreted in view of the developed theories. The classical assumption, however, was recently found to be valid only for systems with rough interfaces.

This presentation will first review the classical descriptions of solid–state sintering (SSS) and then liquid–phase sintering (LPS) as well. For SSS, densification models and kinetics are presented. For LPS, the fundamental difference between two existing models of densification, contact flattening and pore filling, are explained. Microstructural evolution with normal grain growth during SSS and LPS are described.

At the beginning of the 2000s, we found that densification, grain growth and microstructural evolution are largely governed by the structure of grain boundaries (for SSS) and solid/liquid interfaces (for LPS).[1–5] When the driving force is smaller than a critical value, the reaction of atoms at the interface governs the sintering behavior and kinetics for systems with faceted (even partially) boundaries and interfaces. For faceted systems, the classical theories of sintering are, therefore, not valid and new theories need to be developed to properly describe the sintering kinetics and microstructural evolution. Remaining issues are suggested to achieve this goal.

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Reactive metal infiltration for manufacturing of ceramic matrix composites

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The reactive melt infiltration process is a versatile route to manufacture nonoxide fiber reinforced ceramics (CMC). In general a fibrous preform is manufactured with Carbon or SiC fibers. The fibers are surrounded by a porous matrix which shows an adjusted pore morphology for the succeeding melt infiltration process. Depending on the composition of the reactive alloy melt and the desired final matrix state Carbon, SiC or filler particles as borides are introduced in the porous matrix. Ideally all constituents react in the desired manner with the alloy to a more or less dense matrix.

The process strategy to manufacture damage tolerant tough and dense composites is shown. The resulting properties of C/SiC, SiC/SiC as well as ultra high temperature ceramic matrix composites UHTCMC are discussed and correlated with the key aspects of manufacturing steps. One example is the design of the fiber matrix interphase which needs to survive the reactive melt infiltration and furthermore must provide crack deflection in order to prevent brittle failure of the composite.

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RMI-derived ceramic matrix composites based on the liquid-phase pyrolysis of carbon/carbon

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Keywords: ceramic matrix composites, RMI, thermoplastics

Ceramic matrix composites (CMC) manufactured via Reactive Melt Infiltration (RMI) processes, in particular by Liquid Silicon Infiltration (LSI), are well-established structural ceramic materials, used in gas turbines, thermal protection systems of spacecraft or brake systems. Typically, the requirements on these applications differ widely with the consequence that the microstructure should be tailored to different properties.The RMI-process offers unique opportunities for microstructure modifications as the fiber/matrix interphase can be modified easily by thermal fiber pre-treatments which varies the functional groups on the fiber surface. Also, a post-treatment of the amorphic carbon matrix beyond 1600 °C result in different microstructures.

Carbon/Carbon (C/C) composites derived from thermoplastics like PEI or PEEK were pyrolized up to 1000 °C and subsequently carbonized in inert atmosphere up to 2200 °C. The increased carbonization temperature leads to a higher carbon order as well as an incipient stress-induced graphitization of the carbon matrix close to the fiber surface at 2200 °C. The C/C-SiC composites show a maximum flexural strength of 180 MPa and monotonically increasing Young's moduli ranging from 49 GPa with C/C preforms treated at 1600 °C up to 59 GPa after carbonization at 2200 °C. The correlations between the mechanical properties, the microstructure and the material's composition is discussed. whole text should fit to this single page.

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Cold, flash, sparks, nano – where are sintering processes headed?

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Recent times have seen an explosion of innovative means to densify ceramics at significantly lower temperatures and much shorter times. These innovations have capitalized on either massive increases in driving force by using >100 MPa pressures, or exceptional changes in kinetic processes that enable faster diffusion over short-range distances. This presentation analyzes the spectrum of conditions reported using the sintering approaches listed in the title and summarizes these novel processes in terms of sintering driving force differences and mechanistic alterations in transport required for densification of ceramics powders. In the end, we project how these novel sintering processes will impact commercial sintering technology.

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Novel processing for unique porous ceramics

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Keywords: pore, processing, freeze-dry, ceramics, microstructure, mechanical properties

Porous ceramics are now being used for environmental protection such as diesel particulate filters (DPF), coal gasification gas filters, separation membrane supports, and catalyst supports. It is expected that these applications will be further expanded in future, as the concerns over environmental issues become more crucial in all the countries over the world. A number of innovative processing routes developed for critical control of pores are described, along with some important properties. This paper intends to give an overview on the recent progresses of porous ceramics (mainly macro-porous ceramics whose pore size is larger than 50 nm) prepared via powder processing routes. The partial sintering of powder compacts, the most conventional technique for making porous ceramics, has been substantially sophisticated in recent years. Very homogeneous porous ceramics with extremely narrow size dis-

tribution have been successfully prepared through sintering combined with *in-situ* chemical synthesis. Carefully tailored microstructure (size, morphology and orientation of grains and pores, etc.) of porous ceramics has led to unique mechanical properties, which cannot be attained even in the dense materials. Powder processing with various types of the sacrificial fugitives also has been examined for obtaining well-tuned shape and size of pores. The freeze-dry techniques using water or liquid as fugitive materials have been most frequently studied in recent years. Controlling growth of ice during freezing has led to unique porous structures and excellent performances of porous ceramics.

As an novel processing approach for unique porous structure, special emphasis is placed on the advanced gelation-freezing methodology for macroporous ceramic components, that can create nearly honeycomb shaped pore channels, unlike either ellipsoidal or dendric or lamellar structures obtained via conventional aqueous freeze casting. Three main technological features will be discussed in terms of 1) honeycomb shaped porous structures, 2) relationship between carefully selected freezing conditions and cell properties generated, 3) mechanical properties and applications of the obtained porous ceramics. This simple, ecofriendly and versatile approach tailors porous architecture with engineered porosity and yields macro-cellular component with distinctive characteristics of fluid permeability, mechanical properties, machinability, and thermal insulation properties, suitable for a variety of industrial applications.

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Ultra high temperature ceramic matrix composites based on carbon fibres

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Keywords: UHTCMC, carbon fibre, infiltration

Ultra High Temperature Ceramics (UHTCs) are potentially excellent materials for use in severe aerospace environments, for example as nozzle inserts and/or thermal protection systems (TPS). However, although they are refractory materials and have melting temperatures above 3000 °C[1–3], their poor thermal shock means that they need to be reinforced and used as CMCs. The use of carbon fibre reinforcement is possible as long as it can be protected at the application temperatures. In the present work, carbon fibre preforms have been impregnated by different UHTC slurries to fill the inter-tow porosity between the different orientation plies of the preform and then infiltrated with a UHTC matrix using a CVI technique based on radio frequency (RF) heating to fill both the intra-tow porosity and the residual inter-tow porosity. Operating at 150–400 kHz and with a maximum of 4.2 kW, the temperature of the sample was controlled using a 2 colour pyrometer and the pressure used was in the rage of 15–100 mbar. The advantage of RF heating is the inverse temperature profile that develops in the sample, which means that the infiltration starts from inside out. The consequent reduction in process time is significant in comparison with a more conventional CVI process.

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Recent advances in current assisted sintering

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In recent year there has been much excitement and debate about flash sintering, which has reinvigorated interest in other processes involving direct Joule heating. SPS is still the dominant electric current sintering technology and has already been be used to Flash SPS (FSPS) various materials. This talk will discuss some simple methods to evaluate the possibility of flash sintering different materials using SPS equipment. A more complex model of the entire sintering process was also developed. But this required revaluating many assumptions used in the previous work, in light of the highly no equilibrium conditions of flash sintering. With a robust model in place optimized tooling and heating profiles have been developed for FSPS. Thermoelectric materials proved to be an excellent test case for this technique due to the significant effect of microstructure on the functional properties. Skutterudite thermoelectric materials was successfully FSPSed to near full density and samples with unique microstructures and properties were achieved.

Acknowledgements

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Densification strategies for Ultra High Temperature Ceramics prepared by Near-Net-Shaping Techniques

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Components for hypersonic applications have relied on Ultra High Temperature Ceramics to withstand high temperatures, high stagnation pressures, vibrations and extreme oxidation conditions associated with the speed, flight and reentry conditions. These components often require a complex geometry and a fully dense, fine and controlled microstructure. The current state-of-the-art processing of these materials allow their full densification but not the shaping capability. Near-Net-Shaping Techniques involving the colloidal processing of UHTC powders can afford to provide near-net-shaped pieces, but because of the shape, the sintering needs to be done using pressureless conditions. This work will discuss the strategies to enhance the densification of these materials: particle packing in the green bodies (by the control of the interparticle forces in solution), sintering temperature and profiles and additives, and how these results compare with the current state-of-the-art densification. These strategies have allowed to reach 93% TD without sintering aids at 2100 ^{o}C and 98% TD with sintering aids and modified sintering profiles. This work also show some of the shapes and some of the temperature testing performed in samples produced using colloidal processing and pressureless sintering combined approach.

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Effect of sintering temperature on crystallization of nepheline-leucite glass-ceramics

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Ball milling is an effective method of mechanically reducing the crystallite size after crystallisation. However, pre-crystalised glass particles tend to hinder the densification process during sintering. Introducing a green compact to a sintering temperature higher than the crystallisation one can allow for sufficient viscous flow to occur in some cases. However this can result in changes of the crystalline phase/s, size and morphology as well as the residual glassy phase composition. Therefore, the aims of this study were to investigate the effect of sintering temperature on crystallisation of alkali rich alumina silicate glasses. Wherein, two different glass compositions based on a multicomponent system were synthesised using melt-quench method. The experimental glass powders were prepared by ball milling for 2 hours and sieving below <125 µm (mean glass powder particles, D50 = 25µm). Thereafter the prepared powders were divided into two groups one of which (group A, G1 and G2) was left as glass powders for sinter-crystallisation experiment from green compact; whereas the second (group B, GC1 and GC2) was heat-treated to produce glass-ceramics powders. The prepared glass-ceramics were ball milled for 2 hours back to find powders. Thus, sintering experiments were conducted on glass powders (G) and pre-crystalised glass powders (GC). Glasses and glass-ceramics were characterised before and after sintering using differential scanning calorimetry (DSC) Dilatometry (DIL), X-ray diffraction (XRD) and Nuclear Magnetic Resonance (NMR). The crystalline microstructures of the glass-ceramics were analysed using scanning electron microscopy (SEM) before and after sintering. Results illustrated a tendency towards a decrease in grain size with increasing the sintering temperature in group B (GC1 and GC2). This paper will discuss further the sintering results for both groups in relation to crystallisation, different crystalline phase developments, crystallite size and morphology.

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New insights into field assisted sintering through synchrotron X-rays computed tomography investigations

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Keywords: spark plasma sintering, alumina, synchrotron X-ray, computed tomography

The emergence of spark plasma sintering (SPS) has been seen as one of the most effective sintering technologies for powdered materials including metals, ceramics, glass, biomaterials and even polymers.[1–5] Since the first patent of Inoue half a century ago,[6] SPS has been developed based on the assumption that using discharge or plasma induced by pulsed electric currents coupled with the application of uniaxial mechanical pressure could favor the short time and low temperature sintering of advanced nanostructured materials. However, despite the tremendous technological advances in electric current-activated/assisted sintering,[6] a large gap still exists between the numerous experimental studies of the process parameters and the fundamental understanding of the underlying mechanisms of SPS. This difficulty in understanding the salient mechanisms could be due to the numerous physical couplings (electrical–thermal–mechanical)[7,8] encountered in this process. Among the non-elucidated hypothetical mechanisms, such as plasma (or micro-discharge) cleaning of particle surfaces before sintering activation,[9] Joule heating,[10] electromigration,[11] local melting and evaporation, [12] or thermal diffusion by Soret effect, the existence of plasma has been cited routinely without providing evidence or justification. In the present investigation, we propose a novel experimental approach to highlight the SPS mechanisms during early –stage sintering of non-conductive ceramics. We use *ex-situ* synchrotron X-ray beamlight (SSRF Beamline BL13W1), and computed tomography techniques to reveal particular details of the sintering necks and mechanisms during SPS. We discuss these results in the framework of thermal instabilities theories.

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Strong junctions of Alumina to TZM alloy obtained by coupling oxidation of the alloy and diffusion bonding

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Keywords: ceramic to metal joining, diffusion bonding, TZM oxidation, adherence, ASTM C633

The new ceramic to metal junctions must make possible to use the pieces at high temperatures in aggressive environments, with good mechanical properties, including fracture toughness.

First of all, the materials to be joined must have high Tammann's temperatures, for avoiding the effects of unwanted diffusions leading to the recrystallization of the metal and to creep; moreover, their coefficients of thermal expansion (CTE) must be close.

The TZM alloy (Mo99/Ti0.5/Zr0.1) melts at 2600 °C and recrystallizes at 1400 °C, which is better than pure molybdenum, with identical physical and corrosion properties.

Hence it seemed well suited for a ceramic to metal assembly with alumina ($T_F = 2072$ °C), the CTE of which being close to that of TZM, respectively 5.4×10^{-6} and 5.3×10^{-6} K^{-1} at room temperature.

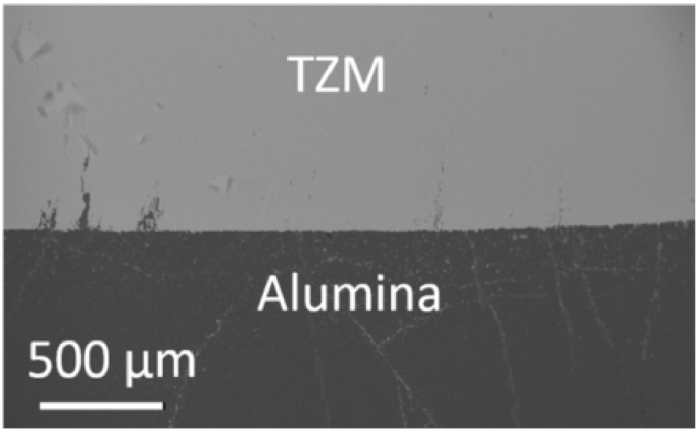

Fig. 1. SEM photograpy of an alumina to TZM interface by diffusion bonding

In this study a joining approach without filler alloys interphases, or metallization is investigated. The proposed method is based on diffusion bonding by thermocompression. Of course, the direct joining of TZM to alumina is thermodynamically impossible and an important preliminary step is required. This step consists in the preoxidation of TZM in air.[1]

The ceramic to metal adherence of the obtained assemblies (Fig. 1) was tested via the mechanical ASTM C633-13 traction test, but the adherence values could not be determined because the fractures occurred in the glue during the test, for a rupture stress of 45 MPa. This means that the adherence of the alumina /TZM adherence was higher than 45 MPa.

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Flash sintering of alumina

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Keywords: flash sintering; alumina; sintering

Flash sintering is an innovative energy saving densification technology, which allows a consistent reduction of the consolidation time and temperature for many ceramic materials.[1,2] Flash sintering belongs to the family of field/current assisted sintering technique; however, it possesses some peculiar characteristics mainly associated to the presence of the so called flash event. This is characterized by a very rapid heating of the specimen based on Joule effect, which is in the order of 10^4 K min^{-1}.[3] Meanwhile, a drop in the electrical resistivity takes place and the material densifies in few seconds. Such phenomenon is also associated to a strong bright light emission.

In this work, we apply flash sintering to 99.8% pure α-alumina using different combinations of DC current/field. Densification and microstructural evolution are studied as a function of the process parameters. Different microstructures are pointed out in proximity to the electrodes. Such asymmetry is very likely associated to partial reduction of the oxide upon the final stage of the process, after the flash event. Finally, the analysis of the light emission points out its fundamental thermal origin.

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Joining steel to yttria doped hafnia with a reactive brazing for a potentiometric oxygen sensor in sodium

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Keywords: SFR, potentiometric sensors, yttria-dopped hafnia, reactive brazing, steel

Within the framework of the development of the fourth generation of nuclear reactors, a Sodium cooled Fast Reactor (SFR), named ASTRID (Advanced Sodium Fast Reactor for Industrial Demonstration) is in a basic design phase. A SFR operates in a specified oxygen content range in order to control the corrosion of the steel structures of the core (claddings…). Potentiometric sensors allow to obtain a fast and specific measure complementary to others devices (plugging indicator). In most advanced designs, the solid electrolyte of the sensor, generally made of yttria-doped thoria (YDT) or more rarely hafnia (YDH) is brazed on a steel with a controlled thermal expansion coefficient, in order to limit the size of the ceramic tube and to insure that it is fully immerged in sodium at constant temperature.

As no potentiometric sensors specifically designed for liquid sodium are commercially available, the CEA decided to develop its own. In the past, brazing was found to be a critical part of the success of the sensor, so a new assembling method was investigated and a reactive brazing was developed and patented.[1] The first tests are conducted on YDH, as a surrogate material for YDT (similar expansion coefficients). Their purpose was to ensure that a correct mechanical strength could be obtained for the joint and to examine the effect of the brazing parameters on the reactive layer.

The brazing between the steel and the oxide ceramic is performed by forming an eutectic between a zirconium foil and the Fe-Ni steel on one interface and by the formation of an oxide layer on the other interface, zirconium reducing the ceramic. The Fe-Ni-Zr eutectic temperature is about 940 °C and the oxygen diffusion in the ceramics must be fast enough so the layer can be formed in a few minutes at the interface. The yttrium doping provides oxygen vacancies, which induce a high ionic conductivity in the oxide.

Tests were performed in induction and tubular furnaces under vacuum at temperatures between 980 °C and 1080 °C. It was found that too high temperatures do not allow good quality joint, because of a too large reduced area in the ceramics and too important wetting of the steel by the zirconium foil. Obviously, the formation of the oxide layer is not limited by the diffusion in the oxide. It was also found that this layer is enriched in iron, which could be a drawback for sodium corrosion resistance of the joint. Cracks were often found at the interface or at 45° in the YDH oxygen depleted zone. Better mechanical resistance and lower cracking were obtained by using a Zr machined ring rather than a foil.

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Emulsion detonation synthesis (EDS) as an alternative route for YSZ outstanding based materials

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Keywords: EDS, Y-TZP, mechanical properties, Metal Matrix Ceramic

Emulsion detonation synthesis (EDS) is a unique manufacturing powder synthesis process that through the high pressure thermodynamic variable enables the manufacture of nanostructured powders with customizable properties and excellent mechanical performance.

Involving a cycle of high temperatures, pressures and rapid quenching, EDS produces nanostructured ceramic powder with extremely favorable properties compared to conventional micro-structured powders ensuring the control of powder chemistry, uniform grain sizes, low sintering temperatures and enhanced physical and chemical properties.

ZrO_2 doped with 2% mol Y_2O_3 ceramic powders was synthesized through this method, obtaining outstanding mechanical properties for sintered ceramics (14 MPa $m^{0.5}$, 1200 MPa and 1250 MPa of fracture toughness, biaxial flexural strength and hardness (HV10) respectively) without being significantly affected by the ageing process typically for 2YSZ ceramics synthesized by other methods.

New Metal Matrix Ceramic (MMC) inter-granular composites with remarkable dielectric, magnetic and mechanical properties can be prepared through EDS. Through the control of the detonation atmosphere (reduced atmosphere), these composites can be supplied to the market with well distributed reduced metal on the surface of the base ceramics. This configuration excludes the reduction step during processing, increasing the yield of the production process of these specialties by the Ceramic Industry.

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Study of the shaping and sintering ability of lanthanide oxide powders

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Keywords: cerium oxide(IV), spent nuclear fuel, powder morphology, sintering

This research is focused on reprocessing and recycling of future spent nuclear fuels. Some previous studies[1,2] have shown that recovering actinides such as uranium and plutonium from the spent nuclear fuels through an oxalic co-conversion process can be a suitable route to synthetize actinide mixed oxides. At last, this latter could be used to fabricate new nuclear fuel.

The main objective of this study is to evaluate the shaping and sintering abilities of these ceramic powders. In particular, it appears critical to find correlations between powder morphology, green body's characteristics and sintering behaviour. This preliminary work was carried out on a surrogate of actinide oxides[3]: ceria CeO_2 and then transposed to the uranium dioxide UO_2. The first experimentations were related to the using of uniaxial pressing followed by pressure-less sintering treatment under air or argon hydrogenated atmosphere.

A commercial powder and a powder synthetized by oxalic precipitation of different morphology (crystallite size, agglomeration state, etc.) were used. They showed different shaping and sintering abilities depending on their initial morphology. First, it appears that the green density of pellets obtained after pressing depends on the size, the morphology and the agglomeration state of the elementary particles. For example, aggregation of particles resulting from the oxalic precipitation way inhibits the compaction ability during shaping. Secondly, the densification phenomenon observed during pressure-less sintering under air occurs in the 1000–1400 °C temperature range for both powders. This temperature remains significantly low compared to the refractoriness of CeO_2 and can be attributed to the high reactivity of submicronic size powder particles. Beyond this temperature, the grain growth becomes quicker and leads to micro-sized grains after sintering. Aggregated nanoparticles obtained from oxalic precipitation way show a differential sintering ability due to firstly the densification of intra-agglomerate porosity at low temperature ($T < 1000$ °C) and secondly to the inter-agglomerate porosity at higher temperature (1000 °C $< T < 1400$°C). To prevent this differential densification, it would be pertinent to improve powder characteristics by employing supplementary grinding and/or deagglomeration step. Finally, green bodies with more uniform crystallite and pore size could be thus obtained leading to higher densification ability and more uniform microstructure evolution during sintering.

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Invasive percolation model for flash sintering of ceramic powders densified by liquid film capillary

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Rapid sintering and densification of ceramic nano-powder compacts by spark plasma sintering (SPS) and flash sintering (FS) are attractive and novel fabrication methods for the near future. During the last decade, enormous efforts invested towards the modeling of the densification mechanisms during the SPS and FS. The high densification rates observed during SPS explained by the formation of local spark and plasma due to the particle surface discharges, materials jets, liquid assisted particle rearrangement and densification, as well as local plastic deformation. However, many aspects of the densification mechanisms during FS are still unclear and subject to scholarly debate. Here invasive percolation model used to describe the universal rapid densification of ceramic powder compacts subjected to flash sintering. The electrical system is composed of two types of resistances of the particles and their contact points. The particle contact points with the highest relative resistance first melt due to preferred local Joule heating followed by thermal runaway. Further local melting has a hierarchical nature and its occurrence propagates as a front. The flash event represents the percolation threshold by invasive nature of melt at the particle surfaces between the two electrodes. The rapid densification is associated with local particle rearrangements due to attractive capillary forces induced by the liquid film at the particle surfaces.

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Microstuctural and electromagnetic study of a CuNiZn ferrite obtained by a non-traditional ceramic process

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Keywords: ferrites, sintering, microstructure, electromagnetic properties, grain size

Ferrite powders containing nickel, zinc and different amounts of copper are typically used as electromagnetic wave absorbers. It is very difficult to control the absorption capacity of a given material, as the attenuation properties of electromagnetic wave absorbers depend on several factors, such as complex permeability, complex permittivity, frequency, and thickness. Moreover, certain magnetic properties such as the saturation magnetic moment depend only on the material's chemical composition, whereas others, such as permeability loss, also depend on other factors, of which material microstructure is the most critical. Thus, for a material to act satisfactorily as an electromagnetic wave absorber, high sintered relative density (low porosity), little average grain size growth, and narrow grain size distribution width are required.

Numerous studies have shown that the mechanical and/or physical properties of ceramic bodies improve when particle-size distribution decreases from the microscale to the nanoscale, but controlling the grain growth of the nanometric particles by a conventional sintering process is really hard work. In this line, a non-traditional ceramic process has been used for sintering nano-sized copper nickel zinc ferrites in order to control the grain growth process. The microstructure of the sintered ferrites has been analysed by SEM and EDX, determining the grain size distribution, pore size distribution, grain boundary morphology and precipitate second phases nature. The electrical permittivity and magnetic permeability of the sintered ferrites has been determined, as well as the evolution of the ferrite absorbance with frequency, and correlated with the microstructure results and with the physical properties of the samples. These results have been compared with the ones obtained by a traditional ceramic process.

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Powder chemistry effects on the sintering of Bayer alumina

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Keywords: sintering, alumina

Commercial high purity Bayer aluminas are typically 99.8%–99.9% pure and contain Na_2O, SiO_2, Fe_2O_3, and CaO as main impurities. During heating these impurities can combine to form a nanometer thick liquid phase at the grain boundary that controls the sintering behavior of the powder. We show that the viscosity and solubility of Al_2O_3 in the liquid phase are strongly affected by impurity chemistry. In this work we systematically show how the sintering kinetics and fundamental sintering mechanisms of Bayer alumina change as a function of the total amount and fractions of the different impurities and dopants. High-resolution TEM and EDS studies reveal how physical and chemical characteristics of the grain boundaries change as a function of powder chemistry, leading to an understanding of the observed sintering behavior. By comparing the sintering kinetics, grain boundary chemistries and structures of MgO-free and MgO-doped Bayer aluminas, we identify when MgO affects sintering and gain some insight about the role of MgO during the sintering of Bayer alumina.

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Densification and mechanical behavior of spark plasma sintered $Ta_{0.8}Hf_{0.2-x}Zr_xC$ (x = 0–0.2)

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Keywords: spark plasma sintering, ultra-high temperature ceramics, carbides, mechanical properties

TaC, HfC and ZrC are known as ultra high temperature ceramics with the melting point above 3400 °C. Spark plasma sintering is a new route for consolidation of materials, specially these UHTCs, which are difficult to be sintered at temperatures lower than 2000 °C. The purpose of this study was to consolidate $Ta_{0.8}Hf_{0.2-x}Zr_xC$ ceramics by spark plasma sintering using $MoSi_2$ and $TaSi_2$ as sintering aid and investigate their mechanical properties. Fully consolidation of $Ta_{0.8}Hf_{0.2-x}Zr_xC$ was achieved in presence of 12 vol.% sintering aid at 1650 °C for 5 min under 30 MPa. Sintering procedure consisted of two stages: the first stage occurred via plastic deformation of sintering aid particles, while the second stage was due to $Ta_{0.8}Hf_{0.2-x}Zr_xC$ solid solution and liquid phase formation. XRD patterns, SEM images and micro indentation test revealed that *insitu* formed SiC significantly increased the fracture toughness.

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Fracture toughness properties of spark plasma sintered boron carbide ceramics using Ti and TiO_2

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Keywords: boron carbide, titanium, titanium oxide, spark plasma sintering, fracture toughness

B_4C-TiB_2 composites were produced by spark plasma sintering (SPS) technique with 5 and 10 vol. % in two different ways. In first set of experiments, metallic titanium with different particle sizes are used to form TiB_2 whereas in second set of experiments reactive spark plasma sintering is attained by adding titanium oxide and C-black to B_4C. All of the experiments were carried out at 1550 °C by applying 40 MPa pressure under vacuum atmosphere with

4 minutes holding time. The final products having hexagonal geometry (61 mm diagonal, 10 mm height, and 31 mm length) were spark plasma sintered for the first time in literature. The relative density were examined by Archimedes method, hardness and fracture toughness of samples were evaluated by the Vickers indentation technique and microstructures of all samples were observed using scanning electron microscopy (SEM).

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Development of translucent silicon nitride ceramics by SPS process with various additives

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Keywords: silicon nitride, translucency, spark plasma sintering, sintering additives

Polycrystalline translucent Si_3N_4 ceramics are receiving a great attention in a special optical application owing to its high mechanical strength and thermal and chemical stability. However, Si_3N_4 is poor in sinterability because of its strong covalent bonding. To achieve the translucency of Si_3N_4 ceramics, appropriate sintering condition and sintering aid are required. High density, fine-grained microstructure and a low content of sintering aid are important to reduce the light scattering by pores, grains and grain boundary phase. The spark plasma sintering (SPS) is effective to produce highly-densified sintered bodies with fine-grained microstructure because of the high heating rate and short-time sintering.

Translucent Si_3N_4 ceramics were tried to fabricate by the SPS process using binary additives of AlN-MgO, AlN-Y_2O_3 and Al_2O_3-Y_2O_3 systems and single additives of MgO and Y_2O_3 systems. The sintering additives of AlN-MgO and AlN-Y_2O_3 systems typically form SiAlON-like composition by reaction with Si_3N_4. In the present systems, a liquid-phase sintering mechanism is expected in SiO_2-Al_2O_3-MgO and SiO_2-Al_2O_3-Y_2O_3 systems, in which Si_3N_4 includes impurity SiO_2 and AlN includes impurity Al_2O_3. MgO and Y_2O_3 also form the oxide liquid phase with SiO_2. The translucency of sintered body was evaluated in visible light region.

Fine α-Si_3N_4 powder with high purity was useful to achieve the high translucency of sintered bodies. When the content of additive was large, α -SiAlON formed in AlN-MgO and AlN-Y_2O_3 systems with a high translucency, and β -SiAlON in Al_2O_3-Y_2O_3 system with a low translucency. On the other hand, β-Si_3N_4 formed at a small content in AlN-MgO, AlN-Y_2O_3 and Al_2O_3-Y_2O_3 systems, and exhibited a high translucency. This means that the crystalline phase is not important for optical translucency. Although the rod-like grain growth of β-Si_3N_4 causes light scattering, the fine-grained β -Si_3N_4 ceramics achieved the high translucency even in Al_2O_3-Y_2O_3 system. In the single additive systems, all sintered bodies were β-Si_3N_4. The high translucency was achieved at a small content of Y_2O_3 but not in a large content. The translucency was low in MgO system at any additive content. The factors on translucency will be discussed on the base of sintered morphology and additive composition.

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Ultra-fast firing: the role of heating rate in flash sintering

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It has recently been reported that in "flash sintering", ceramics can be sintered in a few seconds with the aid of an electric field. It is generally assumed that this dramatic acceleration in sintering rate is directly related to the presence of the electric field. This presentation considers the alternative possibility that the accelerated sintering is instead a consequence of the rapid heating rate involved in flash sintering rather than a direct effect of the electric field on mass transport. The sintering of 3YSZ powder compacts at temperatures of 1100–1300 °C and dwell times of 5 s–2 h was compared with heating rates of between 0.08 and ~100 °C/s. Both flash sintering and alternative heating methods producing rapid heating without the application of an electric field to the specimen were used. The results show that rapid heating can accelerate sintering by over 2 orders of magnitude compared with heating to the same temperature at conventional rates, even without the application of an electric field. It is concluded that much of the acceleration of densification in flash sintering of 3YSZ is a consequence of the rapid heating involved rather than being a direct effect of the electric field. Possible explanations are discussed with reference to the observed microstructures.

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Processing of single phase $EuTiO_3$ bulk ceramics – the effect of processing conditions

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Keywords: perovskite, bulk ceramics, solid-state reactive sintering

The $EuTiO_3$ is frequently studied rare-earth perovskite system, which exhibits in the bulk form incipient ferroelectricity; the ferroelectric behaviour was observed only in the epitaxial thin films under large biaxial compressive strain.[1] It also exhibits anti-ferromagnetic ordering

(G-type) below $T_N \approx 5.3$K.[2] The research of magnetoelectric properties of this material suffers due to problems with processing of this advanced ceramic material. Bulk samples had either phase impurities in the form of pyrochlore ($Eu_2Ti_2O_7$) or high porosity (around 20% t.d.). The absence of thermodynamic data is the crucial issue in the field of novel advanced material processing. In the case of $EuTiO_3$ ceramics, it means that it is not possible to establish the optimal experimental setup by thermodynamic calculations therefore the role of experiment is irreplaceable.

The main objective of this research was the preparation of phase-pure bulk dielectric $EuTiO_3$ ceramics with minimum of microstructural defects. The solid-state reactive sintering experiments were performed with isostatically formed green bodies (300 MPa) at different temperatures in reduction atmosphere with varied hydrogen partial pressure and flow. Processing conditions were optimized with the aim to (i) ensure the chemical reaction of oxide precursors, (ii) allow the reduction of europium from +3 to the +2 oxidation state and (iii) prevent secondary phases and/or microstructural defects formation. The single phase $EuTiO_3$ samples with electric resistivity varied from dielectric to conductor level were prepared during the experiments and the effect of processing conditions on microstructural and functional properties was discussed.

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Spark plasma sintered single phase Ca-α-SiAlON ceramic utilizing nano-sized precursors at lower temperatures

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Keywords: nano-ceramics, SiAlON, silicon nitride, spark plasma sintering

The present work aimed to the development of nitrogen rich single phase alpha(α)-SiAlON by spark plasma sintering (SPS) technique, utilizing nanosized starting powders and incorporating calcium oxide (CaO) as a densification additive. A decrease in sintering temperature along with enhancement of mechanical properties was anticipated.

Spark plasma sintering was used to process single phase Ca-α-SiAlON employing nano-sized precursors at relatively lower temperatures of 1500 °C and 1600 °C for three different holding times (10, 20 & 30 min) at respective sintering temperatures. The chemical composition of nitrogen rich Ca-α-SiAlON was fixed to be $Ca_{0.8}Si_{9.2}Al_{2.8}O_{1.2}N_{14.8}$ for all the samples, corresponding to m and n values of 1.6 and 1.4 respectively in the general formula of Ca-α-SiAlON. The densification and mechanical properties of the sintered ceramics were examined to investigate the effect of sintering temperature and holding time on the properties. All samples were completely densified at each set of processing parameters.

For either sintering temperatures (at all holding times), a remarkable amalgamation of properties, namely hardness and toughness, was obtained for all the samples; and the greatest values for both the properties were attained at 30 min holding time, with Vickers hardness values of 21.6 GPa and 20.5 GPa and fracture toughness values of 7.3 MPa√m and 9.7 MPa√m for sintering temperatures of 1500 °C and 1600 °C, respectively. In order to inspect the variation in mechanical properties, the phases formed during sintering process were identified and correlated to the changes in mechanical properties of the samples. Microstructural analysis of cross-section and fracture surface was carried out for samples sintered at 1500 °C and 1600 °C at 30 min holding time.

The relative lower hardness (20.5 GPa) for sample sintered at 1600 °C and 30 min holding time was associated to the larger grain size as compared to sample sintered at 1500 °C and 30 min holding time. With regard to fracture toughness, sintering at either 1500 °C or 1600 °C for 30 min holding time, the yielded fracture toughness values were consequence of formation of elongated α-SiAlON grains.

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Preparation of zero thermal expansion ceramics by sol-gel and hot pressing

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Keywords: sol-gel, zero thermal expansion, microstructure

Materials which exhibit zero thermal expansion (ZTE) are of major importance for science and technology. Recently, a novel class of ZTE materials was discovered in a Sr and Ba containing zinc-silicate system with the generalized formula $Ba_{1-x}Sr_xZn_{2-y}M_ySi_{2-z}Ge_zO_7$ (M = Mg, Co, Cu, Mn, Ni). Unfortunately, the occurrence of a large anisotropy presents a problem especially regarding the synthesis of compact ceramic specimens and consequently their property determination.

Pressure-less sintering procedures to prepare a solid sample were not successful. For this purpose, a high temperature pressure assisted sintering technique was developed. It is now possible for the first time to prepare compact ceramic samples from the as mentioned solid solution phase, applicable for the determination of the real thermal expansion properties within a polycrystalline structure[1].

Additionally, raw materials prepared by a Sol-Gel route as well as a solid-state reaction technique has been processed to compact samples in order to compare the resulting morphology and their corresponding thermal expansion.

Compact ceramic specimens prepared from powders synthesized by a solid-state reaction show a cracked and porous microstructure and reveal a strong negative thermal expansion certainly with a large hysteresis and a permanent dimensional change. In contrast, powders prepared by a Sol-Gel method show a crack and pore free microstructure. Also, the thermal expansion is no longer negative. It shows now a very low, near zero thermal expansion without a hysteresis or an irreversible change in length.

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Impact of field assisted sintering on porcelain microstructure

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Keywords: porcelain, mullite, microwave sintering, spark plasma sintering, flash sintering, field assisted sintering technique

Sintering of porcelains has been studied extensively to understand and improve densification and phase evolution which directly control the physical and mechanical properties of the products. Recently, considerable attention has been drawn to 'Field Assisted Sintering Techniques (FAST)' to ceramics but only a few studies have dealt with porcelains. In this presentation, we report the effect of rapid heating in spark plasma sintering, flash sintering and microwave sintering on a porcelain body compared to conventional sintering. The FAST-densified samples were characterized using XRD, SEM, TEM and microindentation. The effect of FAST on the densification and phase evolution of mullite, glass formation and quartz dissolution will be discussed. For example, densification in porcelains using FAST was fast due to rapid glass formation. Different mullite morphologies were observed. SPS produced mullite oriented perpendicular to the compressive plane whilst microwaves produced randomly oriented and fibre-like mullite. Flash sintered samples contained large volumes of glass and dendritic mullite.

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Theoretical and experimental study of the transition from open to closed porosity sintering stage

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Keywords: oxide ceramics, sintering, porosity, hot isostatic pressing, transparent ceramics

Capsule-free hot isostatic pressing (HIP) is advanced sintering technique for processing of fully dense ceramic materials with variety of high-tech applications.[1] For successful HIP treatment the presintered samples have to be gas-tight, which means to be at the stage of closed porosity. The research in the field of transition from open to closed porosity stage is rarely published in the relevant literature, therefore the deep experimental study of pore closure has been carried out for alumina, magnesia-alumina spinel, tetragonal and cubic zirconia. The results were compared with three theoretical models[2–4] and arising differences were analysed in detail.[5] Furthermore two-step presintering,[6] as an innovative approach within capsule-free HIP technique, was utilized as a tool for obtaining Er-doped alumina exhibiting high optical transparency in combination with visible and infrared luminescence and exceptional hardness.

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Solid solution formation and mechanical properties of ZRC ceramics enhanced by tic particles and graphene

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Keywords: ZrC based ceramics, solid solution, graphene, spark plasma sintering

ZrC ceramic is characterized by an excellent combination of properties comprising high melting point, hardness, wear resistance, thermal conductivity, good creep resistance, and excellent chemical stability. However, consolidation difficulties, poor fracture toughness generally restrict the extensive applications of monolithic ZrC. Studies in recent years have indicated that graphene nanoplatelets (GNP) addition can significantly improve the mechanical properties of ceramic matrices. In this study, ZrC–TiC–Graphene composites containing 11–20 vol% TiC and in the range of 1.0–9.0 vol% graphene were prepared by spark plasma sintering at temperatures of 1700 °C for 300 s under a pressure of 40 MPa. Fully dense ZrC–TiC–GNP composites with a relative density of more than 98% were obtained. The microstructure and mechanical properties of the ceramics have been characterised. It was observed that TiC additions effectively promoted the densification process by forming (Zr,Ti)C solid solution. The sintered composites were then characterized with respect to their densification, microstructure, and mechanical properties change with the combination of TiC and graphene nanoplatelets. Increasing amount of GNP up to 3.0 vol% improve the fracture toughness, and leads to decrease the hardness.

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Spark plasma sintering of silicon nitride with the crystallization and phase transformation in the absence of sintering additive

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Keywords: spark plasma sintering, silicon nitride, mechanical alloying

Silicon nitride (Si_3N_4) shows high strength, high hardness and high toughness which is the reason why it can be utilized as mechanical parts. The Si_3N_4 exhibits two kinds of the crystal structures of α and β forms with hexagonal. The compact of α form shows high hardness and the β form shows the characteristics of high toughness. The phase transition from α to β forms of Si_3N_4 takes place at about 1400 ^oC, and it decomposes above1800 ^oC which often depends on the bulk density of Si_3N_4 compact, that is, how loose and/or dense. The Si_3N_4 powder is also known to be hard to sinter due to the low self-diffusion coefficient because of nature of strong covalent bond in the Si-N. For this reason, Si_3N_4 powders are often sintered with a sintering additive such as Al_2O_3 and Y_2O_3 through the liquid sintering process in which the powders densify with the grain growth. Although the sinterability of the powders can be improved with the additives, they make the high-temperature strength of the compact decrease. On the other hand, our group found that a stacking-sequence disordered silicon carbide (SiC) prepared by high energy ball milling of elementary Si and C can be sintered with the transformation to the ordered form in the absence of any additives[1-3]. The high energy ball milling of Si_3N_4 also made the crystal forms amorphous. In this work, we describe the effect of the milling time on the formation of amorphous Si_3N_4 from the crystal form, and the full consolidation by spark plasma sintering (SPS) of the amorphous powders with the crystallization and phase transformation in the absence of sintering additive.

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From wet sponges to optoceramics

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Keywords: alumina, ceramics, transparent, spark plasma sintering, doping, texture analysis, luminescence

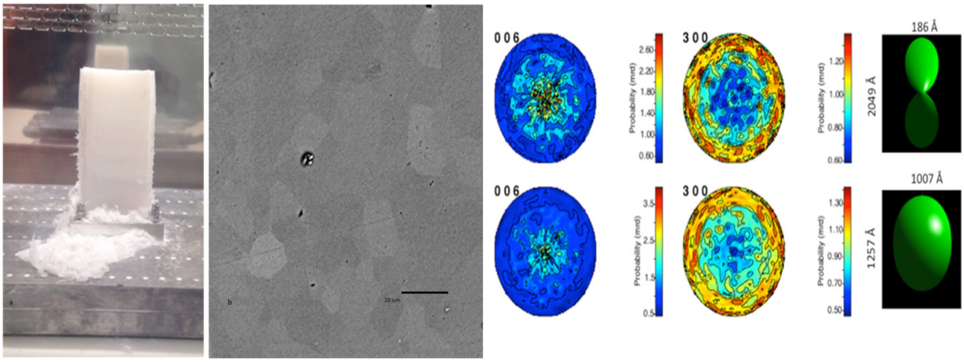

Fig. 1. Growing alumina monolith in the climate chamber (a), backscattered electron image of the sintered ceramic (b) and pole figures with crystallite shapes from the XRD texture analysis (c)

Polycrystalline alumina ceramics are abundantly used in industry due to their chemical inertness, good insulating qualities and fascinating mechanical, thermal, and optical properties. Spinel ceramics have lately been in the limelight because of their promising nanoscale self-healing properties[1], which make them perfect for the pursuit of highly tolerant materials in the nuclear fusion power plants. The self-healing is only efficient for grain sizes below 100 nm. Thus starting powder with uniformly small crystallite/particle size is of utmost importance. There are a lot of different commercial alumina powders available but they tend to have wide particle size distributions. This leads us to revitalize the technique of aluminum oxidation through liquid mercury-silver layer[2] developed in our workgroup some years ago. This room-temperature synthesis (see Fig. 1a) leads to uniform ultraporous monoliths of hydrated alumina fibers, which can be easily doped by vapor or liquid. In this communication we will present the preliminary results of using alumina monoliths to produce alumina (see Fig. 1b), spinel and mullite ceramics with different grain sizes and optical properties. Comparison will be made using commercially available alumina powders. Texture study of a high-pressure sintered alumina ceramic will be presented (see Fig. 1c). Spark plasma sintering with two previously established[3] heating cycles was used to consolidate the materials. Optoelectronical properties of received materials were studied via cathodoluminescence.

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Optimisation of impregnated SiC_f/SiC preforms for microwave chemical vapour infiltration

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Keywords: microwave, chemical vapour infiltration, ceramic matrix composite, SiC, SiC fibre

To deliver the succeeding generation of aerospace propulsion systems, major modification to the materials used and their manufacture are required to replace dating in service components. High-temperature ceramic fibre reinforced ceramic matrix composites (HT-CMCs), specifically SiC_f/SiC, have been identified as potential candidates to operate in the hostile aero-thermo-chemical environments experienced in service without compromising on structural integrity whilst keeping mass at a premium.[1] Presently a lack the high-temperature properties and durability that is essential for long-life at the temperatures envisioned is preventing widespread utilisation of these properties.[2] Current advanced manufacturing techniques are able to produce HT-CMCs and have been utilised in aerospace applications but none of these techniques to date have been capable of unlocking SiC_f/SiC full potential.

One of these advanced methods, chemical vapour infiltration (CVI) is an effective manufacturing route capable of creating near fully dense components with an extremely refined microstructure with little or no preform degradation and minimal residual stresses[3] but its current material output is microstructurally defective and susceptible to failure in the more demanding conditions the aerospace industry encounters. CVI's issues are three fold[4]; processing is incredibly slow using isothermal heating rates so batch production is 2–3 months, secondly premature closure results in residual porosity, which requires subsequent machining stages to re-open the closed channels which reduces the efficiency of the process to between >10%. Lastly, as a consequence of the previous two points, associated costs are very high and the product expensive. Microwave energy has been proposed to offer a potential solution to heat the preform for CVI, it produces a favourable inverse temperature profile meaning temperature is hottest in the centre of the component, the contrast of conventional CVI. This inverse profile is more energy efficient and initiates densification at the centre of the sample thus avoiding surface porosity closure, and hence facilitating reactant gas transport throughout the entire structure. It is expected that the use of microwave enhanced CVI processing routes could yield near fully dense products in 72–96 hours.[5]

Current work has been dedicated to preparation of SiC fibre preforms prior to microwave processing with regard to decreasing processing times further. This study has been a multidisciplinary approach building on previous research has investigated the impregnation of SiC fibre preform with SiC powder.[6] This factor along with other important parameters have also been considered; dielectric properties of constituent materials, uniformity of powder application, pore distribution and size and permeability of the composites to facilitate the production of optimum preform characteristics for infiltration.

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Insitu study of densification at high heating rates

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The fast sintering techniques attract high attention not only due to economic reasons. From the scientific point of view there are many questions about the mechanisms of rapid sintering which should be answered. Among fast sintering techniques, Spark Plasma Sintering (SPS) is fast developing consolidation technique, due to the synergy of fast heating rate, uniaxial pressure and pulsed electrical field. Recently, enhanced densification of tetragonal ZrO_2 sintered by rapid heating rates (hundreds of °C/min), has been reported even during pressure-less sintering[1,2] and the role of electromagnetic field was questioned.[3]

In this work, ZrO_2 ceramics were sintered by SPS with various heating rates, ranging from units °C/min up to several hundred °C/min. The sample shrinkage was continuously monitored during the whole sintering. The apparent activation energy of densification was evaluated by means of newly developed Master Shrinkage Curve model designed for anisotropic shrinkage. The effect of the heating rate on the value of apparent sintering activation energy is evaluated and discussed.

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Al_2O_3-$Y_3Al_5O_{12}$ composites with submicron microstructure by hot pressing of yttrium aluminate glass microspheres

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Yttrium aluminate glass microspheres with composition of the eutectic in a pseudobinary system Al_2O_3-$Y_3Al_5O_{12}$ (YAG) were prepared by feeding a polycrystalline powder precursor into methane-oxygen flame. Kinetics of crystallization of the glass was studied in detail by differential thermal analysis. The glass crystallized in several stages, with initial formation of YAG in two steps (937 and 1000 °C), with subsequent crystallization of α-Al_2O_3 at $T > 1300$ °C. The obtained information was utilized for preparation of bulk materials by hot pressing in the temperature range 840–1600 °C and pressures up to 80 MPa, with isothermal dwell 0120 min. Depending on the conditions of hot pressing experiments dense composites with various microstructures and phased composition were prepared. Hot pressing at 1600 °C without isothermal dwell yielded dense composite with fine two phase microstructure with α-Al_2O_3 and YAG phases percolating at a submicrometre level and Vickers hardness ~ 15 GPa. Extension of the isothermal dwell at 1600 °C resulted in microstructure coarsening and decrease of Vickers hardness.

Acknowledgments

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Grain growth transitions in perovskite ceramics: bimodal microstructures, anisotropy and point defects

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Perovskite materials are widely used in a variety of electronic devices, e.g. capacitors, oxygen conductors, PTC (positive temperature coefficient) heaters and piezoelectric actuators. Many macroscopic properties of polycrystalline perovskites are governed by their grain boundaries and, therefore, depend strongly on microstructure evolution (sintering and grain growth) during processing.

Several perovskite ceramics are known to show a non-Arrhenius type of grain growth. Strontium titanate has a grain growth rate transition that has been well documented, with decreasing growth rates between 1350 °C and 1425 °C. Other materials such as barium titanate, lithium lanthanum titanate and barium strontium titanate show similar grain growth rate transitions. The growth transitions are coupled to the formation of bimodal microstructures and are postulated to be caused by grain boundary structural transitions.

This talk reviews our current understanding of the grain growth rate transitions in perovskite ceramics. A simple mean field approach is often used for quantifying these effects on a macroscopic scale. However, this approach fails to capture the underlying physics of bimodal anisotropic grain growth that occurs in ceramic perovskites. Important factors including anisotropy, atomistic boundary structure, segregation, wetting, faceting, boundary stoichiometry, space charge and interfacial drag need to be considered explicitly. A discussion of open questions and future directions will be presented.

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Inverse hall-petch relation in nanostructured oxide ceramics fabricated by high-pressure SPS

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Keywords: spinel, YSZ, SPS, inverse hall-patch

High pressure (up to 1 GPa) spark plasma sintering (HPSPS) technique allows to fabricate nanostructured (20–30 nm) polycrystalline ceramics at relatively low temperatures with short sintering time. The specimens obtained by HPSPS technique display a unique combination of optical and mechanical properties, comparable or even better than the best results reported in literature for a two-stage fabrication process (pressureless sintering followed by hot isostatic pressing or vacuum sintering).

Our recent experimental results on densification of polycrystalline transparent magnesium aluminate spinel (PMAS) and yttria stabilized zirconia (YSZ) has raised some fundamental questions related to microstructure evolution, densification and grain growth kinetics. Furthermore, for the first time, the minimal grain size (of about 40 nm) where a Hall-Petch relation is valid was established and an inverse Hall-Petch correlation was clearly observed for ceramics with grain size less than 30 nm.

The present work focuses on the understanding of sintering behavior during HPSPS process and on clarification of the grain growth mechanism. A model explaining the effect of grain size on the mechanical properties, was developed and will be discussed.

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Effect of metal doping on heat transfer in Spark Plasma Sintering process

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Keywords: Spark Plasma Sintering, metal doping, heat transfer

Spark Plasma Sintering (SPS) is one of the novel sintering processes accompanied with unique kind of heating – pulsing electrical current. The benefits of the pulsing electric current is the oft-repeated claim that electric pulsing creates a plasma which activates surfaces of powder particles through removal of surface layers.[1,2] However, so far convincing evidence of this conditions is absent.[3] In spite of conflicting results, pulsing in SPS is also able to influence particle movements due to its strong electromagnetic field when doping conductive metals (e.g., iron) to nonconductive matrix.

In this study, γ-Al2O3 powders doped with various metals (Fe, Cu, and Ni) were sintered via SPS. Two heating modes–auto and manual mode were applied to observe the role of electromagnetic field on sintering. Phase transformation of γ to α-Al2O3 serves as direct indicator of internal temperature, independently on measured outside temperature.

Particle movement and altering of heat transfer method were proofed during the SPS process of electrically nonconductive materials doped by metals. Shrinkage, density, temperature and microstructure were investigated to analysis and quantify the impact of metal dopants on heat transfer in SPS process.

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Flash joining of CVD-SiC coated ceramic matrix composites

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Keywords: flash joining, diffusion bonding, Spark Plasma Sintering, C_f/SiC composites, Ti interlayer

The purpose of this work was, for the first time, to bring together the flash processing and the joining of ceramic materials, thus allowing flash joining of ceramics. Flash joining of CVD-SiC coated C_f/SiC samples with a Ti interlayer was achieved using a Spark Plasma Sintering machine. The influence of different heating powers and discharge times were investigated. The sample flash joined at a maximum heating power of 2.2 kW (peak electric current of 370 A) within 7 seconds showed the highest apparent shear strength of 31.4 MPa, which corresponds to the interlaminar shear strength of the composites. A maximum joining temperature of ~ 1237 °C was reached during the flash joining. An extremely rapid heating rate of 9,600 °C/min combined with a very short processing time hindered any reaction between the CVD-SiC coating and the Ti interlayer. A defect-free interface was obtained, and no transverse cracks were observed in the Ti interlayer. The Ti foil did not melt or shrink during joining, resulted in the limited diffusion of Si and C from the CMCs into the Ti. Therefore, the formation of Ti_3SiC_2 was not observed. T a sound joint was obtained by forming a metallic kind of joint (Ti-based) at the joining temperature, in which the absence of any reaction phases (titanium silicides, carbides or ternary phases) significantly shortened the time necessary for the solid-state diffusion bonding. The Ti interlayer also partially filled up the surface cracks in the CVD coating on the CMCs due to plastic flow. This is believed to strengthen the joint.

The apparent shear strength of the flash joint was higher when compared to the apparent shear strength of the C_f/SiC joints when joined with Ti (both 30 and 130 µm) using a standard SPS process at 1700 °C with a heating rate of 100 °C/min and a dwell time of 5 minutes. This constitutes a significant reduction in a processing time and the maximum temperature required, which in turn leads to energy savings and potentially higher industrial interest in the process. The present work clearly demonstrates that, when the right conditions are achieved, a strong joint can be obtained within 7 seconds using flash joining.

Acknowledgments
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Effects of processing and sintering conditions on density and microstructure of microinjection molded oxide CMCs

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Keywords: CMC, fiber orientation, sintering, microstructure, grain growth, density, ceramic injection molding

Ceramic matrix composites (CMCs) are created by adding fibers with variety of fiber structure into various ceramic materials to provide condition / task adapted properties. On the other hand, ceramic injection molding is an automated net shaping process that can produce the ceramic parts with complex geometry and good surface quality without the requirement for a post-processing step. In this study, we produced aluminum oxide CMCs (Al2O3 powder: TMDAR, Taimicron; Al2O3 chopped fibers: 3M Nextel 610) by using ceramic μ-injection molding process. Each step such as feedstock preparation, molding step, debinding or sintering, has significant effect on the final properties of the CMCs parts. Measurement of density as a function of time, temperature, fiber content or -orientation coupled with the examination of the final microstructure is a useful method to evaluate the ceramic parts. At 1200 °C relative density decreased at about 35% with increasing amount of oxide chopped fibers. The reason of such a low sintering temperature for aluminum oxide based material is to prevent the grain growth in the fibers.[1] In addition, the form of the injection mold defines the fiber orientation that differentiate the density of the sintered parts. The difference between tensile specimen (higher orientation) and disc form (random orientation) is about from 1 to 10% depending on temperature and the amount of fiber in the material.

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Formation of molybdenum boride layers on TZM alloy by spark plasma sintering process

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Keywords: TZM alloy, molybdenum boride, boriding, spark plasma sintering

TZM alloy is one of the most important molybdenum (Mo) based alloy which has a nominal composition containing 0.5–0.8 wt% titanium (Ti), 0.08–0.1 wt% zirconium (Zr) and 0.016–0.02 wt% carbon (C). It is a possible candidate for high temperature applications in a variety of industries. However, the rapid oxidation of TZM alloys at high temperature in air and low wear resistance are considered to be the main drawbacks.[1–5] In this study molybdenum boride phase was formed on the surface of TZM alloy by spark plasma sintering (SPS) process. Boron carbide (B_4C) was used as a boron source during the boriding. Both sintering and boriding process were performed in a single step at constant temperature of 1420 °C in various pressure (40–60 MPa) and holding time (5–15 min) under vacuum. The effect formation Molybdenum Boride layers and sintering parameters on the microstructure, surface hardness, wear resistance and oxidation resistance were investigated. The results showed that boride layers composed of MoB and Mo_2B have a thickness in the range of 137–213 µ. Moreover, increase in pressure and holding time result in increase in density, hardness, wear and oxidation resistance of the alloy.

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Conversion of MAX phase single crystals in highly porous carbides by high temperature chlorination

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Keywords: MAX phase, chromium carbides, CVD chlorination, porosity, magneto-transport

We apply high temperature chlorination to the exfoliation of the chemically sensitive A-atom planes of single crystals of nano-lamellar MAX phases[1,2,3]. This allows us to synthesize highly porous and electrically conducting refractory carbides. Focusing on the case of porous Cr_3C_2[4], we investigate the dependence of the layer morphology, structure and formation kinetics on processing parameters such as temperature and time. Many properties, such as porosity and specific surface area, can be controlled and optimised through an appropriate choice of parameters, which may expand the application range already covered by the previously developed processing techniques. XRD analysis shows that the porous material exhibits a preferential crystalline orientation.The Raman signature of Cr_3C_2 and Cr_7C_3 is determined for the first time, and allows us to follow the creation and elimination of the various phases as a function of processing time and temperature. Variation of electrical resistivity and magnetoresistance *versus* temperature and magnetic field is also investigated.

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Poster presentations

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Synthesis of reaction-sintered silicon carbide ceramics by a two-stage siliconizing method

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Keywords: silicon carbide ceramics, siliconizing, reaction-sintered SiC

Since the 20th century silicon carbide ceramics are well known, and thanks to its unique physical and chemical properties has been widely used in aerospace, aviation, automobile and semiconductor industries.[1] There are many kinds of SiC ceramics are exist and most of which the reaction sintering siliconizing fabrication process of the carbon filler or skeleton are used.[2] This process is carried out in a vacuum or in an inert atmosphere at a temperature of 1600–1800 °C and provides impregnating of workpiece by silicon forming a reaction-bonded silicon carbide. However, this method has some limitations on the thickness of the preform, since silicon penetrates into detail begins to react with carbon, resulting the formation of silicon carbide having a higher melting point and which stops the impregnation of liquid silicon into the deep of the detail. This effect reduces the density of ceramics increasing its porosity, resulting in degradation of the product technical performance. For neutralization of this effect, the two-step siliconizing method for oversized substrates with a diameter up to 200 mm and a thickness of 15 mm was developed and applied.

Essence of the method in the following: onto the surface of C-SiC composite preformed workpiece placed in a graphite crucible, silicon powder is sprinkled. Crucible is tightly closed with a graphite lid and placed in a high temperature vacuum furnace chamber. After vacuum pumping till $2 \cdot 10^{-2}$ torr pressure the heating of furnace till temperatures of 1500 °C is produced and followed by aging. This operation is leads to the complete melting of silicon and impregnated throughout the entire volume of the preform that corresponds to the first stage of the process. At the second stage of the process the temperature raises to 1800 °C at which the reactions sintering of carbon constitutes the composite and melt silicon forming a reaction-sintered silicon carbide is take place. The x-ray studies showed that the resulting oversized product consists of 6-H and C-3 polytypes of silicon carbide with minor inclusions of free silicon. The mechanisms of silicon infiltration, including capillary effect and diffusion of silicon atoms through carbon mesh, are discussed. Obtained results indicate the perspectives of using of this method for fabrication of silicon carbide oversized details.

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Optimization of the thermal insulation of the die during SPS sintering

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Keywords: Spark Plasma Sintering, finite element modeling, thermal insulation

Based on the simultaneous application of axial pressure and elevated temperature generated by a high current flow, Spark Plasma Sintering (SPS) is one of the most attractive consolidation techniques. The sintering is achieved at a lower temperature and a shorter duration compared to conventional techniques, which allow to enhance the mechanical or physical properties of the materials.

Finite element modeling has contributed to investigate the influence of several experimental parameters on the temperature distribution, which is of crucial importance to the SPS processing, since it directly affects the microstructure homogeneity and the final properties of the sintered materials.

In the present work, the influence of the thermal insulation of the die is investigated using a finite element model based on the thermoelectric coupling during SPS sintering, that allowed to simulate the temperature distribution in the sample. It is sown that in the case of alumina, chosen as a model for non-conductive materials, a partial thermal insulation of the die is more effective to reduce the radial temperature gradients within the sample, than the commonly used total insulation. The model is used to determine the optimized height of the thermal felt necessary to minimize the radial gradient and to discuss the effect of the sample dimensions.

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Effect of ceramic addition on structural and mechanical properties of steel alloys

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Keywords: attrition milling, Spark Plasma Sintering (SPS), Nano-size ceramic powders, submicron sized structure, mechanical and structural properties

The powder metallurgy technology provides more controlled microstructure, a homogeneous dispersion of nano-sized oxide particles in the metal matrix and tailored properties in terms of strength and radiation resistance.[1] Oxide-dispersion strengthened (ODS) steels are good candidates for use in nuclear reactors generation IV and the first fusion power plants because of its neutron resistant property.[2] The application of ODS steels strongly depends on the availability of large batches of materials.[3] The Höganäs 316L stainless steel powder and four nano-sized ceramic powders: Y_2O_3, Al_2O_3, Si_3N_4 and SiC have been used to study the effect of ceramic addition on the structural and mechanical properties of steel alloys. Eight alloys have been prepared during this work. Homogenous dispersion of the nano-size ceramic particles on the surface of the stainless steel grains has been achieved by high efficient attrition milling for five hours. A good coverage of steel grains by ceramic particles has been observed. The morphological changes of the stainless steel grains, the covering and the dispersion of the ceramic particles have been observed by Scanning Electron Microscopy (SEM) and verified by Energy-dispersive X-ray spectroscopy (EDS). A fast sintering of powder mixtures has been performed by Spark Plasma Sintering (SPS) in order to obtain submicron sized structure. The mechanical properties of the solid samples have been presented and tested using tensile, three and four points bending, tribology and hardness tests. The effect of ceramic addition on the structural and mechanical properties of the 316L Höganäs Stainless steel has been clearly observed by SEM, EDS, X-ray Diffraction (XRD) and Transmission Electron Microscopy TEM.

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Ca-doped Magnesium Aluminate (Spinel) synthesized by precipitation route in alcoholic medium

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Keywords: magnesium aluminate, precipitation, nanomaterials

Magnesium aluminate ($MgAl_2O_4$), also called Spinel, presents excellent refractory and mechanical properties, low density and high optical transmission in visible and mid-wavelength infrared spectra. Many dopants are used in order to obtain nanometric particle distribution and properties improvement. Magnesium aluminate particle size is also affected by the synthesis route. Samples of Ca-doped magnesium aluminate were prepared using a precipitation route with NH_4OH, aluminum and magnesium nitrates, calcium carbonate as dopant and ethanol as solvent. Ethanol is used to avoid the problem of the hydroxides different solubility depending on pH in aqueous solution. The hydroxides precipitate was calcined at 900 °C to obtain magnesium aluminate oxide and then milled. Samples were characterized by XRD, Infrared, Surface Area Analysis (BET), Dilatometry and SEM. Resulting powders presented particle size range between 3–10 nm and the only identified crystalline phase, despite the amount of dopant, was $MgAl_2O_4$. Conventional sinter tests were carried out in different conditions and the obtained sintered pellets were translucent and highly dense. The increase in the dopant's concentration favors the particle size decrease and also densification and sinterability. SPS sinter tests and mechanical properties determination of the sintered pellets are being carried out.

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Crystal structure and piezoelectric properties of (LiCeNd)-multidoped $CaBi_2Nb_2O_9$ Aurivillius type ceramics

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Keywords: Rietveld-refinement, structure properties, piezoelectric properties, $CaBi_2Nb_2O_9$

(LiCeNd)-mutlidoped $CaBi_2Nb_2O_9$ Aurivillius phase ceramics were prepared via a conventional solid state sintering route. The crystal structure, micro-structure, dielectric and piezoelectric properties were systematically investigated. XRD patterns showed a single crystal structure, indicated (LiCeNd) dopants entered into lattice point and formed solid solutions.

The Rietveld-refinement showed a gradual change in crystal structure from orthorhombic to tetragonal with increasing (LiCeNd) doping concentration. The $Ca_{0.85}(Li_{0.5}Ce_{0.25}Nd_{0.25})_{0.15}Bi_2Nb_2O_9$ (CBN-LCNd15) ceramics possess the optimum properties, and the d_{33} and T_c values were found to be ~13.1 pC/N and ~900 °C, respectively. The thermal depoling behavior also demonstrated that the CBN-LCNd15 ceramics possess outstanding thermal stability of piezoelectric properties (d_{33}~11.3 pC/N, T= 850 °C for 2h). This demonstrates that the (LiCeNd)-mutlidoped CBN-based ceramics are a promising candidate for ultrahigh temperature applications.

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In-situ X-ray diffraction study of alumina α-Al_2O_3 behavior

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We determined the crystalline characteristics of the hexagonal α-alumina phase by X-ray diffraction at high temperatures between 293 and 2308K under dynamic vacuum. Our experimental values allow us to deduce an anisotropy of the ‘c’ direction compared to the ‘a’ direction of approximately 12% in the range of 293K–1760K: Such an anisotropy is related to internal constraints in the alumina structure which may cause plastic deformation. There is quite a difference in the range 1760K–2308K: no further anisotropy remains. The perfect isotropic expansion of the alumina cell leads us to conclude the absence of any internal constraint above 1760K. As the anisotropy which characterizes the alumina structure is a direct consequence of the fact that the aluminum atoms occupy two thirds of the octahedral sites in the compact hexagonal subnetwork formed by the oxygen atoms, we believe that the isotropy in question must surely translate an equal occupation for all octahedral sites so that the site contains statistically 2/3 Aluminium atom.

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Nitrogen and fluorine effect on the crosslink density of some aluminosilicate glasses

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Keywords: glasses, oxynitrides, oxifluoronitrides, crosslink density, nitrogen, fluorine

The effects of fluorine and nitrogen substitution for oxygen in calcium–(magnesium)–(yttrium) aluminosilicate glass have been examined. Forty-two glasses in the Ca–(Mg)–(Y)–Si–Al–O–(N)–(F) system have been prepared and characterized with respect to Density (ρ), molar volume (MV), compactness (C), free volume (FV), DTA glass transition temperature ($T_{g,DTA}$), dilatometric glass transition temperature ($T_{g,dil}$), dilatometric softening point (T_{DS}) microhardness (µHv) and Young's modulus (E).

This paper reviews factors affecting the physical, thermal and mechanical properties of three different oxyfluoronitride glass systems, showing how composition variables can be used in additive equations to understand important predictors of property values. A modified method for calculating glass crosslink densities has been used, which takes into account increased partitioning of aluminium from the network to a modifier role as fluorine content increase. This method allows to explain changes in thermal properties with composition (as glass transition temperature) but not changes in mechanical properties (as Young's modulus or microhardness), which are controlled by glass compactness (packing density).

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Oxyacetylene and Oxypropane torch flame characterisation for UHTC and UHTCMC screening tests

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Keywords: UHTC, UHTCMC, torch testing

The development of material systems suitable for ultra high temperature application is currently of great scientific interest. Ultra high temperature ceramics (UHTCs), which have high melting temperature around 3000 °C[1], and ultra high temperature ceramic matrix composites (UHTCMCs) based on carbon or silicon carbide fibre reinforcement, have been extensively investigated for aerospace applications as sharp leading edge components and thermal protection system which require resistance to these temperatures[2]. To enable this investigation the development of characterisation methods to examine how materials behave at these temperatures is vital[3]. A number of methods can be used to heat materials to these temperatures, some cannot recreate hypersonic flight conditions such as static furnace oxidation testing and other such as plasma wind tunnel testing and arc-jet testing are very expensive. The use of gas torches currently offers a comparatively simple and low cost technique of characterising and initial screening of potential UHTC materials[4]. They have this potential because they can easily achieve the temperatures required and offer high heating rates, however to allow the results to be compared with those from other techniques the velocity and heat flux of the flame gas must be known. The current work has been focus on characterisation of the oxyacetylene and oxypropane torch flame gas velocity and heat flux measurements of oxypropane torch. After that, different UHTCMCs were tested at different distance from the tip nozzle using both torches.

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Friction and wear of Al_2O_3-GO/RGO composites

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Keywords: Alumina, ceramic matrix composites, graphene oxide, wear resistance, friction behaviour

This paper presents the results of the study of the properties of alumina ceramics-GO/RGO composites during the friction and wear studies. Based on the previous experiments, two types of the Al_2O_3 matrix composites were produced: reinforced with graphene oxide (GO) synthesized by a modified Hummer's method[1] and reinforced with modified graphene oxide nanoplatelets (RGO-Al_2O_3).[2] All samples were prepared by powder metallurgy and consolidated by Spark Plasma Sintering (SPS). Friction tests using the ball-on-disc method and wear tests as dry machining on C45 steel were executed. Coefficients of friction, wear rate of disc and ball as well as cutting tool life and roughness parameter Ra of machined steel surface were analyzed. Scanning Electron Microscopy (SEM) observations for samples after tests were also carried out, to reveal the types of wear. The work compares also cutting and friction performance of produced composites with those of commercial ceramic cutting tools.

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Ni catalysts derived from hydrotalcite for the dry reforming reaction of methane. Effect of the addition of Si

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Keywords: CH_4, CO_2, hydrotalcite, sintering

CO_2 reforming of methane shows a growing interest from the both industrial and environmental point of view. CO_2 and CH_4 are undesirable greenhouse gases and both are consumed by the proposed reaction. NiMgAl, NiAl, NiAlSi, NiMgAlSi were prepared by coprecipitation at constant basic pH and calcined at 800 °C. The non-calcined compounds exhibit the characteristic diffractions of hydrotalcite-like layered double hydroxide materials confirmed by infrared spectroscopy. Samples containing sillicium show a poor cristallinity. Nevertheless, after calcination the hydroltacite-like structure is completely destroyed. The BET surface area results, after calcination at 800 °C, showed some differences among the catalysts. The results of H_2-TPR measurements of the calcined samples indicated that NiAl and NiAlSi present reduction profiles at lower temperature. NiMgAl and NiMgAlSi present reduction profiles at high temperature. The dry reforming of methane by carbon dioxide in presence of various catalysts is studied at 750 °C. For NiAl and NiAlSi catalysts CH_4 conversions were close to 70.0%, with a H_2/CO ratio close to 0.9. In the NiMgAlSi sample the CH_4 conversion decrease to 50%, and the H_2/CO ratio reaches values lower than unity. The NiMgAl sample exhibit a higher conversion 95.0% close to stoichiometric values and a H_2/CO ratio of almost 1, which can explained by the high stability of the support and the resistance to sintering of particles, maintaining a very high specific surface (ca. 100 m^2/g), after the reducing treatment.[1] Overall, it appears that the catalytic performances of the catalysts decreased as a function of sintering, in the following sequence NiMgAl> NiAlSi> NiAl> NiMgAlSi.

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To sinter water and oxygen sensitive materials using Spark Plasma Sintering

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The state of the art Spark plasma sintering unit with capacity of sintering samples up to 20 mm diameter placed in the argon atmosphere glove box. This makes it possible to limit the input of oxygen and water in the materials. The entire process can be done in a protective atmosphere from the powder handling and loading the mold to the sintering without breaking the protective chain. In that way air sensitive materials can be sintered and also the effect of water and oxygen on sintering process can be investigated. The effect of water on sintering of zirconia has been investigated by calcinating powder in vacuum at different temperatures prior sintering. The sintering was done without exposion to the air as well the comparison has been done with calcination in air and sintering at the same conditions. The sintering behaviour and microstuctures has been investigated and compared.

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Spark Plasma Sintering: an advanced processing route for spring magnet fabrication

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Keywords: permanent magnets, spring magnet, spark plasma sintering, nano-structured ceramics

Spark Plasma Sintering (SPS) is a non-conventional sintering technique that allows densifying materials reducing sintering time, preventing grain growth and even preserving an epitaxial arrangement at interface in composite materials[1]. To the best of our knowledge, SPS was seldom used to produce spring magnetic composites. In most of the cases hard and soft oxides nanoparticles (NPs) are co-sintered[1,2]. Unfortunately, the reached maximal magnetic energy $(BH)_{max}$ of resulting nanostructures, remains small compared to that of their bulk counterparts. In this work we proposed to prepare cobalt ferrite (CFO) and iron metallic (F) nanocomposites presenting spring magnet effect; using SPS and starting from polyol–made CFO and F NPs. Our main aim is to obtain permanent magnets with as high as possible $(BH)_{max}$ values varying material processing conditions: size of CFO NPs, CFO/F nominal atomic ratio, SPS pressure and temperature. The microstructure and the magnetic properties of the produced CFO-F nanocomposites are investigated and compared.

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Parameters and sinterability of Al_2O_3-SiO_2-Zro_2 (y_2o_3) nanoparticles

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Keywords: sol-gel synthesis, thermal plasma synthesis, nanopowders, spark plasma sintering, nanostructural mullite

Mullite-zirconia ceramics due to high refractivity, thermal shock resistance, good chemical stability and improved mechanical resistance are promising material for structural and functional application. However, the parameters of ceramic are determined by sintering method, raw materials, their purity, particle size and activity. The objective of this work was to compare parameters and sinterability of nanosized powders, prepared in Al_2O_3-SiO_2-ZrO_2(Y_2O_3) system by synthesis in thermal plasma flow (PL) and by well-known sol-gel combustion synthesis (SG). Thermal plasma synthesis was based on evaporation of coarse-grained (10–40 µm) Al_2O_3, SiO_2, ZrO_2, and Y_2O_3 powders in radio frequency air plasma. Formation of the products via vapour phase led to obtaining homogeneous composites with spherical shape and relatively wide particle size distribution in the range of 20–100 nm. This could be explained by different growth conditions of particles due to temperature distribution of plasma flow and by the collisions of the liquid particles. The sol-gel combustion synthesis was performed by mixing water solutions of Al, Zr and Y nitrates with TEOS ethanol solution at 100 °C for 1 h. Molar ratio of Al and Si was 3:2. Additive of zirconia with 3 mol% of yttria was 5; 10 or 20 wt.%. Glycine water solution was added to the solution of precursors and temperature was increased up to 120 °C. The formed gel was calcinated at 500 °C for 2 h and after this the temperature was increased to 1000 °C. The as-prepared by both methods powders contained t-, m-ZrO_2 and X-ray amorphous phases. Additional calcination of SG and PL prepared samples led to formation of mullite at 1250–1300 °C and 940–990 °C respectively depending on the content of zirconia. Densification of as-prepared partially X-ray amorphous SG particles with specific surface area of 20–28 m^2/g started at 10150–1150 °C depending on the content of zirconia. Final relative density of the samples was reached at 1500 °C during 3 min. Densification of PL powders with specific surface area of 32-41 m^2/g started at 900 °C and final relative density (99.3%) was reached at 1400 °C during 3 min due to regular shape of the particles. All sintered bodies contained mullite, t-ZrO_2 and m-ZrO_2 phases. SEM studies showed grain size mainly in the range of 0.8–1.5 µm. SG samples contained also rod-like mullite crystals with diameter of 1.2 µm. Hardness of the bulk materials was in the range

of 13.20–13.85 GPa. Spark plasma sintering of the partially X-ray amorphous Al_2O_3-SiO_2-ZrO_2(Y_2O_3) nanosized powders allowed to decrease sintering temperature and to obtaine materials with fine-grained microstructure.

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Microstructural and magnetic properties of SPS and hot-magnetic press consolidated Sr-ferrite ceramics

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Keywords: Sr-ferrite, spark plasma sintering, hot-pressing

In the last years, much effort has been again devoted to the research of ferrite-based permanent magnets, due to the so called “rare-earth crisis.”[1,2] In particular, a quest to enhance maximum energy product (BH_{max}), which is a figure of merit in permanent magnets, is still underway. Large BH_{max} values are found in magnets combining substantial magnetization at remanence with high coercivity. Both parameters are influenced by materials properties, such as crystalline and shape anisotropy (remanence), particle’ size (coercivity). In this study, we will present how initial particle size, shape and sintering conditions influence microstructure and consequently magnetic properties of sintered Sr-ferrite ceramics.

Two sets of powders and sintering conditions are being used. Namely, commercial Sr-ferrite (SFO) with a particle size in the micron range and isotropic shape, and hydrothermally synthesized Sr-ferrite with hexagonally shaped platelets with a diameter up to 500 nm and thickness up to 50 nm. Both powders are being sintered with two different sintering set-ups; spark plasma sintering (SPS) and consolidation with a hot-magnetic press. Sintering with SPS promotes the alignment of hydrothermally synthesized SFO particles in the direction of the applied pressure, which is also the direction of materials’ easy axis and thus the enhancement in remanence is perceived. Moreover, no grain growth was observed, which is beneficial for maintaining particle’ size at the nanoscale and thus exploiting advantages of nanosized induced phenomena. On the other hand, consolidation in the hot-magnetic press, due to the applied external magnetic field, results in orienting spins in the shape-wise, isotropic material (commercial SFO), which leads to the enhancement of BH_{max} of commercial SFO powders.

Starting powders were examined by transmission (TEM) and scanning electron microscopy (SEM), while the microstructural characterization of consolidated magnets was done with SEM. Magnetic properties of starting powders and consolidated SFO ceramic magnets were evaluated with vibrating sample magnetometer and permeameter.

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Preparation of transparent ALON ceramics by using spark plasma sintering

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Keywords: current activated pressure assisted sintering, AC electric field-assisted sintering, nanocrystalline boron carbide

Boron carbide (B_4C) with its high hardness, wear resistance and rather low density is quite a promising material for lightweight armor, blasting nozzles, grinding wheels and other industrial applications. Ceramics based on boron carbide can be obtained by various methods.[1–3] Field assisted sintering technique is a modern technique of sintering under pressure and it is widely used for the manufacture of refractory ceramics in nowadays. We studied two methods for sintering of boron carbide: spark-plasma sintering and (SPS) and high-voltage consolidation (HVC). The effect of spark-plasma sintering regimes and high-voltage consolidation regimes on the microstructure and mechanical properties boron carbide ceramics was investigated. It is established that the achievement of high density of compacts from boron carbide is possible for solid-phase sintering / consolidation by both methods. It is shown that for the investigated SPS regimes the maximum level of boron carbide sample density is observed at a sintering temperature of 1850–1950 °C. Also, high-voltage consolidation of boron carbide powders was carried out. The high-voltage consolidation consists in the affect of a discharge with a high current density (≈ 100 kA*cm^{-2}) and a short pulse duration (less than 300 µs) on the powder compact. The increase in the density of the material, its microhardness with increasing voltage of a high-voltage discharge is shown.

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Flash sintering of a three-phase alumina, spinel, and yttria-stabilized zirconia composite

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Three-phase ceramic composites constituted from equal volume fractions of α-Al_2O_3, $MgAl_2O_4$ spinel and cubic 8 mol% Y_2O_3-stabilized ZrO_2 (8YSZ) were flash-sintered under the influence of DC electric fields from 50 to 500 V/cm. Experiments were conducted either by using a constant heating rate with a set voltage or isothermal experiments with increasing voltage. Higher electric fields inhibited grain growth due to the lowering of the flash temperature and an accelerated sintering rate. During flash sintering, alumina reacted with the spinel phase to form a high-alumina spinel solid solution, identified by electron dispersive spectroscopy and from a decrease in the spinel lattice parameter as measured by X-ray diffraction. Synchrotron *in-situ* X-ray diffraction experiments demonstrate that the formation of high-alumina spinel occurs in less than 3 seconds along with the formation of a transient phase. The influence of 8YSZ content on flash behavior of the composite is reported.

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The SPS sintering of different size and morphological forms of silicon carbide powders

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Keywords: silicon carbide, SPS, ceramic, microstructure, liquid phase sintering

Several sintering experiments of different SiC powders were performed using SPS method. The studies involved different geometry and size of powder particles: equiaxed micro particles, nanopowder and whiskers. There were significant differences in the microstructure

and the basic mechanical properties (hardness, Young's modulus) arising from the morphology of the used powders. One of the greatest drawbacks in the manufacturing of SiC is the difficulty to sinter dense samples without the use of additives. For the purpose of comparison the sintering additives Al_2O_3 and Y_2O_3 were used. It has been found that obtaining dense sinters is possible due to the presence of phases activating mechanisms of mass transport, thus facilitating densification process during sintering. The use of yttria and alumina as sintering additives cause a liquid phase presence during the sintering and intensifying process. Particularly interesting microstructure characterized by open porosity was obtained using powder with whisker morphology. This type of microstructure is suitable for production of filters operating at high temperatures.

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An original concept for the rapid elaboration of C/C composites: the film boiling chemical infiltration

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Keywords: kalamazoo, pyrocarbone (PyC), chemical vapour deposition (CVD), Chemical Vapour Infiltration (CVI)

A work based on the development of an original process for the fabrication of a C/C composite for aeronautic and nuclear industries is presented: the "film boiling" densification.

Nowadays C/C composite are mostly elaborated by CVI (Chemical Vapour Infiltration). This process is long and restrictive, indeed the elaboration takes several weeks. Using "film boiling process" for the densification of a carbon fiber preform allows a large reducing of the processing time with respect to CVI (50 to 100 faster).[1,2]

The carbon preform is immersed into a carbon precursor and heated up above the precursor decomposition temperature. The precursor in contact with hot surfaces will vaporize and form a "vapour film boiling" at the interface. The preform, heated up above the precursor decomposition temperature, the vapours will decomposed leading to the deposition of C inside the preform. The immersion in a liquid allows the precursor high concentration thus the process is not limited by the diffusion of the species, leading to a rapid densification. Experiments were first carry out with hydrocarbure precursors. Several experiments parameters were tuned, such as deposition temperature, time or pressure, to estimate their influence on the deposition kinetics and the obtained matrix.

The presented work will focus on the PyC deposition from cyclohexane in order to better understand the deposition mechanisms. Indeed several types of PyC can be observed in the literature: Dark laminar PyC (DL), Smooth laminar PyC (SL), Rough laminar PyC (RL) and

Regenerative Laminar (ReL). Understanding all the deposition mechanisms will help the chemists to tune experimental set up to obtain the suitable PyC.

Microstructural, liquid phase and gas phase analysis were carried by polarized light optical microscopy (PLOM), Fourier transform infra-red (FTIR) and gas chromatography coupled to mass spectroscopy (GC-MS) to answer this question.

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Mixed electronic and ionic conductivity and stability of 8YSZ/graphene bulk composites

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Keywords: YSZ, graphene, CMC, SPS, sintering

Graphene is added to structural oxide and non-oxide ceramics to improve the mechanical, electrical and tribological properties. Examples include Al_2O_3, SiC and Si_3N_4, among others.[1] Similar improvements have been reported in Yttria-stabilized Zirconia, YSZ-graphene composites.[2] YSZ is a well-known oxygen-ion conductor and is used as solid oxide fuel cell electrolytes in past decades. YSZ-graphene composites should therefore display mixed ionic and electronic conductivity, exploited for several electrochemical high-temperature devices and processes. Perovskites with mixed-valence transition metals in the B-site are typically used, but these materials are prone to thermo-chemical and mechanical degradation.

This study will characterize the mixed electronic and ionic conductivity of YSZ/graphene composites prepared by spark plasma sintering (SPS), as a function of graphene loading, and compare them to alternative sintering methods. Starting from a 8YSZ suspension with graphene nanoplatelets (GNPs) powders, we establish a protocol to obtain dense and homogeneous composites, as confirmed by SEM and Raman performed on fractured surfaces. As expected the GNPs concentrate along the grain boundaries and tend to align perpendicularly to the pressure during SPS. Impedance spectroscopy with increasing GNP loading established a percolation limit between 2.5 and 3.75 wt.% and an increase of total conductivity by 10^5, with activation energy of 0.4 eV.

The stability of composites was established at isothermal conditions and varying the oxygen partial pressure (pO2). Composites are stable in reducing conditions $pO_2<10^{-4}$ atm) up to 600 °C for several hours. However, Nyquist plots at 350 °C and 0.21 atm show an irreversible transition from electron to ion conductor behaviour, and increased grain boundaries resistance by 20 fold, compared to simple YSZ with identical grain size. We conclude that graphene blocks ion diffusion at the grain boundaries and establish a stability domain of operation conditions for YSZ-graphene composites. Results are compared with samples sintered at different atmospheres and heating rates.

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Influence of niobium on silicate glasses for nuclear waste immobilization

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Keywords: nuclear waste, niobium, vitrification

Nuclear waste immobilization by vitrification process is a potential route because it allows many elements to be incorporated into the glass and consequently the final waste volume is reduced up to 80% its initial volume.[1] The effect of Nb addition into silicate glasses modified by B_2O_3 and Al_2O_3 additions was studied. In this work, compositions of the system CaO-Na_2O-SiO_2-RxOy[2] were studied, where RxOy represent modifications with additions of B_2O_3 and Al_2O_3. In these compositions, the B_2O_3 was gradually substituted by Nb_2O_5 and the effects of this substitution were evaluated. The gasses, obtained by traditional quenching method, were characterized by X-ray diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FTIR), Raman Spectroscopy and Differential Thermal Analysis (DTA). The XRD diffraction patterns confirmed that the materials are completely amorphous and the DTA analysis revealed that the glass-transition-temperature (Tg) slightly increases by increasing the Nb content, which suggests that the Nb might be participating in the glass structure. Similar tendency was verified by determination of the Hrubÿ parameter,[3] which is related to the stability of the glasses against devitrification. The formation of metaborate rings and boroxol goups was apparently stimulated by the addition of less than 1.0 mol% of Nb, indicating a competition between borum and niobium for positions in the glass network. It was also observed that Nb induces the glass network to the predominance of SiO_4 Q_3 units, which is directly associated to an increase in the chemical stability of the glasses. Such results are indicative that the chemical durability of the studied glasses might be improved by the Nb addition. This compositional system might be a promising alternative to the production of a new family of glasses suitable for the immobilization of nuclear wastes.

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Microstructure and strength composites beta-sialon – boron nitride obtained by spark-plasma sintering

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Keywords: combustion synthesis, spark plasma sintering, beta-sialon, boron nitride

Composites β-SIALON – BN are highly promising for metallurgical applications such as tubes for metal pouring, pipe heaters, nozzles, dozer units, annular breakers, buckets, crucibles, lining plates, thermocouple casing, etc.[1] Combustion synthesis (CS) is a convenient technique for production of SIALON powders with desired composition, particle size, and morphology.[2] Spark plasma sintering (SPS) is a newly developed process that allows pulsed direct current to pass through the die and sample to heat them. Compared with conventional hot pressing, SPS allows higher heating rates and a very short holding time.[3] The spark plasma sintering of β-SiAlON/0–30 wt % BN ceramic composites was investigated. It was studied the microstructure and the strength of the samples (β-SIALON – BN) consolidated by SPS. The raw materials (β-Si_5AlON_7 and BN powders) were prepared by infiltration-mediated combustion synthesis. Experimentally established were the following process parameters for SPS of composites with high relative density (>95%) and flexural strength of 250–300 MPa: (a) heating rate 50 deg/min, (b) maximum temperature 1650–1750 °C, (c) and holding time 5 min. High-density β-SiAlON–BN ceramic composites with improved strength properties were prepared by spark plasma sintering of combustion synthesis-produced β-Si_5AlON_7 and BN powders. Thus obtained machinable ceramics seem promising for fabrication of machine parts and items operating in severe conditions of strong thermal shock and corrosion-active media.

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Oxidation behavior of stainless steel and polymer derived ceramic coatings with passive fillers

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Keywords: PDC ceramics, glass microspheres, hydrothermal corrosion, high temperature oxidation

Polymer-derived ceramics (PDCs) have been investigated in the past few decades for several applications, such as bulk materials, ceramic fibers and porous ceramics. Additionally, the PDC approach has proven to be a suitable alternative for the processing of functional coating systems with protective properties against oxidation and corrosion, high optical emissivity, and many others.[1,2] In this work, the development of a novel thermal barrier coating system based on polymer-derived ceramics, applied by simple lacquer methods is reported. The system consists of a polysilazane (PHPS) bond-coat and an insulating layer formed by the combination of passive yttria-stabilized zirconia (YSZ), commercial barium silicate glasses (G018-311 and G018-385), glass microspheres and an (organo)silazane (Durazane 1800). The aim of this study is to investigate the oxidation resistance of a AISI441 stainless steel with and without the coating. The high temperature oxidation behaviour of these materials in a flow-through oxygen atmosphere and water vapour was investigated at the temperatures of 900 °C, 950 °C and 1100 °C and the exposure times in the range of 1–48 hours. Uncoated substrate (ferritic steel grade AISI 441) was used as a reference. The rate of oxidation in pure flow-through oxygen atmosphere and water vapour were determined, and the oxide scales formed after different exposures times and temperatures on coated and uncoated samples were characterized by SEM/EDS and XRD, including detailed microstructural and phase analysis of the oxide scales formed in the atmosphere of oxygen. X-ray diffraction confirmed extensive corrosion of the uncoated AISI441 stainless steel accompanied by formation of a Cr_2O_3, TiO_2 and a $(Mn, Cr)_3O_4$ spinel containing layer of corrosion products. Beneficial effect of the PDC coating was observed at the temperature of 900 °C, demonstrated by marked reduction of the weight gain of coated steel after 48 h of exposure to flowing oxygen. At higher temperatures the protective action of the PDC coating was observed moderately, and a thick layer of oxidation products was formed at the steel/coating interface.

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Preparation of SiC/SiC_f and SiC/C_f nanocomposites

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Keywords: nanocomposites, SiC/SiC composites, carbon nanofibers, sintering

Type SiC/SiC and SiC/C composites made by addition of SiC and C nanofibers to the SiC matrix were fabricated by two kinds of sintering process: with liquid phase of silicon and by solid state reaction with boron and boron carbide as sintering additives.

In this work ceramic slurries were used to prepare granulates by freeze granulation method, which provided a uniform arrangement of all components in the whole volume of the specimen. As a result lamellas like structured SiC/SiC composites were obtained after sintering. Changes in thermal and mechanical properties caused by addition of SiC and C nanofibers were the subject of further researches. It was observed that additives such as SiC and C nanofibers to SiC matrix has significant influence on the flexural strength and thermal diffusivity of SiC/SiC and SiC/C composites.

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Influence of carbon form on sinterability of silicon carbide

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Keywords: carbon, silicon carbide, sintering, SPS, ceramic, ceramic matrix composites

Strong covalent bonds occurring in silicon carbide (SiC) or silicon nitride (Si3N4) cause to retard solid-phase sintering, because of the slow bulk occurring in this group of materials.[1] As was shown by Prochazka dense SiC can be sintered by using carbon and boron sintering aids.[2] Moreover, in work[3] it was reported that the morphology of used carbon has a strong influence on phase structure and relative density.

In this work the mechanical properties and the microstructure changes of samples sintered with different additions (0.5, 1, 1.5, 2, 2.5, 3 wt%) of six forms of carbon were examined. The following sources of carbon were used: 1. Multilayer graphene (MLG); 2. Highly oriented pyrolytic graphite (HOPG); 3. Graphite, 4. Amorphous Carbon, 5. Active Carbon and 6. Carbon Black. In order to determine the morphology of used carbon the specific surface area, total porosity, shape of pores and Raman spectra were measured. The sinters were consolidated at 1900 °C using the Spark Plasma Sintering method (SPS). The influence of morphology of carbon on density, hardness, fracture toughness and phase structure of the sintered samples was investigated.

A high rate of densification was observed for samples with varied amounts of carbon, depending on the used form. Moreover, samples with the highest relative density show the highest value of hardness, an almost single-phase structure and equiaxed grains.

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Development of silicon nitride based CNT/graphene composite using hot isostatic pressing (HIP) technique

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Keywords: hot pressing, Si_3N_4 composites, SIALON, oxynitrides, CNT, graphene

Different weight percent of CNTs and multilayer graphene (MLG) reinforced silicon nitride based composites were prepared by hot iso-static pressing (HIP) to investigate the effect of the CNTs and graphene on mechanical properties of composite. Composite material was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) for structural analysis, morphology and incorporation of CNT and graphene into matrix. Mechanical testing and sliding wear tests were carried out to observe the effect of CNTs and graphene on mechanical and tribological properties. Significant improvement in the micro-harness, tensile strength but slightly improvement in wear resistance was observed through addition of CNTs and multi layered graphene in Si_3N_4 ceramic matrix. The improvement in the mechanical properties is mainly attributed to grain refinement, uniform dispersion and pinning effect caused by the addition of CNTs and graphene. Si_3N_4 particles were observed at the bottom of the dimples at the fracture site, more likely voids ignition occurred at the Si_3N_4/CNTs, graphene interfaces regions. The mechanical properties, electrical and thermal properties of Si_3N_4 can be enhanced by the addition of CNT and graphene in optimum conditions.

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Preparation of transparent AlON ceramics by using spark plasma sintering

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Keywords: AlON, aluminium oxynitride, spark plasma sintering, transparent, powder solid state reaction

Polycrystalline aluminum oxynitride (AlON, $Al_{(64+x)/3}O_{(32-x)}N_x$, $0 \leq x \leq 8$) is an ideal material for transparent armor owing to its high strength and high hardness, highly resistant to rain and sand damage, and excellent optical properties.[1,2] Al_2O_3 and AlN powder mixtures were used to synthesise AlON ceramics using the reactive spark plasma sintering (SPS) method at temperature 1700 °C for 30 min at 40 MPa and a heating rate of 100 °C/min under nitrogen. The starting components were taken by the following proportion: 64.3 at.% of Al_2O_3 and 35.7 at.%. of AlN.[3] The powders were mixed by specified proportion in alcohol in an ultrasonic disperser in alcohol for 40 minutes, and then air dried. The solid-phase synthesis of ALON with the spark-plasma sintering yielded positive results. The densification, microstructure and mechanical properties of the produced ceramics were analysed. The highest hardness value was recorded to be 18.8 GPa, and the tensile strength of the sample with the highest AlON ratio was measured to be 187 MPa.

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Role of particle–particle contacts in the thermophysical behaviour of green ceramic bodies during drying and firing

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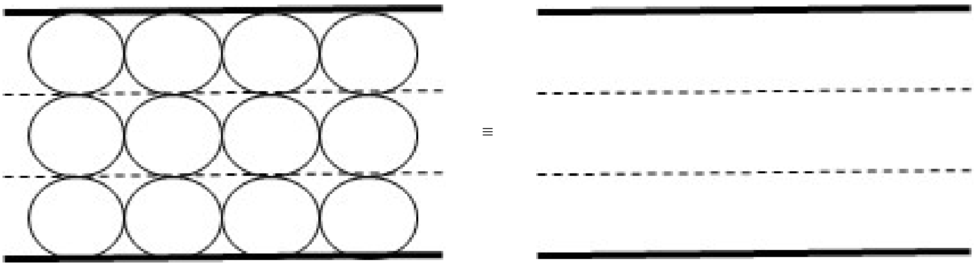
Keywords: ceramic green body, thermal conductivity, particle–particle contacts, drying, firing

After the forming step, a green body is constituted of a compacted powder associated with typically 40–60% pore volume fraction. Further processing than involves thermal treatments to remove excess water with a drying step, if needed, and to consolidate the ceramic body into its final shape during firing. A key aspect, controlling heat and mass transfers in the green body, is the nature and area of the particle–particle contacts in the compacted powder. The work presented in this report examines the relation between particle–particle contact area and thermal conductivity of green ceramic bodies (alumina, zirconia, tin oxide, kaolin clay...).

A model system of metal beads has been studied with flowmeter thermal resistance measurements to illustrate the role of interface planes in the overall thermal conductivity of a granular assembly. This leads to a simplified model based on a series of interface planes across the sample to describe the thermal conductivity of the green body.



As a first example, the approach is used to explain the strong decrease of thermal conductivity of alumina green bodies during the last stage of drying. In particular a marked increase in the thermal resistance of equivalent interface planes occurs as water is removed from the neck regions of the grain assembly, i.e. just next to the particle–particle contacts. In a second example with a nanometric tin oxide powder, BET measurements are used to evaluate the evolution of the particle–particle contact area compared to the particle–pore surface area. A significant increase in thermal conductivity can be attributed to an increase of particle–particle contact area from 5% in the green body to 33% after thermal treatment at 600 °C. Similar behaviour is observed in zirconia ceramics.

It is concluded that the thermal response time of the green body, controlling the temperature distribution within the ceramic body during firing, is strongly sensitive to the state of the particle–particle contacts in the microstructure.

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Production of functionally graded silicon carbide-titanium diboride-aluminium composites by spark plasma sintering technique and their characterization

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Keywords: functionally graded materials, ceramic-metal composites, spark plasma sintering, silicon carbide, titanium diboride, mechanical properties

In this study, production of functionally graded silicon carbide-titanium diboride-aluminium composites by spark plasma sintering technique was investigated. Silicon carbide-titanium diboride-aluminium powder mixtures containing 70–90 weight % silicon carbide-titanium diboride and 10–30 weight % aluminium were sintered at 1600–1900 ºC for 5 minutes by spark plasma sintering.

SiC-TiB_2-Al composites were sintered in a single step by using the spark plasma sintering method. Furthermore, the produced SiC-TiB_2-Al composites were designed as functionally graded composite material (FGM) layers having different compositions and/or residual porosity levels. Phase analysis of the functionally graded composites layers were characterized by x-ray diffraction, and their microstructure was investigated by using a scanning electron microscope attached with an energy dispersive x-ray spectrometer. Hardness, compressive strength values, and densities of the functionally graded composite layer were measured.

Results obtained show that produced composite FGM's have a microstructure characterized by a co-continuous ceramic-metal network. Furthermore, it was determined that the bulk density of the produced functionally graded composite layers was always above 99.5%, the hardness gradually decreased from the front layer to the back layer, while the compressive strength decreased in just the opposite manner.

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Cutting performance of alumina matrix composites reinforced with nickel-coated graphene

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Keywords: cutting tool, machining, SPS sintering, ceramic, ceramic matrix composites

Despite many advantages of graphene, preparation of composites reinforced with Gn still causes many problems.[1] One of the most imported is ceramic matrix – reinforcing phase interface.[2] Lack of bonding between graphene and the matrix create voids on the interface.

It will act as a stress concentrator and reduce fracture toughness (which is critical for cutting tool materials) of the composite. The problem can be solved by modification of graphene surface by application of the nickel layer.[3]

This paper discusses the influence of nickel-coated graphene addition to alumina matrix and its impact on mechanical and cutting performance of obtained composites. The composites were prepared via powder metallurgy processing using the SPS method to consolidate powder mixtures. Applied method due to lowering the sintering temperature and time (in comparison to conventional sintering methods) leads to limiting the grain growth of alumina matrix. It has great impact on physical properties of produced sinters. Basic physical properties of obtained composites such as density, fracture toughness were analysed and compared with composites reinforced with unmodified graphene. Moreover, machining test and tribotest of sinters were made and compared with commercially available cutting tool. The results show that produced cutting tools are characterized with good cutting performance comparable with commercial cutting tool.

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Effect of the initial stress on the densification behavior of nanostructured tetragonal zirconia by sinter-forging below 1000 °C

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Keywords: zirconia, gelcasting, sinter-forging, nanoceramics

Since the discovery of transformation toughening, partially stabilized tetragonal ZrO_2 has become one of the major high-performance ceramic materials, while comparatively little attention has been payed to its optical properties. For noncubic ceramics, the optical anisotropy causes diffuse scattering due to birefringence at grain boundaries. Thus, the transparency of tetragonal ZrO_2 polycrystal (TZP) basically increases as reducing the grain size at extremely low porosities.

Recently, our group successfully fabricated the densely packed green body by gelcasting of zirconia nano-slurry with the solids loading of 7.0 vol%.[1] The initial compact prepared by the gelcasting in our study had the densely packed structure with a narrow pore-size distribution and high connectivity in the particle network. It was found that the coarsening of the pores, which is thought to be the important obstacle of the densification in nanoceramics, was not remarkable in the sintering of the densely packed compact. The suppression of the pore coarsening resulted in the lowering the sintering temperature. Almost fully dense sample with 99.5% of theoretical density was successfully obtained by the pressureless sintering at 1100 °C for 2 h. The sample sintered at 1100 °C maintained the nanometric structure with the grain size of 79 nm. The accordingly sintered sample with nanoceramic structure exhibited the optical translucency, not to say transparency.

It is well known that the application of an external pressure enhances densification kinetic, and results in the reduction of the sintering temperature. The optical transparency is supposed to be improved by lowering the sintering temperature. In this study, the sinter-forging characteristic of densely packed compacts of ultrafine TZP particles was investigated below the temperature of 1000 °C.

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Thermal decomposition of gallium nitride crystal growth on different conditions

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Keywords: thermal decomposition, gallium nitride, hot isostatic pressing

Gallium nitride is characterized by unique properties, which determine its use in many electronic devices. The most important features are as follow: high chemical resistance, piezo- and pyroelectric properties, energy gap about 3.45 eV, high thermal conductivity. Properties listed above give clear evidence that gallium nitride is a perfect material for advanced electronic applications.

The aim of the work was to determine the decomposition temperature of synthesised gallium nitride single crystals. The single crystals were growing from GaN nanopowder and a powder mixture: GaN and GaOOH in presence of metallic gallium in conditions of elevated pressure and temperature in hot isostic pressing.

The obtained results showed influence of hold time of gallium nitride single crystal at maximum temperature in the conditions of high nitrogen pressure on temperatures of their decomposition. Therefore decomosition temperature of gallium nitride depends on the size of their single crystal formed in hot isostatic press.

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Flash sintering of difficult-to-densify ceramics from soft die and hard green body

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Keywords: flash sintering, UHTCs, colloidal processing, microstructure

Ceramics could be sintered in a spark plasma sintering (SPS) furnace in a flash way, the highlight of this process is densification could be completed in less than 1 min; therefore, a huge energy was saved by this approach compared to the one taken at normal SPS conditions. However, due to the designs on the heating system of SPS, the ceramic bodies for flash SPS (FSPS) have to be partially sintered in a separate run in order to achieve an enough high compressive strength, which can afford the initial loading (~5–6 kN) and thermal shock later applied during FSPS. In this presentation, two novel approaches to avoid the pre-sintering stage of ceramic bodies for FSPS will be demonstrated. Texture free HfB_2 based ceramics with relative density over 95% were achieved in 40 s by optimizing the power and loading during FSPS. A combination of microscopy analyses including SEM, TEM and EBSD were used to explore the microstructure features in the as-flashed body, its mechanical property in terms of hardness and strength will also be reported.

T03: Advanced structural ceramics

Invited lectures

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Multiscale mechanical testing and characterization of SiC/SiC composites for accident tolerant nuclear fuel

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Keywords: silicon carbide, composites

Silicon carbide ceramics are a candidate material for the use in nuclear power generation and are suggested to be used in novel accident tolerant fuel (ATF) cladding designs due to its favorable properties, in particular reduced (compared to Zircaloy) oxidation under accident conditions, good neutronic performance, high temperature strength and stability under irradiation. Due to its inherent brittleness, it is suggested to be used in the form of SiC-fiber reinforced SiC-matrix composite. In order to reliably model behavior of highly non-uniform and anisotropic composite materials the knowledge of the individual properties of fiber and matrix, and, crucially, the fiber-matrix interfaces, is required. In addition, nuclear fuel cladding materials are exposed to elevated temperatures during their operation, and therefore the understanding of the temperature dependences of the relevant properties is essential. Micromechanical testing techniques, such as nanoindentation and microcantilever beam fracture, allow determination of such localized properties, and can be implemented in the wide range of temperatures.

In this contribution we present the results of the nanoindentation hardness measurements and microcantilever fracture tests performed on SiC-SiC fiber composite grown by chemical vapor infiltration (CVI) method (General Atomic, US), with tests performed both at room and at different elevated temperatures (up to 600 ºC) in vacuum. In the measurements performed at room temperature it was found that there is a significant difference in the values of hardness between the matrix and the fiber materials, with fiber being significantly softer and radially non-uniform in hardness (~17 GPa in the center, ~40 GPa at the periphery, comparable to the matrix). Matrix hardness is seen to drop from ~45GPa at room temperature to ~35GPa at 500 °C. This can be correlated with the results of elemental mapping using energy-dispersive X-ray spectroscopy (EDX), which indicate that within the fiber material the grain boundaries are decorated with excess carbon, abundant in the center and almost absent on the periphery of the fibers.

Using focused ion beam (FIB) milling, microcantilevers were manufactured at the interphases, within individual fibers and in the bulk matrix. The local microstructure has been investigated using transmission electron microscopy (TEM), using FIB-machined lift-out samples, so that the local preferred direction of the grain growth could have been directly observed and cantilevers in the matrix could have been oriented differently with regard to it. It was found that interphases are weak spots (fracture stress ~2.5 GPa), matrix is the strongest (~20 GPa) and fiber intermediate (~7.5 GPa). TEM was also used on fractured cantilevers in order to determine the character of crack propagation. It was found that within the matrix fracture is transgranular, and observed fracture stress is independent on the orientation of the cantilever axis relative to the direction of the elongated grains in the matrix, within the fiber it can be both trans- and intergranular, depending on the amount of excess carbon decorating the grain boundaries, and at the interfaces it follows the interlayer-fiber boundary.

Presented results suggest a methodology enabling to better understand and predict the properties of SiC fiber composite, in advanced fission and fusion designs, as well as in non-nuclear applications.

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Toughened, wear resistant and damage tolerant silicon carbide ceramics by adding graphene-based fillers

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Keywords: toughness, strength, wear, damage, graphene, ceramic composites

Silicon carbide (SiC) ceramics are one of the most demanded engineering ceramics due to the combination of their outstanding tribological and thermal properties jointly with a good mechanical response at high temperature. However, the Achilles' heel of these materials is still their relatively low toughness and limited machinability. To overcome these difficulties, we have manufactured SiC composites containing graphene-based fillers, in particular, graphene nanoplatelets (GNPs) or graphene oxide sheets (GOs), which were further reduced to graphene (rGOs) during the spark plasma sintering process. The macro- and micro-mechanical response of SiC/graphene composites as a function of the filler source and content has been analysed, the mechanical performance being closely linked to the wear properties.

Fracture toughness (K_{IC}) and strength (σ_f) measurements evidenced that composites containing just 5 vol.% of rGOs exhibited an outstanding mechanical performance,[1] increasing both K_{IC} and σ_f by ~162% and ~60%, respectively, when compared to monolithic SiC. In the case of GNPs composites, filler contents up to 10 vol.% are required to promote a larger occurrence of crack shielding mechanisms, with K_{IC} increments of 86%. Furthermore, the contact damage resistance of SiC was clearly enhanced when adding graphene fillers, as Hertzian contact damage tests using the bonding-interface technique demonstrated. Graphene fillers, especially rGOs, promoted the formation of a quasi-plastic damage zone beneath the contact, redistributing the stress field and limiting the subsurface Hertzian cone cracks growth. That improved damage resistance enhanced the machinability of the composites. Finally, the wear resistance of SiC materials under dry sliding conditions significantly enhanced with the addition of graphene fillers,[2] with maximum improvements of ~70% for 20 vol.% GNPs composites, mainly due to the formation of a wear protecting graphene-based tribofilm.

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Progress in manufacturing ultra-high temperature ceramic matrix composites (UHTCMCs)

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Keyword: UHTCMC

There is an increasing demand for advanced materials, for aerospace and other applications, with temperature capability ranging from 1500 ^{o}C to well over 2000 °C and able to survive highly corrosive environments whilst subject to intense heat fluxes and mechanical stresses. The interaction of environmental conditions together with the requirement that dimensional stability is maintained makes the selection of suitable materials extremely challenging. This paper discusses the design, development, manufacture and testing of a new class of ceramic matrix composites based on C fibre and SiC preforms enriched with ultra-high temperature ceramic (UHTC) powders and with a matrix infiltrated by either RF- or microwave-heated chemical vapour infiltration (CVI). These composites will form of suite of materials suitable for application in severe aerospace environments.

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Mechanical behavior of zirconia-based composites with transformation-induced plasticity

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Keywords: zirconia, tetragonal to monoclinic transformation, toughness, Weibull analysis

Yttria-stabilized (Y-TZP) zirconia ceramics are increasingly used for developing metal-free restorations and are now considered as promising alternatives to titanium as dental implants. Zirconia indeed possesses high strength and good toughness for a ceramic, together with excellent bio-integration and biocompatibility. However, Y-TZP ceramics are still considered as brittle ceramics, since transformation induced toughening occurs after cracks start to propagate. Also, in some circumstances, Y-TZP may be prone to aging. Our current research is focusing on strategies to improve the LTD resistance of Y-TZP but also to develop alternative composites with better stability *in vivo* and higher degree of ductility. In this work the mechanical characterization of a new type of very-stable zirconia-based composites is presented. These materials are composed of ceria-stabilized zirconia (84 vol%Ce-TZP) containing two second-phases (alumina and strontium hexa-aluminate) and exhibit exceptional strength, toughness and ductility. In other words, in these composites, quite extensive transformation-induced plastic deformation occurs before failure, which leads to mechanical behavior laws similar to metallic alloys.

Acknowledgements

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Nano-mechanical testing of advanced ceramics

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The deformation and damage characteristics of differently oriented WC grains/crystals in WC – Co, Si_3N_4 grains/crystals in reaction bonded Si_3N_4 system and ZrB_2 grains/crystals in ZrB_2 polycrystal were investigated. Depth-sensing nano-indentation and scratch tests of grains and micro-compression tests of micropillars prepared by focused ion beam from oriented facets of grains were studied. Electron backscatter diffraction (EBSD), atomic force microscopy (AFM) and scanning electron microscopy (SEM) investigations were performed to determine the grain orientation and to study the surface morphology and the resulting deformation and damage mechanisms around the indents and in micropillars.

The hardness and scratch resistance of the differently orientated grains showed significant angle dependence from the basal towards the prismatic directions. A strong influence of the grains orientation on compressive yield stress and rupture stress values was found during the micropillar test, too. The active slip systems for individual ceramics have been recognized. The different properties of the basal and prismatic planes was found to be connected with the different deformation mechanisms – slip and dislocation activities.

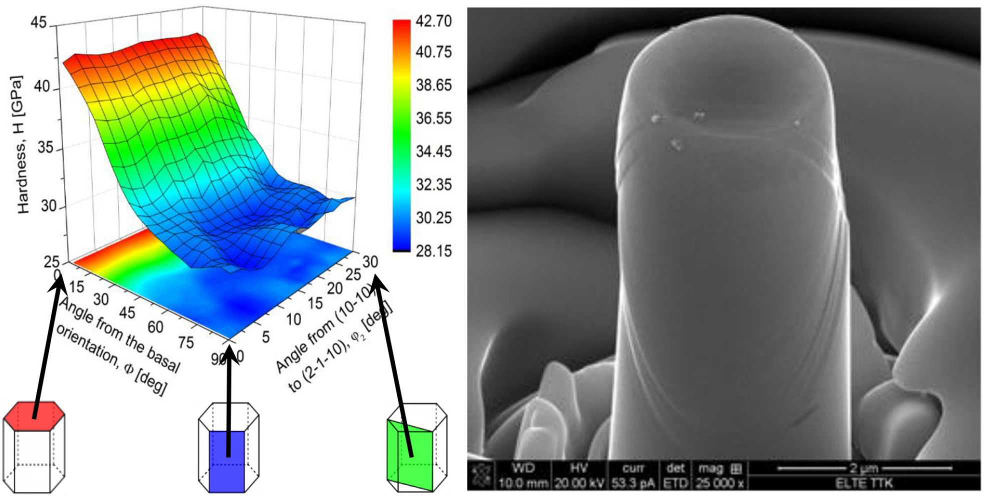

Fig. 1. Hardness anisotropy in WC grains and micropillar deformation of ZrB_2 micropillar

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Ultra-high temperature mechanical behavior of ZrB_2-based laminates

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A combined experimental and computational approach has been used to study the elevated temperature fracture behavior of ZrB_2-based ceramics. Experimentally, laminate structures consisting of alternating layers of ZrB_2 and graphite/ZrB_2 were produced. After densification, the strength of the laminates was tested at temperatures up to 2000 °C. The inelastic work of fracture was estimated from load deflection curves, which showed that the laminates consumed significantly more energy during fracture than conventional ZrB_2 ceramics. Analysis revealed extensive crack deflection due to the laminate structure. In parallel, multi-phase-field (MPF) models based on the regularized formulation of energy functionals in Griffith theory were developed to study crack initiation, propagation, and branching in two dimensions. Models were built by first simulating fracture behavior in single crystal ZrB_2 for comparison to predictions from classic fracture mechanics. Then, propagation of intergranular and transgranular cracks was simulated by considering the effects of grain boundary energy anisotropy and crack surface energy in polycrystalline ZrB_2 and ZrB_2-based laminates. Simulations were able to reproduce crack deflection/branching behavior in laminates using realistic properties for the constituent phases. The presentation will discuss new insight into fracture behavior at elevated temperatures from the combined experimental and computational approach.

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New sintering process for high density and limited grain growth with plastic deformation as dominating mechanism

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Keywords: sintering, sintering process, plastic deformation, densification mechanism

Traditionally, sintering is the densification process of powder compacts, in which interparticle pores are eliminated by atomic diffusion driven by thermal energy. The atomic diffusion may cause also grain growth, besides contributes to densification. For polycrystalline materials, higher density generally results in improvement of properties like strength and toughness, while the undesirable grain growth results in degradation. Attempts have been made to gain full density, while keep the grains with limited growth.

A new method was proposed to sinter ceramic powders at a lower temperature close to the onset point of grain growth, at the same time apply a higher pressure to the compact. Fully dense micro-sized or nano-sized ceramics with limited grain growth were made by the new

route. The sample shows excellent mechanical properties. The plastic deformation under high pressure and at high temperature is proved to be the dominating mechanism for the densification process.

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Chemical vapor deposition of SiC environmental coating for SiC/SiC composite

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Keywords: laser chemical vapor deposition, SiC/SiC composite, SiC coating

SiC fiber-reinforced SiC matrix composite (SiC/SiC composite) is an excellent structural ceramic material because of its high strength, high ductility and light weight. Although MI (Metal Infiltration) and PIP (Polymer Impregnation Pyrolysis) have been studied to fabricate SiC/SiC composite, CVD (Chemical Vapor Deposition) could be the most promising because high corrosion resistant SiC can be prepared. CVD SiC coating has been usually prepared by using halide precursors such as MTS (Methyltrichlorosilane) and $SiCl_4$ (halide CVD). The deposition rate of halide CVD is low and by-product HCl would degrade SiC fibers. In the present study, laser enhanced CVD (LCVD) was applied by using non-corrosive metalorganic precursors, hexamethyldisilane, polycarbosilane and $SiH((NCH_3)_2)_3$ precursors. CO_2, Nd:YAG and semiconductor (InGaAs) lasers (~250 W) were employed. The laser beam was expanded to around 20 mm in diameter enabling a wide-scale deposition with scanning laser. LCVD can prepare highly crystallized β-SiC film at deposition rate of several 100 times higher and at deposition temperature several 100 K lower than conventional MOCVD. β-SiC film was prepared at 2200 μm/h at 1500 K by using CO_2 laser. α-SiC (2H) film was prepared at 70–195 μm/h using $SiH((NCH_3)_2)_3$ precursor at ~1000 K. Plasma can also enhance the deposition of films in CVD. By combining microwave (2.45 GHz, 0–1.5 kW) and magnetic field (0.0875 T), much active electron-cyclotron-resonance (ECR) plasma can be formed. The ECR plasma is highly stable even at a higher pressure, and ionizes gases more than radio-frequency and micro-wave plasma. We have applied both laser and ECR plasma in CVD (laser-plasma CVD). The deposition temperature was further decreased in the laser-plasma CVD. Highly crystallized β-SiC film was prepared by laser-plasma CVD at a significantly low temperature 1123 K, 150–400 K lower than that of halide CVD, at a deposition rate of 138 μm/h, 10 to 100 times higher than that of MOCVD. Laser CVD was also used to prepare $Yb_2Si_2O_7$ and SiAlON bonding layer between SiC fiber and SiC matrix in SiC/SiC composite.

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Van der Waals interactions in refractive index matched nanoparticle dispersions

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Van der Waals forces have a strong influence on the dispersion quality of ceramic slurries and finally affect the resulting properties of ceramic parts, filled polymers, hybrid materials and nanocomposites in general. Reducing the van der Waals forces and therefore, matching the refractive index between the filler and the matrix should improve dispersion in hybrid materials, as already experimentally shown by Wozniak et al.[1] As an alternative, steric stabilization offers a tool to improve the stability and to modify the rheological behaviour.[2,3]

However, the dispersion quality of refractive index matched dispersion cannot be assessed by SLS or DLS based particle size measurement techniques. We present here the rheology based results of a study applying model dispersions containing silica nanoparticles and as a solvent mixture a matched 1-butanol and benzyl alcohol system. The refractive index of the solvent was changed by varying the mixing ratio, and the effect of index difference on the filler-matrix interaction being investigated. In agreement with the theory, a stronger gel network was observed when the refractive index of filler and solvent were matched. If the difference in refractive index of the two materials became too large, particles and solvent interaction was reduced, and agglomerates were formed. This resulted in a weaker gel network.

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Diamond reinforced ceramic materials: potential wear resistant components

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Materials with enhanced wear resistance are of great interest for modern industry. In many cases, advanced ceramics show high wear resistance at room and high temperatures. Nevertheless, there is a demand of a further improvement of the wear and tribological behavior of these materials. The reinforcement of ceramic materials with super hard particles like cubic BN (cBN) or diamond is one possibility to overcome the rising requirements. At normal sintering conditions of ceramic materials, diamond and cubic boron nitride are metastable modifications and transform into the soft hexagonal modifications. Therefore, special approaches have to be applied to obtain dense materials with high hardness, wear resistance and thermal properties. The possibilities and constraints of diamond-ceramic composites are reviewed. The most promising way for the production of diamond/SiC components was found to be the reaction bonding of diamond by silicon infiltration. During this process a three dimensional skeleton of SiC is formed. Due to the epitaxial growth of the SiC on diamond, a strong interface between diamond and SiC is formed resulting in super-hard wear resistant components with high thermal conductivity and low thermal expansion coefficients. Such materials can be produced as bulk materials or as SiSiC ceramic components with a silicon carbide bonded diamond layer. The layer thickness can be between several 100 µm up to several millimetres. This allows a cost effective production of large wear parts with complex shapes.

Correlations between preparation, microstructure and wear resistance, mechanical and thermal properties are given. The results show the great potential of these materials for a wide range of applications.

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Temperature dependence of thermal properties for high thermal conductive silicon nitride ceramics

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Keywords: silicon nitride, thermal conductivity, thermal expansion coefficient, metalized substrate

Silicon nitride has attracted much attention as advanced insulating substrates for power module because of its excellent mechanical properties with intrinsic high thermal conductivity. So far extensive research works have been carried out for increasing thermal conductivity without degrading the mechanical properties. Our group has succeeded in fabricating high

thermal conductive silicon nitrides by nitrideing Si powder compacts with sintering additives, followed by post sintering process[1]. When applying the developed silicon nitride as metalized substrates in power modules, it is very essential to understand temperature dependence of thermal properties such as thermal conductivity, and coefficient of thermal expansion, CTE for designing structures of power modules. Because it is well known that these thermal properties exhibit strong temperature dependence around room temperature. In this investigation thermal properties of silicon nitrides possessing different thermal conductivities was examined in the temperature range between –50 to 400 ºC. It was revealed that variation of thermal conductivity with temperature was significant in higher thermal conductive Si3N4. In addition the material with the highest thermal conductivity (180 W/(m·K) at RT) kept about 100 W/(m·K) even at 250 ºC. On the contrary, there was little difference between CTEs of Si3N4 with different thermal conductivities.

In general ceramic substrates are used in the form of metalized substrates in order to ensure heat conduction from device to heat sink as well as to keep mechanical reliability. Cu metalized silicon nitride substrates start to be used in high-power modules. Large difference of CTE between Cu and Si_3N_4 might affect thermal expansion behaviour of Cu /Si_3N_4 substrates. The thermal expansion of metalized substrates was examined in the temperature range between –40 to 250 ºC. It was revealed that the thermal expansion and contraction curves exhibited hysteresis due to plastic deformation of Cu. In addition transition points corresponding to elastic to plastic deformation of Cu were observed. CTE of the substrate in the elastic region substantially matched the estimated value based on the Turner model[2] using measured CTE values.

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SiAlON based ceramics for cutting tool applications

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Keywords: α/β-SiAlON, intergranular phase chemistry, machining, cast iron, superalloy

SiAlONs are ceramic materials with a range of technically important applications, from cutting tools to wear parts and the properties of SiAlONs can be tailored for specific applications. Although there many ongoing studies on new materials development for cutting tool applications, α/β -SiAlONs have been widely used for machining of cast irons and superalloys. Wear performance of the cutting tools are governed by material properties which are affected by microstructure. Microstructure of α/β -SiAlONs can be controlled by types and amount of liquid phase sintering additives, which affect the distribution and crystallinity of intergranular phase, remnant of the additives after sintering. In this presentation, the effect of various types of sintering additives on the intergranular phase chemistry and microstructures will be reported for α/β -SiAlONs that are developed to be used in cast iron turning and in high speed superalloy milling. It will be shown that additive types play an important role in intergranular phase crystallinity and its wetting behaviour of grain boundaries and hence the cutting performance in cast iron machining. However, for high speed superalloy milling, chemical interactions between the superalloy and SiAlON cutting tool material is more important.

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High thermal conductivity of liquid-phase sintered silicon carbide ceramics

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Keywords: SiC, thermal conductivity

In this paper, factors affecting the thermal conductivity of LPS-SiC will be presented. The results suggest that (1) the oxygen impurity in SiC lattice was detrimental in increasing the thermal conductivity of LPS-SiC; (2) the Al-containing additive compositions should be avoided for improving the thermal conductivity of LPS-SiC; (3) the N-doping has little effect on thermal conductivity of LPS-SiC; (4) the occurrence of β→α phase transformation was detrimental in increasing the thermal conductivity of LPS-SiC; and (5) the selection of additive compositions which could pick-up oxygen from SiC lattice was important in improving the thermal conductivity of LPS-SiC ceramics. Based on the above understanding, a fully dense SiC ceramic with a room temperature thermal conductivity of 262 $W(m\cdot K)^{-1}$ was obtained via spark plasma sintering β-SiC powder containing Y_2O_3-Sc_2O_3. The high thermal conductivity of the SiC ceramic could be attributed to (1) oxygen content reductions in the SiC lattice from 6700 ppm to 1770 ppm during SPS processing, (2) the presence of clean SiC-SiC boundaries, which increased contiguity between SiC grains, and (3) the lack of Y solubility within the SiC lattice due to large ionic size differences of the elements.

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Engineering design and processing of silicon nitride ceramics for industrial applications

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Keywords: silicon nitride ceramics, ceramic substrate, power electronics

Silicon nitride (Si_3N_4) ceramics, so-called self-reinforced ceramic materials, exhibit a very unique microstructure containing whisker-like elongated grains plus fine matrix grains. The class of Si_3N_4 ceramics in general shows very good mechanical properties combined with good resistance to wear, corrosion, and oxidation. Therefore, many government funded ceramic turbine related programs were initialed globally in 1990 to design and implement them as high temperature structural components such as hot section vane, blade, and turbo rotor for gas turbine and microturbine engine. These integrated global research efforts conducted by academia, research institution, industrial sectors, and government during the last four decades allow the ceramic community to gain a much better understanding on how to control such a microstructure and the interfaces and continuous intergranular films as they relate to mechanisms for enhanced toughness in a self-reinforced ceramic. In addition, it is also now known that the oxide additives could influence the alpha-beta Si_3N_4 phase transformation, microstructural evolution, microstructural and chemical bonding of interfacial thin film during the processing and sintering procedures. Recently, great attentions on Si_3N_4 ceramic have been on its application as an insulator substrate for power electronic components; i.e., IGBT and LED due to its excellent performance in mechanical properties and reliability to overcome the increased thermal stress generated during application condition. This presentation will focus on engineering design and processing of chemical compositions and also microstructure of Si_3N_4 ceramics to achieve a combined physical and mechanical property targeted for a specific component application. The implications and challenges to achieve the aimed properties and performances learned through the course of these studies would also be presented and discussed in the paper.

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Dual scale composite architectures for high temperature structural applications

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Dual composite (DC) architectures have been shown to increase wear resistance while maintaining or increasing fracture toughness in WC-Co composites for room-temperature applications by the use of multiple, discretely segregated engineered microstructures.

Composites of zirconium diboride (ZrB_2) and molybdenum disilicide ($MoSi_2$) are candidates for similar dual composite architectures for high-temperature structural use in corrosive environments, due to the high-temperature ductility and oxidation resistance of $MoSi_2$.

Multiple DC architectures were prepared by hot-pressing dispersing pre-sintered granules of known volumetric amount, size and composition in a continuous matrix made of different loose powder mixtures. Granules were produced by the freeze-spray granulation. Conventional composites of the only compositions representative of granules and matrices were hot pressed for comparison.

Microstructures were investigated and correlated to mechanical properties including elastic modulus, thermal expansion, flexure strength and fracture toughness at room temperature up to 1500 °C in air, and compared to corresponding traditional particulate sub-composites.

Shared themes of T03: novel processing, microstructure-property relationships, ceramics for extreme conditions, oxide and non-oxide structural ceramics, testing and characterisation of advanced ceramics.

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A short review on the mechanical properties of pure fully-dense boron carbide fine ceramics

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Boron carbide is the third hardest material in Nature after diamond and the cubic phase of boron nitride. This fact, together with its light weight, high corrosion resistance and chemical stability makes this material a promising candidate for structural application under extreme environments. Unfortunately, applicability has been restricted by the severe difficulty for sintering pure dense specimens at moderate temperatures. This drawback has been partially overcome recently: fine-grained, (average grain size as low as 150 nm) pure near-fully dense specimens can be prepared by spark plasma sintering under optimized conditions.

This presentation will outline the room temperature fracture and wear properties as a function of the grain size as well as the high-temperature creep plasticity. The main features making this material a unique material will be emphasized as well as the parts requiring further investigation.

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Ceramic-based composites with complex architectures

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The advance of many technological fields, from healthcare to aeronautics, demands new materials with unconventional combinations of mechanical and functional properties. Among these, ceramics are of great interest due to their corrosion and wear resistance, enhanced chemical and thermal stability, high flexural strength and hardness that make them suitable for demanding applications. However, the performance of ceramics is often limited by their low fracture resistance. Significant advances have been achieved in the development of tougher ceramics-based composites and one of the themes that recurrently appears is the need to control the materials architecture at multiple length scales from the nano-level and up. In this respect natural materials such as bone or nacre provide blueprints for the use highly complex, hierarchical microstructures to enhance fracture resistance. Mineralized natural materials are composites where the inorganic phase is cleverly interlayered with an organic component that acts as compliant phase. These composites exhibit characteristic structural features on multiple length scales from molecular to macroscopic dimension resulting in strong, damage tolerant materials. In this presentation we will review some advances on the use of top down methods such as freeze casting or robotic assisted deposition for the fabrication of damage-tolerant composites whose design takes hints from Nature. These composites combine technical ceramics with a “soft” phase (metals, polymer or carbon) in complex architectures. The parameters that determine the material structure and its influence on the mechanical and functional response will be reviewed. The objective is to discuss the difficulties associated with the design and fabrication of synthetic structures that mimic the structural and mechanical characteristics of natural counterparts and to point out possible directions of research.

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Electrically conductive ceramics – processing and properties

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Keywords: alumina, silicon nitride, silicon carbide, electrical conductivity

Si_3N_4 and Al_2O_3 ceramics are insulating materials, SiC is a semiconductor. All of this type of ceramics are widely used for the engineering applications because of their excellent mechanical and chemical properties. Hardness is one of those which belong to the most important. This brings also a problem with final machining of these materials. Introduction of the electrically conductive elements without substantial decreasing of the other properties of ceramics is a way how to apply the electrical discharging machining also for this class of materials. Present paper deals with the processing of three types of ceramics with increased electrical conductivity. NbTiC electrically conductive phase was used for SiC ceramics, carbon nanofibres were used for Si_3N_4 ceramics and carbon nanotubes were used for Al_2O_3 ceramics. In all types the increased electrical conductivity was observed, 2700 S/m for SiC ceramics, 1300 S/m for Si_3N_4 ceramics and 1800 S/m for Al_2O_3 ceramics. The way of conductive phase introduction and its influence on the mechanical properties will be discussed. For the processing was used hot-pressing as well as rapid hot-pressing.

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Texturing and mechanical properties of MAX phase ceramics and Zr(Hf)B_2-base ultra-high temperature ceramics

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Keywords: MAX phase, high temperature ceramics, textured ceramics

The controlled development of texture is one of the ways for effectively improving properties of ceramics. We have demonstrated a new processing of textured ceramics with a feeble magnetic susceptibility by colloidal processing in a high magnetic field and subsequent heating[1]. The principle of the process is that a crystal with an anisotropic magnetic susceptibility will rotate to an angle minimizing the system energy when placed in a magnetic field. This processing can be applied to fabricate many kinds of textured ceramics with non-cubic structure. Here, processing of textured MAX phase ceramics and Zr(Hf)B2-base ultra-high temperature ceramics is demonstrated.

MAX phases are the layered ternary ceramics with the general formula Mn+1AXn (where M is an early transition metal, A is an A group element in the periodic table, X is a C or N, and n = 1, 2, 3). They show unique combination of metallic and ceramic properties, which were derived from their layered hexagonal structure and the anisotropy of the bonding strength. There are strong M-X bonds and weak M-A bonds in the nano-laminate. As examples of MAX phase ceramics improved mechanical properties of textured Nb_3AlC_2, Ti_2AlN and Ti_3SiC_2 ceramics are demonstrated[2]. Textured Nb_4AlC_3 with plate-like grains shows a high flexural strength (about 1200 MPa) and the fracture toughness (about 18 MPa•m$^{1/2}$).

Also some anisotropic properties of textured Zr(Hf)B_2-base ultra-high temperature ceramics are demonstrated[3].

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Local mechanical properties of advanced structural ceramics measured using microcantilever beam specimens

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Keywords: Microcantilever beam specimen, strength, toughness, Si_3N_4, SiC, ion-exchange glass

Local mechanical properties are important to understand the nature of the mechanical properties of bulk ceramics and glass. In this study, the local mechanical properties of several kinds of ceramics and glass were measured using microcantilever beam specimens prepared by focused ion beam technique. The size of the sample was about 2.5 × 2 × 15 µm and their section profile was pentagonal. A sharp single notch was also machined along a target to measure the fracture toughness. After bending test, the bending strength was calculated by the fracture load and the second moment of area, and the fracture toughness was estimated by displacement extrapolation method based on finite element analysis. Although Si_3N_4 ceramics are often utilized as structural components in the Al casting industry and they occasionally suffer breakage after long-term use, degradation mechanism has not been clarified, yet. The degradation behaviour of Si_3N_4 ceramic surfaces soaked in molten Al in short periods of time was evaluated using microcantilever beam specimens. The bending strength of the ceramic surface before and after contact with molten Al was 5.89 ± 1.33and 3.03 ± 0.28 GPa, respectively. The fracture toughness of the corroded layer in Si_3N_4 ceramics also decreased compared to that of the polished surface. Using fractography by observation with scanning electron microscopy, it was shown that changes in the grain boundary glassy phase resulted in the degradation of strength and fracture toughness. From this mechanism, the Lu_2O_3 additive was proposed to make highly durable Si_3N_4 ceramics. In the ion-exchange glass, an improvement in the strength resulted from compressive stress by replacement of Na^+ with K^+. Such ion-exchange should cause structure change, which means that the ion-exchange possibly results in change in the mechanical properties in the compressive layer. The bending strength of compressive layer in ion-exchanged glass measured using microcantilever specimens is about 40% higher than that of as-polished glass. There is no significant variation with the fracture toughness before and after ion-exchange. Young's modulus of ion-exchanged glass was higher than that as-polished glass. Consequently, it was shown that the strengthening of the ion-exchanged glass resulted from the improvement of Young's modulus. Furthermore, the strength of a neck region of porous SiC ceramics measured using microcantilever beam specimens was 18.8 GPa. It was found that the strength of bulk porous SiC ceramics was quantitatively explained by maximum pore size, neck radius and neck strength.

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Micro-mechanical test method for searching toughening mechanisms operating at nano-scale

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Keywords: fracture toughness, R-curve, stishovite, silica, transformation toughening

The development of strong, tough, and damage-tolerant ceramics requires nano/microstructure design to utilize toughening mechanisms operating at different length scales. The toughening mechanisms so far known are effective in micro-scale. Here, we developed a micromechanical test method using micro-cantilever beam specimens to determine the very early part of resistance-curve. This testing method is a powerful tool to search for toughening mechanisms that may operate at nanoscale for attaining both reliability and strength of structural materials. A case study is presented here.

Silica (silicon dioxide, SiO_2) is a common mineral found in many rocks and sands. However, quartz and glass are brittle and easily broken. Recently, Nishiyama[1] found that the brittle glass is transformed to nanocrystalline SiO_2 stishovite, which is tough (13 MPa m1/2) and very hard (33 GPa), by high-pressure synthesis. Stishovite is a high-pressure polymorph of silica stable at pressures above 9 GPa. The finding of “fracture-induced amorphization” in stishovite lead to a proposal of a new type of transformation toughening by the direct transition from crystal to amorphous state[2], which is different from the classical martensitic transformation of zirconia. We investigated strength and toughness of nanocrystalline stishovite by using micro-cantilever beam specimens. The crack growth resistance curve (R-curve) rose steeply with crack extension of only a few μm[3], and reached to a plateau value of 10.9 MPa $m^{1/2}$. The sharply rising R-curve is the result of very narrow transformation zone width of nanocrystalline stishovite. We discussed the effects of grain size,and microstrain on the critical stress, the transformation zone width, and thereby, the fracture toughness[4].

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Thermal insulation ceramics initiative: from crystal structure modification to morphology design

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Keywords: thermal insulation materials, E/TBC, porous materials

High efficiency engine and propulsion system strictly challenge extensive thermal insulator candidates by pushing them to their critical property limits in extreme conditions. A critical demand has been addressed to the simultaneous optimizations on high temperature thermal/chemical stability and extremely low thermal conductivity. How do we discover new thermal insulation materials through adoption of novel concept or mechanism in order to achieve giant thermal resistance? This presentation includes our recently progresses on crystal chemistry modification of rare-earth silicates as E/TBC candidates[1–3] and morphology design of highly porous silicates[4,5] and nano-carbides[6,7] as super thermal insulation materials. Our works showed the strategic engineering of phonon behaviours and nano-scale heat conduction may initiate and fasten breakthroughs of advanced thermal insulation ceramics in extreme environments.

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Making ceramics tolerant to damage by forming nanolaminated structures: from MAX phases to MAB phases

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Keywords: non-oxide ceramics, nanolaminated structures, MAX phases, MAB phases, structure-property relationships

Non-oxide ceramics are potential materials for extreme environment applications such as scramjet engine components, leading edges and thermal protection systems for hypersonic vehicles, and cladding materials in generation IV nuclear reactors. However, the defect sensitivity and poor thermal shock resistance are the main obstacles to impede their near-term applications. The origin of brittleness is the nature of strong covalent bonding, which makes the activation of slip systems extremely difficult. Formation of nanolaminated structures like MAX phases ($M_{n+1}AX_n$, where M is an earlier transition metal, A is a group-A element, X is carbon or nitrogen, n = 1–6), has been proven an effective approach to overcome the brittleness of transition metal carbides and nitrides. Inspired by the success in development of MAX phases, nanolaminated ternary borides called MAB phases (where M is a transition metal, A is a group-III_A or IV_A element, B is boron) were recently proposed. In this presentation, the structure and properties of MAX phases will be introduced first. These materials are characterized by a transition metal carbide or nitride layer ($M_{n+1}X_n$) interleaved by a close packed A-group element layer, which exhibit a unique combination of the merits of both metals and ceramics. The chemical bondings in these materials are anisotropic with strong covalent M-X bond and weak M-A bond. The origin of damage tolerance is the presence of weak τ-type bond between A atom and the adjacent M-X bond chain, which results in low shear deformation resistance. Similar to MAX phases, MAB phases also exhibit anisotropic electrical and mechanical properties, low shear deformation resistance and are tolerant to damage. The high stiffness is originated from the strong covalent B-B or M-B bonds, while the low shear deformation resistance and easy slip are due to the presence of metallic M-B or A-A bonds. Slip systems of the new MAB phases will be given and their correlations to the electronic structure and chemical bonding will be discussed.

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Oral presentations

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Processing and oxidation behavior of ZrB_2-SiC-AlN composites

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The effects of AlN substitution on sintering, oxidation and thermal properties of ZrB_2-SiC were investigated. Up to 10 vol% AlN was substituted into ZrB_2-SiC by replacing ZrB_2 or SiC. Samples were all sintered to nearly full density (93.5%~99.4% depending on compositions) by pressureless sintering. AlN substitutions limited the grain growth of ZrB_2. Oxidation resistance of the composites were tested at several temperatures up to 2000 °C using both static and cyclic oxidation tests. AlN substitutions affected the oxidation behavior by formation of Al_2O_3 and/or aluminosilicates. X-ray photoelectron spectroscopy (XPS) showed the presence of Al_2O_3 and SiO_2 on the surface. Presence of Al_2O_3 could possibly lead to a modification in the viscosity of the glassy oxide scale as well as decrease the viscosity of SiO_2 scale at a higher temperature (1600 °C). Replacement of ZrB_2 by AlN resulted in a more protective scale both at 1000 °C and 1600 °C. Substitution of SiC by AlN resulted in a compromise of the oxidation behavior at 1600 °C due to devitrification of the scale. Several samples were also cycled between 2000 °C with plasma heating in a 100 torr air pressure (21% oxygen). Volatility diagrams were constructed to assess the thermal stability of the oxides formed. A delicate balance in ZrB_2, SiC and AlN is required for optimal performance.

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Environmental barrier coatings (EBC) for silicon-based ceramic composites

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The need to increase the cycle efficiency and reduce noise and NO_x emissions from jet engine turbine has promoted the development of ceramic matrix composites (CMC) such as silicon carbide fibre-reinforced silicon carbide (SiC-SiC). Use of CMCs will lead to a significant improvement in fuel consumption and thrust-to-weight ratio compared to metal alloys. In addition, the low density of CMCs allows weight savings of up to 30% compared to Ni-based super alloys equating to about 1000 kg/engine thus leading to vastly improved fuel consumption. However, silicon (Si)-based ceramics such as SiC-SiC have poor environmental durability in high velocity combustion environments. Si-based ceramics have excellent oxidation resistance due to formation of a protective silica layer on reacting with dry air making them stable at temperatures up to 1200 °C for long-term application. On the other hand, the same silica layer will react with water vapour to form gaseous silicon hydroxide, leading to high recession and component failure. To avoid this behaviour, a prophylactic environmental barrier coating (EBC) is required. A variety of EBCs have been developed in the past, which consists of a minimum of 4 layers requiring a costly application method such as plasma spraying. In this work, five rare earth monosilicates are being examined as potential EBCs: Y_2SiO_5, Yb_2SiO_5, Lu_2SiO_5, Gd_2SiO_5 and Er_2SiO_5. Their performance in steam environments is being studied at 1200–1350 °C for different times as a first step to determine which EBC candidate is most promising for protecting SiC-SiC CMCs in the jet engine environment. The main aim of this study is to develop a reliable single layer of EBC instead of multilayers and to develop a low cost method of applying the EBC.

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Influence of composition on optical properties of Y-α-SiAlONs

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Keywords: SiAlON, phase composition, SPS, microstructure, optical properties

Traditional transparent materials are not suitable for many applications such as; transparent armors, night vision vehicles, high-speed infrared guided missiles on transparent materials field focused on development of new materials those have superior mechanical and thermal properties as well as good optic and IR transmission. SiAlON ceramics generally designed for use in structural applications under extremely harsh conditions because of their high strength, good thermal shock resistance and chemical stability. In recent years, serious attention was taken to improve SiAlON ceramics optical properties.

In this study, translucent Y-α-SiAlON ceramics with different compositions were produced by using spark plasma sintering (SPS) technique. The IR transmittance, microstructure and phase assemblages of the sintered samples characterized by using FTIR, SEM and XRD techniques, respectively. According to the results, the m and n values in the α-SiAlON general formula influenced the densification behavior, grain morphology (size, size distribution and shape), phase assemblages of α-SiAlON and also the composition and distribution of intergranular glassy phase, therefore, affecting the optical and IR transmission.

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High-porosity foamed geopolymers by the frothing/peroxide route for water purification and thermal insulation

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Keywords: geopolymer foams, water purification, thermal insulation, porosity

High-porosity metakaolin-based geopolymer foams were fabricated by a gelcasting technique using hydrogen peroxide (foaming agent) in combination with Tween 80 (surfactant). Slurries processed in optimized conditions enabled to fabricate potassium based geopolymer foams with a total porosity in the range of ~67 to ~86 vol% (~62 to ~84 vol% open), thermal conductivity from ~0.289 to ~ 0.091 W/mK, and possessing a compressive strength from ~0.3 to ~9.4 MPa. Moreover, parameters influencing the compressive strength, the porosity, the thermal conductivity, and the cell size distribution were investigated. The results showed that the cell size and size distribution can be controlled by adding different content of surfactant and foaming agent. The foamed geopoymer can also be used as adsorbents for the removal of copper and ammonium ions from wastewater. The foams, due to their low thermal conductivity, could also be used for thermal insulation.

It was also possible to produce geopolymer formulations that could be printed using additive manufacturing technology (Direct Ink writing), which enabled to produce components with non-stochastic porosity.

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Anisotropic mechanical, thermal and electrical properties of SPSed aluminum nitride-graphene platelets composites

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Keywords: graphene platelets, AlN, fracture toughness, thermal properties, electrical conductivity

Graphene as an allotrope of carbon consisting of a single layer of sp^2 bonded carbon atoms has high thermal conductivity, superior charge carrier mobility, large specific surface area and outstanding mechanical properties such as high Young's modulus (1 TPa) and fracture strength. This unique set of properties makes graphene promising candidate as a second phase

for ceramic matrix composite to increase application areas by improving their mechanical, thermal and electrical properties. Additionally, the uniaxial load applied during production in the SPS resulted in the preferential orientation of graphene in the microstructure of composites.[1,2]

Therefore, the motivation of this study was to investigate the effects of graphene platelets (GPLs) addition in different amounts on mechanical, thermal, electrical properties and microstructures of SPSed aluminium nitride (AlN) matrix composites as a function of anisotropy. For these purposes, 1, 2, 4 and 8 wt % GPLs added to the AlN and sintered in the SPS furnace at 1825 °C for 15 minutes. All the mechanical, thermal and electrical measurements were made in parallel and perpendicular directions to the SPS pressing axis.

The microstructure investigations indicated that the basal planes of the GPLs oriented perpendicular to the SPS axis in the composite, leads to anisotropic microstructures. The fracture toughness increased by ~30% in parallel direction and by ~33% in perpendicular direction with the addition of 1 wt % GPLs into the AlN. The mean toughening mechanisms are crack deflection and crack bridging in parallel and perpendicular directions, respectively.

The addition of 1 wt % GPLs into AlN resulted the ~37% decrease in both parallel and perpendicular directions thermal conductivities. As the GPLs addition increased from 1 to 8 wt %, the thermal conductivity tended to decrease in the parallel direction whereas it increased in the perpendicular direction. The perpendicular direction conductivity higher by 2.4% than parallel direction conductivity in the 1 wt % GPLs added AlN and this value increased up to 90.2% when the added GPLs amount was increased to 8 wt % at room temperature, thereby indicating the anisotropic effects increased as the added GPLs increased in the composites. The electrical conductivity values of all composites in perpendicular direction were higher than in parallel direction. Furthermore, the composites became an electrically conductive with the addition of 1 wt % GPLs in both directions.

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SiC based materials for next generation nuclear power plants

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Next generation nuclear reactors are expected to operate with increased efficiency, safety, proliferation resistance and accident damage tolerance. The feasibility of Generation IV nuclear reactor designs is highly dependent upon the development of advanced materials that can withstand the designed operating conditions. Silicon carbide possesses many of the ideal material properties necessary and is therefore being explored for various applications in these reactors. In this presentation, the challenge and opportunities of using SiC based materials in nuclear power plants will be presented.

Following the broad overview, the feasibility of using the polymer derived ceramics (PDC) processing route for nuclear SiC will be discussed. Results will be presented to show the versatility of the PDC route, to tailor the composition, nanostructure and the resultant polytypes of SiC to enhance radiation stability. It is also an attractive approach to make a variety of needed shapes and forms including porous materials, and matrices for composites. Finally, results will be presented on the use of the PDC approach to make coatings and joints for SiC based materials. Results on the use of continuum mechanics to process reliable and crack free coatings and joints and their mechanical properties will be presented.

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Sintering resistance of advanced plasma-sprayed thermal barrier coatings with vertical cracks and columnar structures

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Thermal barrier coatings (TBCs) are required for enhanced performance of advanced industrial and aero gas-turbines, as one of the key technologies of thermal protection. Air-plasma spraying (APS) is widely employed to prepare coatings due to its cost-efficiency. Excellent thermal insulation, and also a certain amount of strain tolerance in thermal cyclic loading, can be provided by the lamellar microstructure of APS coatings. In order to further improve the thermal shock resistance, dense vertical cracks have been implemented in conventional APS coatings. Based on APS technology, suspension plasma spraying (SPS) has been developed recently. By using suspension feedstock, advanced coatings, with vertical cracks and columnar structures, can be fabricated. These microstructural features significantly improve the strain tolerance. However, during high temperature service, TBCs go through a degradation process called sintering, in which Young's modulus and viscosity increase irreversibly. Sintering induced mechanical degradation is one of the main causes of premature failure.

In this study, the effects of strain tolerant microstructures (e.g. vertically cracked and columnar structured) on the sintering resistance of APS and SPS TBCs are investigated experimentally and numerically. *In-situ* bending tests are conducted on free-standing coatings in the thermomechanical analysis device, which integrates conventional three-point bending test in a furnace. Evolution of Young's modulus and viscosity are measured by periodic loading, during annealing treatment at 1200 °C. Based on experimental observation, finite element models are constructed for both APS and SPS coatings. The effect of sintering on the mechanical properties is depicted by a constitutive relation, which is developed following the variational principle. The mechanisms of hardening, induced by sintering, are elucidated by comparisons between experimental and numerical results. Additionally, this study lays foundation to the optimized design of structurally graded TBCs, for further improvement of sintering resistance.

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Chemical interaction of CMAS with yttrium silicate environmental barrier coatings materials in combustion environments

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Rare earth silicates, such as yttrium silicates, are potential materials for improved oxidation and erosion protection due to their high melting point, low volatilization rate, low thermal expansion coefficient, and low oxygen permeation constant. Thus, yttrium silicates have potential applications as a high-temperature ceramic and environmental/thermal barrier coatings for structural Si-based ceramic materials such as SiC or Si_3N_4.

However, these rare earth silicates tend to induce chemical reactions between different underlying layers in an EBC multilayer system and they are susceptible to attack by vitreous melts, such as molten deposits. These molten deposits are based on calcium-magnesium alumino-silicates (CMAS) that, originating from siliceous debris ingested with the intake air, react with the Y_2SiO_5 topcoat and cause degradation and cracking. Therefore represents a fundamental threat to progress in gas turbine technology by limiting lifetime of yttrium silicate as environmental barrier coatings.

The objective of this work is to study the chemical interaction of yttrium silicate environmental barrier coating, Y_2SiO_5, synthesized by different methods with CMAS at combustion environment conditions.

The phase transformation and the microstructural evolution due to this exposure were studied by X-ray diffraction (XRD), quantitative phase analysis reference intensity ratio (RIR), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively.

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Heat treatment effect on the microstructural changes in the vicinity of fibre matrix interfaces of SiOC based composites

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Keywords: CMSs, SiOC, pyrolysis, interface, microstructure, TEM

The interface properties between matrix and reinforcement in the composites play important role and influence resulting mechanical properties significantly. The quality of the interface predetermines overall behaviour of the composite. Composite behaviour is given by the efficiency of the load transfer from matrix to the reinforcement. Weak interfaces lead to the reliable tough composite material but with low strength. Contrary, strong interfaces result in high strength accompanied by low fracture resistance.[1] Composite materials applicable at high temperatures usually use ceramic fibres as reinforcement. Therefore microstructural changes at the interface and its vicinity is crucial aspect for the long term application at high temperatures.[2]

The aim of this work is to describe in detail microstructural changes with various thermal treatment of SiOC based unidirectionally reinforced composite materials prepared via pyrolysis of polysiloxane preforms reinforced by ceramic fibres. The standard mechanical test were used to determine basic mechanical properties of the composites as elastic modulus, strength and fracture toughness.[3–5] These properties were further correlated with the microstructural changes found in the vicinity of interfaces. The transmission electron microscopy was employed to determine microstructural changes of the interfaces of selectively prepared TEM lamellae. The lamellae were prepared from neighbouring fibres selected on the polished cross-section of the composite using a focused ion beam build in SEM. Both the EDS analyses and the selected area diffraction analyses in TEM were employed to obtain both the chemical and the crystallographic information, respectively. It was found that with increasing temperature of heat treatment the microstructure of matrix was changed only slightly contrary the fibre microstructure which significantly developed and formation of new crystalline phases was observed.

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Elastic constants of carbon fibres derived from nanoindentation of a 2D-C/SiC composite system

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Keywords: elastic constants, carbon fibre, nanoindentation, micromechanical model

Elastic constants of single carbon fibres were estimated by a novel nanoindentation based method and subsequently predicted by a modified micromechanical model. The method was proposed for carbon fibres but can be applied generally to any transversely isotropic material. This case study was carried out on a T-300 PAN-based carbon fibre reinforced SiC composite material (2D-C/SiC) at room temperature. Transversal and longitudinal cross-sections of individual fibres were indented by a sharp Berkovich tip up to the maximum depth of 150 nm. Assuming transverse isotropy of the fibres, their five elastic constants were deduced from the measured indentation moduli using numerical and analytical models (Vlassak and Nix[1], Delafargue and Ulm[2]) and finite element method simulation. The elastic constants were estimated to $c_{11} = 30.9$, $c_{12} = 9.7$, $c_{13} = 12.2$, $c_{33} = 237.3$ and $c_{44} = 10.9$ GPa. The complete set of measured elastic constants were analyzed and then predicted by a modified two- and three-phase Eshelby-Mori-Tanaka (EMT) micromechanical model. The analysis revealed that an anisotropic 'amorphous' matrix should be assumed to achieve an appropriate fit with experimental results.

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On the fracture toughness testing of ceramics

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Ceramics are very brittle materials. Fracture toughness, which characterizes the resistance against crack propagation, is therefore extremely significant for them. But – compared to the situation of metals – fracture toughness testing is not routinely measured in ceramics characterization and fracture toughness is rarely used for design.

This is mainly caused by two reasons. First, specimens with geometries like those used for metals fracture toughness testing are much too large, complicated and expensive to be machined from ceramics. Second, fracture toughness testing requires a well-defined and sharp pre-crack in the specimen. In metallic materials such cracks can be obtained by fatigue pre-cracking. This is not practicable in ceramics, because they are not highly susceptible to cyclic fatigue. Some alternative methods for the generation of the pre-crack have been developed in the past. They lead to controversial discussions about the validity of fracture toughness testing results.

The state of the art of fracture toughness measurement techniques for ceramics will be critically discussed. Furthermore, examples for new methods, that are especially applicable to small specimens (a need in material's development), will be presented.

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Influence of HIP post-treatment on microstructure and density of silicon carbide sintered by SPS

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Keywords: silicon carbide, Spark Plasma Sintering, Hot Isostatic Pressing

To prevent damages caused by impact of a small-calibre projectile on a structure or human, dual hardness armour is generally used. It is composed by a ceramic layer in front pressed on a bottom face, called “backing”, in metal or composite material. The aim of this ceramics is to break up the projectile and to distribute loading on the backing. The backing is used to support ceramic layer and to take over fragments.

Silicon carbide is the ceramic which presents the best cost/efficiency ratio for ballistic applications, especially in dual hardness armour because of its high compressive strength, high hardness and low density. The use of this ceramic would permit to offer better mobility and autonomy to the armoured vehicles with equivalent protection. In this view, studies are currently performed to increase ballistic performances of materials used, in other words improve and optimize their mechanical properties and thus their microstructure.

The development of highly dense ceramics is essential for ballistic applications. Indeed, the presence of porosity involves defects in the pellet which could initiate the brittle failure of the latter. Sintering of silicon carbide is particularly difficult because of the high covalent character of its chemical bonds and the important effects of interface energy in grain boundaries. A fine control of initial powder characteristics (particles size, morphology, purity …) would permit to improve green body compactness and to favour densifying mechanisms. These two aspects are favourable to obtain dense materials with fine and homogeneous microstructure and high mechanical resistance. The choice of sintering process is essential to control the evolution of microstructure and reach the expected properties.

The aim of this PhD work is to develop dense ceramics in silicon carbide by Spark Plasma Sintering combined with Hot Isostatic Pressing post-treatment from a powder synthesized by laser pyrolysis. The effects of structural characteristics and purity of powders on sintering behaviour will be particularly controlled, as well as mechanical properties of obtained material.

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Bio-inspired CNT reinforced ceramic composite materials

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Keywords: biomimetic, CNT, composite, freeze casting, alumina

Carbon nanomaterials such as carbon nanotubes (CNTs) are often considered to be the ultimate reinforcement material for strong and light organic and inorganic composite materials. However, research on CNT composites has been hindered by the fact that commercially available CNTs are often tightly agglomerated and hence require sophisticated dispersion techniques to detangle them before they can be employed as fillers or reinforcements. Recent developments in the production and up scaling of nanotubes in the nanomaterials by design group at Oxford have paved the way towards the successful exploitation of CNT properties for the generation of multifunctional composite materials. Combining this with biomimetic ceramic microstructure architectures which are manufactured using new developments in freeze-casting, this promises to deliver a novel material that improves current ceramic materials significantly.

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Advanced oxide ceramic composites based on graphene

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Graphene is a 2D carbonaceous material with extraordinary mechanical and electrical properties which is very suitable to be exploited as reinforcement in ceramic matrix composites (CMC) for achieving superior performance. Different from previous intensively studied carbon based reinforcement such as carbon fiber and carbon nanotube, the extremely thin 2D feature of graphene can profoundly change the properties of CMC especially in the case of oxides. In alumina composite, a percolation threshold as low as 0.38 vol.% is achieved and the electrical conductivity surpasses 10^3 Sm $^{-1}$ when graphene content is only 2.35 vol.%. More interestingly, it is found that the charge carrier type changes from p- to n-type as graphene content becomes higher, as a result of synergistic doping effect between graphene and oxide matrix. Further study reveals that the doping level can be manipulated by tuning the concentration of oxygen vacancy of matrix, which is realized in yttria stabilized zirconia composite as a proof of concept. In addition, the graphene based oxide CMC also shows outstanding mechanical properties, as exemplified by alumina composite in which an unprecedented increase of strain tolerance by ~40%, completely retained fracture strength (417MPa) and enhanced fracture toughness (5.3MPam$^{1/2}$) are simultaneously realized at merely 2.18vol.% of filler loading. Therefore, it is believed that the graphene based oxide ceramic composites are very promising material for the application requiring both advanced functional and mechanical properties.

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Effect of graphene content on the tribological behaviour of 3YTZP reinforced with graphene nanoplatelets

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Keywords: 3YTZP, GNP, friction, wear, tribofilm

Zirconia-based ceramics have a wide range of structural and functional applications in industry, including cutting tools, bearing parts, solid oxide fuel cells, oxygen sensors, ceramic membranes and medical prostheses owing to their excellent mechanical properties, good ionic conductivity and high temperature stability. Although the inherent brittleness of these materials prevents their use in applications where tribological aspects are involved, the use carbon-based reinforcements, such as CNTs or graphene, has a positive impact in fracture behaviour. Besides, these carbon-based materials are prone to exhibit good lubricating properties due to the well-known behaviour of graphite as a solid lubricant[1].

Tribological studies using graphene as reinforcement in ceramic bodies have revealed that, in general, incorporation of graphene to the composites improves their wear resistance and reduces their friction coefficient. Different mechanisms have been proposed to explain this behaviour, such as formation of a graphene-rich lubricating tribolayer due to exfoliation of embedded graphene platelets or graphene-induced fracture toughness improvement that positively affects the wear resistance.

In this work, the tribological behaviour of yttria tetragonal zirconia reinforced with different GNP amounts (2.5, 5, 10 and 20 vol%) is described. Friction and wear results are compared to monolithic 3YTZP used as a reference material. In tests performed at normal loads above 10 N, the presence of wear debris at the tracks influenced the friction coefficient and wear rates, being these parameters lower for higher GNPs content. Electron microscopy studies and an extensive Raman analysis were performed to determine the nature of a transfer layer deposited on the composites wear track during tribological tests.

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Anisotropy of properties of silicon carbide – graphene composites

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Keywords: silicon carbide, graphene nanoplatelets, graphene oxide, *in-situ* graphene, anisotropy

Graphene as a single layer of sp^2 bonded carbon atoms has excellent mechanical, thermal and electrical properties[1–6] and due to that fact is widely used as a filler in various polymer, metal and ceramic matrix composites. This work focuses on SiC based composites with addition of 1, 3 and 5 wt. % of graphene nanoplatelets (GNP) or as synthesized graphene oxide (GO). Rapid hot pressing (RHP) was used for sintering at 1800 °C (heating rate 100 °C/min) and load of 50 MPa for 5 minutes in vacuum. Dense silicon carbide/graphene nanoplatelets (GNPs) and silicon carbide/graphene oxide (GO) with yttrium oxide and aluminium oxide as a sintering additives were prepared by this technique. Functional properties (electrical conductivity and thermal diffusivity) and mechanical properties (hardness, fracture toughness and elastic modulus) of such sintered composites were studied in parallel and perpendicular direction to the RHP pressing axis. In reference sample SiC-Y_2O_3-Al_2O_3, without any artificial addition of graphene, sintered by electrically assisted sintering technique – rapid hot press formation of graphene domains were observed. Comparative sintering of reference powders in conventional hot press was performed. For confirmation of presence graphene domains in RHP reference sample Raman spectroscopy, SEM and TEM were used. Also anisotropy of functional and mechanical properties of reference samples prepared by conventional hot press and rapid hot press was studied and compared.

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Characterisation of anisotropic thermal conductivity of ceramic/metal composites using freeze casted ceramic preform

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Keywords: freeze casting, ice templating, ceramic/metal composite, anisotropy, thermal conductivity

Freeze casting by ice templating was used for processing ceramic preforms. The porosity was then filled by metal using a low-pressure infiltration technique and ceramic/metal composites were obtained. Two ceramic materials were studied, alumina and zirconia, and the preforms exhibit an anisotropic lamellar structure with ellipsoidal pores ranging from 35 µm to 40 µm and porosity from 64 to 67%. This processing route leads the anisotropic morphology to be conserved after metal infiltration. The aim of the present work was to study the anisotropic thermal conductivity of such composite with different ceramic materials. Thermal conductivities were ranging from about 13 $W.m^{-1}.K^{-1}$ to 80 $W.m^{-1}. K^{-1}$ perpendicular and parallel to the freezing direction respectively, for zirconia/metal composite. The thermal diffusivity of the composites was determined by Flash measurements on flat disk in order to calculate the thermal conductivity as a function of structure orientation. A simple model based on Maxwell equation was used in order to evaluate the influence of residual porosity and to predict thermal conductivity.

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Wear damage and fracture of SiC based composites with graphene and carbon nanotubes

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Keywords: SiC, CNT, graphene, TiNbC, mechanical properties, electrical conductivity

SiC based ceramic materials with nano carbon additives, namely with *in-situ* grown carbon nanotubes (CNT) and multilayered graphene platelets (GPL) were prepared and studied. The materials were compacted by hot pressing.

As a reference material a single phase SiC was prepared by the same way, too. The microstructure and chemical composition of the resulting materials were studied by SEM/EDX. Hardness and fracture toughness of prepared materials were evaluated and propagation of indentation cracks was analyzed. The electric conductivity as function of fraction of additives was determined. Self-mated friction and wear was measured by ball-on-disc technique in dry conditions under load of 5 N.

Six materials with 0–6 wt. % GPL were prepared. GPL had preferential orientation given by the hot pressing direction and often remained in stacks. With increasing amount of GPL hardness (21 GPa -> 15 GPa) and elasticity (440 GPa -> 380 GPa) decreased. Toughness and strength improved as mechanisms of crack bridging and deflection by GPLs acted as toughening mechanisms. Coefficient of friction in all materials was between 0.4 and 0.6, GPL did not affect it. Wear rate was improved by higher amounts of GPLs 10^{-6} – 10^{-5} mm^3/Nm. Wear mechanisms were similar in all materials, mostly governed by cracking and oxidation.

Electrical conductivity was very low, far insufficient for electric discharge machining (EDM). Higher amounts and better distribution of carbon phases is required for EDM to be considered possible.

In the systems SiC-CNT a novel way to prepare the CNTs with high quality and excellent distribution grown *in-situ* by CCVD on iron nanoparticle pre-cursor was designed. The prepared mixtures were subsequently compacted by hot pressing. Three SiC-CNT composites together with reference SiC-(Fe) were prepared by CCVD and HP. Microstructure studies proved excellent quality and distribution of CNT. However, full densification is still a challenge and residual porosity remains. Hardness was good considering the porosity. With presence of CNT moderate decrease, from 24 GPa for down to 17–19 GPa, was observed. Indentation fracture toughness behaved similarly, i.e. decreased from ~7 MPa.m$^{1/2}$ for the monolith down to ~4 MPa.m$^{1/2}$ for highest amount of CNT. Electric conductivity increased with amount of CNT and for higher amounts (5 and 10% CNT) exceeded 1000 S/m (1448 S/m and 2873 S/m, resp.) which shows a potential for sufficient values. Preliminary friction studies found COF ~ 0.4 and showed weak effect of CNTs. Main wear mechanisms were again cracking and oxidation.

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Thermo-chemical properties of re-silicate environmental barrier coatings

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Keywords: environmental barrier coatings, Y_2SiO_5, SiC, oxidation, corrosion

The improvement of the gas turbine inlet temperature is a key factor involved in increasing the fuel efficiency and reducing the carbon emissions of a gas turbine. Due to the high limit point of temperature capability, non-oxide silicon-based ceramics, such as SiC/SiC$_f$, Si_3N_4 and SiC,[1] have been investigated extensively as potential structural material for hot gas parts for next-generation gas turbines. Owing to the presence of oxygen and high-temperature water vapor in the combustion environment, SiC based ceramics was degraded by recession due to chemical reaction under steam environment. In order to solve this problem, the protecting layer, called EBC (environmental barrier coatings), is necessary.[2] In the present study, the influence of isothermal heat treatment on thermo-chemical properties of Y_2SiO_5 coatings on SiC was investigated.

Y_2SiO_5 coatings have been deposited by flame spray technique as protection layer of SiC substrate from oxidation and steam corrosion. In this work, Y_2SiO_5 coatings are heat treated by different temperature and different exposed times in air environment condition. The thermal behaviors such as phase transformation, microstructure change and TGO growth has been examined by XRD, SEM, and EDS analysis. The hot corrosion between Y_2SiO_5 coatings and CMAS was examined by isothermal heating at 1400 °C in air during 1~50 hrs.

In addition, the mechanical properties are evaluated by nano-indentation test. The thickness of corrosive region at top surface of Y_2SiO_5 by the reaction between Y_2SiO_5 coating and CMAS was increased with increasing the heat treatment time.

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Investigation of the mechanical behavior of MAX phases by acoustic emission technique

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Keywords: carbides, acoustic emission, mechanical properties, high temperature

Since the last two decades, MAX phases have attracted researcher's attention. Due to their chemical composition and structure, they provide a unique combination of metal-like and ceramics-like properties.[1] Their name, $M_{n+1}AX_n$ phases with n = 1, 2 or 3, refers to their chemical composition, where M is an early transition metal, A is an A-group element (Si, Al, etc.) and X is carbon or nitrogen.

Mechanical properties of two ternary carbides, Ti_3SiC_2 and Ti_2AlC, were investigated under cyclic bending tests with simultaneous acoustic emission monitoring (AE) at room temperature. Results show significant differences between both of them in terms of observed microstructural changes associated with acoustic emission response. Thanks to this technique coupled with an accurate SEM investigation, mechanisms such as debonding of layers in MAX phases grains or damage occurrence in secondary intermetallic phases (microcracking) were identified and their specific acoustic signatures separated populations of AE signals were distinguished.

In addition, ultrasonic pulse echography in "long bar mode" (US) and acoustic emission (AE) techniques were applied for high-temperature investigations. Results for both materials show a decrease of the Young's modulus with increasing temperature which is more marked around maximal temperature of the thermal cycle for Ti_2AlC material. Additionally, AE activity during heating (up to 1473 K and 1632 K) and cooling stages was recorded. The increase of the maximal temperature of the thermal cycle influences the number of recorded cumulated hits. This difference in acoustic response might indicate the beginning of microstructural changes or activation of other deformation mechanisms. Both measurements (US+AE) highlights the role of the plastic deformation mechanism activated over the brittle-to-plastic transition temperature.

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Material development, processing and testing of a silicon nitride turbine rotor

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Micro gas turbines with cogeneration of heat and power are very suitable for peripheral energy supply. To increase efficiency and decrease pollutant emissions, higher operating temperatures or lower cooling efforts of the turbine stage are aspired. Subsequently, this leads to thermal loads at the turbine components that cannot be suffered by superalloys for long term applications. High performance ceramics promise a higher temperature capability and strength. This makes them candidates for being the future generation turbine material. Silicon nitride (Si_3N_4) is one of the most refractory ceramics, providing a good balance of thermal stability and mechanical properties.

For this reason a silicon nitride rotor for a radial flow micro gas turbine with 30 kW_{el} was developed. The illustration of a realistic profile of operational demands via simulative coupling of thermal and (fluid-) mechanical loads was the groundwork for material development. A further verification of the materials suitability was performed via stress considerations, non-destructive testing and burst testing. A field test verified the suitability of silicon nitride for the highest loaded components of gas turbines.

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The investigation of zirconia based precursors and ceramics via thermodynamic approaches

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Keywords: stabilized zirconia ceramics, sol-gel synthesis, STA, EMF, high temperature mass spectroscopy

Due to their exceptional anion conductivity at high temperatures cubic zirconia solid solutions are widely used as solid electrolyte (SE) materials in different electrochemical devices. However the search of the optimal ceramic compositions for their long-term use in the aggressive atmosphere of industrial processes remains a great challenge for science and technology. The precise knowledge of the thermochemical data on thermal prehistory, temperature and concentration dependence of the electromotive force (EMF) on ambient oxygen,

ion transfer number of SE as well as the evaporation features in ZrO_2 based systems at high temperatures makes it possible to develop high-performance zirconia based SE for *in-situ* measurements at extremely high temperatures in aggressive ambiance. Thus the goal of the present work was the detailed investigation of thermochemical behaviour of M_xO_y-ZrO_2 systems (M = Ca^{2+}, Y^{3+}, Ce^{4+}, La^{4+}) via the systematic thermochemical approach that includes simultaneous thermal analysis (STA), EMF measurement and high-temperature mass spectroscopy. The synthesis of precursors powders was performed by reversed co-precipitation from aqueous solutions under the optimal conditions and by conventional solid state synthesis including milling into a planetary mill. The phase transitions, so as possible exo- and endo-effects were investigated by STA. Then the precursors was cold pressed into the pellets and hydrostatically pressed. The pellets were annealed at 1600 °C for 2 hours. Following galvanic cell O_2 ($P_{O2}(1)$), Pt | SE | Pt, ($P_{O2}(2) = 0.21$ atm) was used for SE sensor properties investigation. The evaporation experiments were carried out using Knudsen effusion technique combined with mass spectrometric analysis of vapor composition. It was show that the value of crystallization enthalpy up on the phase transition “amorphous precursor → crystalline solid solution” can serve the criteria for crystallization completeness of metastable cubic solid solutions in CaO-ZrO_2 system. Phase stabilization of the metastable crystalline solid solution at 400–1000 °C is due to kinetic factors. YSZ ceramics manufactured from powders with the mean particle size 40–140 nm shows the highest values of oxygen ion transfer number i.e. 0.97–0.98 at 600–800 °C. SE manufactured from precursors with the mean particle size 40–140 nm shows higher sensor characteristic i.e. temperature and oxygen concentration EMF dependencies, EMF (E_{Nernst} - $Ereal$), t_{ion}, response time, then ceramics, manufactured by conventional solid state synthesis. The components of La_2O_3-ZrO_2 system evaporate separately: there is no temperature range where lanthanum and zirconium gaseous species are present together. It was found that the activities of lantania in all concentration range of condensed phase have low negative deviation from ideal case whereas zirconia activities has strong negative deviation from ideal case.

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UHTC based matrix as a protection for C/C composites for very high temperature use: original manufacturing and oxidation resistance

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Keywords: aerospace, propulsion, UHTC, RMI, oxidation, oxy-acetylene torch testing

Propulsion applications in aerospace require materials that can withstand extreme conditions: temperatures rising above 2000 °C in oxidizing and corrosive atmospheres. In a constant need to improve the protection of carbon/carbon composites, the SiC-based protective coatings are not efficient enough. Ultra High Temperature Ceramics (UHTCs) such as borides, carbides and nitrides present high melting points, high hardness, chemical inertness and relatively good resistance to oxidation in severe environments. More specifically, diboride-based compounds such as ZrB_2 and HfB_2 are of special interest.[1] During oxidation, the growth of a multi-oxide scales composed of a skeleton of a refractory oxide filled with a glass makes their oxidation resistance better.[2,3] The addition of SiC has shown better oxidation resistance than single phase material, 20%vol. SiC seemed optimal for hypersonic applications.

The aim of this work is to prepare a protective matrix, instead of usual coatings, based on this reference composition. A two-step manufacturing process is carried out to obtain C_f/C-UHTC composites. By varying the powder mixtures introduced by slurry impregnation and metal compositions during reactive melt infiltration (RMI), a wide range of matrix' compositions are generated. The reactive systems involved during manufacturing lead to matrices composed of ZrB_2 and SiC phases, and may contain ZrC or residual metal compounds.

The oxidation resistance evaluation is done under oxy-acetylene torch. Tests are performed in presence of oxygen and water in the flame during at least 3 minutes at maximum temperature around 2000 °C. Samples characterisation allows determining weight change, scale thickness and scale compositions. Oxidation kinetics is determined and allows comparing the protection ability of each composition.

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Measuring fracture toughness of Y-TZP

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Keywords: fracture toughness, transformation

Yttria-stabilized tetragonal zirconia ceramics (Y-TZPs) are not only used for engineering applications but also – to an increasing extent – for medical and dental restorations. While the knowledge of materials properties like strength and toughness is necessary for a safe design of structural parts in the first case, these properties are material specifications with standardized lower bounds in the other case. Robust test methods are thus a need for all fields of application regarding Y-TZPs.

For the determination of fracture toughness of ceramics a number of test methods has been standardized so far. Generally these methods require a pre-crack (or a suitable substitute) to be introduced into a bar-shaped specimen, which is then fractured in bending. Not all methods are equally suited for all kinds of ceramics. Especially fine grained Y-TZPs seem to be a material class that is particularly difficult to test. Indentation pre-cracking for the SCF method can usually not be achieved with a Knoop indenter, instead the more complicated cracks associated with Vickers indenters have to be used. Bridge pre-cracking for the SEPB test requires extremely high loads due to the high toughness of the material. The robust and easy to use SEVNB method requires a notch with a tip radius that is comparable in size to the grain size of the material. Even though fine notches with radii down to a few micrometers can be produced, it seems to be impossible to fulfil this criterion for materials with typical grain sizes of just a few hundred nanometers.

Some of these problems may arise from the fact that Y-TZPs are metastable materials where the tetragonal zirconia grains transform to the monoclinic phase under externally applied load or during machining. This transformation toughening causes compressive stresses to appear in the transformed regions. Apparently, such compressive stresses in the vicinity of a honed notch in a SEVNB fracture toughness specimen will lead to incorrect results.

In this study we investigate the SEVNB fracture toughness of Y-TZP. Notches with different radii are produced and tested. Two groups of specimens are compared: specimens in the as-notched state and specimens after a heat treatment that re-transformed the m-ZrO_2 to the tetragonal polymorph and removed the residual stresses. The amount of m-ZrO_2 and residual stresses are measured in the vicinity of the notch roots using Raman spectroscopy. The measured fracture toughness values are compared to values obtained with alternative methods that use sharp pre-cracks. It is shown that below a critical notch root radius the fracture toughness can be correctly measured with the SEVNB method if annealed specimens are used.

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Silica membranes for selective separation of small gasses under hydrothermal conditions

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Keywords: hydrothermal stability, hybrid silica, gas separation, microporous membrane, MAP coating

The hydrothermal stability of microporous ceramic membranes is of high importance for implementation of these membranes in industry, as a lot of industrial processes include steam. Often the hydrothermal stability of these ceramic membranes is only tested for either the mesoporous intermediate membrane layer or the microporous separation layer of the ceramic membrane.

Here, we present the results of a study on the hydrothermal stability of a ceramic membrane system consisting of an intermediate γ-alumina layer and a hybrid, ethylene-bridged, silica separation layer. Also, the influence is investigated of the addition of a monoaluminumphosphate (MAP) coating between the α-alumina support and the γ-alumina layer on the membrane stability. The results show that the hybrid silica on γ-alumina retains its gas separation performance after a hydrothermal treatment albeit with a lower mechanical adhesion between the hybrid silica and the γ-alumina layer, while a bare γ-alumina layer is degraded during a hydrothermal treatment. On the other hand, the hybrid silica on a MAP-modified γ-alumina membrane did not show any signs of delamination after hydrothermal testing. Moreover, a hydrothermal treatment of the hybrid silica on a MAP modified γ-alumina membrane results in a significant increase in the H_2/N_2 (perm)selectivity of a factor 3.

Also by tuning the sol-gel chemistry, the influence of the amount of water on the dip-coating/gelation process was examined. First, membranes were coated on a support with a controlled low water content (RH < 0.5%) and no detectable permeation of N_2 and CH_4 was observed. Second, the system was pretreated at 90% RH while applying the coating, resulting a significantly higher N_2 permeation. The formation of larger pores can be understood by a higher condensation rate and longer drying times when more water is present. This results in a stronger network that better withstands the compressive forces during drying. By limiting both the water and acid contents in the dip sol, a more dense pore structure is obtained that gives the highest H_2/N_2 and CO_2/CH_4 (perm)selectivity's found to date for hybrid silica membranes.

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Near zero thermal expansion ZrW_2O_8/ZrO_2 composites

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Keywords: zirconium tungstate, zirconia, spark plasma sintering, thermal expansion coefficient

A zirconium tungstate (ZrW_2O_8) precursor was synthesized by a novel sol-gel method with zirconium oxychloride and tungstic acid as the zirconium and tungsten sources, respectively. This precursor could readily be crystallized at 600 °C, which in turn provided the desired nanoparticle sizes for the composite production. For synthesis of ZrW_2O_8/ZrO_2 composite system, both conventional and spark plasma sintering methods were experimented and respective results were compared and composition ranges that provide composites with almost zero thermal expansion coefficient's (CTE's) were determined. The composites that were conventionally sintered at 1200 °C for 24 hours with Al_2O_3 as the sintering aid, showed a CTE of 0.20×10^{-6}/K for the compositions fixed at 35% ZrW_2O_8 and 65% ZrO_2. On the other hand, with the spark plasma sintering method, which was conducted at 1000 °C for 5 minutes without a sintering aid, a composition of 55% ZrW_2O_8 and 45% ZrO_2 showed a CTE of 0.94×10^{-6}/K. For characterization of the products X-ray diffraction (XRD), scanning electron microscopy (SEM), photon correlation spectroscopy (PCS), and thermal and dilatometer analyses (DTA/TGA/DMA) were used. The observed differences in the obedience to rule of mixtures in the two sintering methods and identified pressure induced phase transitions in the interparticle regions will be discussed.

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Synthesis and characterization of a new $[Ti_1\text{-}_{\varepsilon}Cu_{\varepsilon}]3[Al(1\text{-}x)Cu_x]C_2$ max phase solid solution with adjustable substitution rates

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Keywords: MAX phase, solid solution, powder metallurgy, microstructural characterization.

Ti_3AlC_2 is a member of the MAX phase compounds having the general formula $Mn_{+1}AX_n$ (n = 1-3), where M is an early transition metal, A is an A group element (from IIIA to VIA), and X is either carbon or nitrogen. In these materials, the $M_{n+1}X_n$ layers, characterized by strong covalent M-X bonds, are interleaved with A layers through weak M-A bonds. This inherent nanolayered structure provides a unique combination of metal-like and ceramic-like properties.

In this work, Ti_3AlC_2 MAX phase powders were first prepared at 1450 °C for 2 hours from 1.9TiC:1.05Al:1.0Ti reactant mixture. High-energy milling of Ti_3AlC_2 and Cu (40vol.%) powders was then performed to form large aggregates containing alternative lamellas of both compounds. Finally, a new $[Ti_{1-\varepsilon}Cu_{\varepsilon}]_3[Al_{(1-x)}Cu_x]C_2$-Cu Metal Matrix Composite has been produced by sintering Ti_3AlC_2 and Cu co-milled powders. Using XRD and TEM-EDXS, it has been demonstrated that Cu can enter the crystallographic structure of the Ti_3AlC_2 MAX phase, whereas a Cu(Al) solid solution is formed during thermal treatment. TEM-EELS analyses have demonstrated that Cu is mainly located on the A site of the MAX phase. The composition of the MAX phase solid solution, determined after selective chemical etching of the Cu(Al) matrix, by analyzing the filtrate and the solid phase using ICP-OES end EDXS methods respectively, is $Ti_3(Al_{0.5}Cu_{0.5})C_{2.}$ Thus, Al atoms are substituted preferentially compared to Ti atoms. Using X-ray diffraction and neutron diffraction, it is demonstrated that the Cu mixing into the Al site is accompanied by lattice distortion that lead to symmetry reduction into the monoclinic structure.

Moreover, by varying the Cu content in the range 10-50 vol. % in the initial Ti_3AlC_2-Cu reactant mixture, it is demonstrated that the substitution rate of Al by Cu atoms can be adjusted in the $[Ti_{1-\varepsilon}Cu_{\varepsilon}]_3[Al_{(1-x)}Cu_x]C_2$ solid solution. Finally, Rietveld refinement allows demonstrating that the lattice parameters of the monoclinic MAX phase vary linearly with Cu content on the A site implying that the Vegard's law is obeyed.

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Towards sandphobic thermal barrier coatings (TBCs) – characterization of YSZ-based TBCs exposed to sand laden combustion flows

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Keywords: YSZ, TBCs, CMAS, microstructural evolution, thermal cycling

The increasing operating temperatures of gas-turbine engines has led to the deterioration of protective thermal barrier coatings by deposition and infiltration of solidified molten sand, salt, and volcanic ash particulates, typically composed of calcia-magnesia-alumina-silicates

(CMAS). Future thermal and environmental barrier coatings (TBC/EBCs) will operate at increasingly higher temperatures and must simultaneously provide improved thermo-mechanical performance and resistance to CMAS-induced damage. This work presents ongoing efforts on the development of 'sandphobic' tailored YSZ based coatings deposited onto Ni superalloy substrates. Tailoring of YSZ coating microstructures is performed by using various coating techniques including air plasma spray (APS), solution precursor plasma spray (SPPS), and electron beam physical vapor deposition (EB-PVD). Coatings are further tailored for CMAS resistance by incorporating Gd_2O_3 and $Gd_2Zr_2O_7$ topcoat layers and blended YSZ/Gd_2O_3 compositions. A sand ingestion gas turbine engine rig was utilized in order to evaluate the coatings under realistic operating conditions. The coatings are exposed to a sand laden combustion environment with air flow temperatures of ~1400 °C. Exposed coatings are evaluated using confocal microscopy, scanning acoustic microscopy (SAM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), electron backscattered diffraction (EBSD), and focus ion beam (FIB) cross-sectioning in order to characterize the effectiveness of the coatings in preventing CMAS infiltration, CMAS induced spallation, and build-up of CMAS deposits.

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Microstructure and mechanical properties of NbB_2/SiC-GNP composites

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Keywords: NbB_2 based ceramics, ultra high temperature ceramics, graphene, spark plasma sintering

Niobium diboride (NbB_2), as a typical ultra high temperature ceramic, has a good combination of properties, such as high melting point (~3040 °C), high hardness (~21 GPa), high thermal conductivity (~17 W/m·K) and good thermal shock resistance. However, difficulties in densification, low fracture toughness and poor oxidation resistance of NbB_2 limit the use of these materials. A number of studies have shown that addition of SiC improves the oxidation resistance by forming a protective SiO_2-rich layer and improve fracture toughness of transition borides. Moreover, recent studies have demonstrated that graphene nanoplatelets (GNP) addition can significantly enhance the mechanical properties of ceramic matrices. In this study, GNPs were incorporated into (20-x)SiC-80NbB_2 (vol.%) composite powder with x = 0, 0.5, 3, 5, 7 and 10 vol.% contents. The resulting powder mixtures were sintered by spark plasma sintering (SPS) at 1750 °C under 50 MPa with a 5 min holding time. The prepared composites were then characterized in terms of their densification, microstructure, oxidation behavior and mechanical properties. Improvement in oxidation resistance as a result of formation of protective layers and fracture mode change with the incorporation of SiC and GNPs will be discussed in this presentation.

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Microstructural characterization of commercial ceramic materials for ballistic applications

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Keywords: ceramic, microstructure, Vickers hardness, Weibull modulus, indentation toughness, average grain size, grain size distribution, EBSD, XRD, TEM, Raman spectroscopy, armour

Room temperature microstructural properties of near fully-dense Al_2O_3 (Corbit 997), B_4C (Bocadur) and SiC (Sicadur) commercial ceramics for ballistic applications were studied.

Residual porosities were estimated by image analysing of polished surfaces both on cross section and on impact surface. The results demonstrate anisotropic properties: the grains pull-out phenomenon is more pronounced on the impact surface in respect to its cross section. Results of image analyses and other technical methods for porosity determinations were compared.

Vickers indentation hardness were measured at different loads. The results confirm the typical ceramic behaviour already known as indentation size effect[1]. Furthermore the hardness results were statistically evaluated on the basis of Weibull analysis. Weibull's approach to flaw statistics is based on "weakest link statistics" so that failure of one element of a body leads to failure of the whole body. Weibull moduli were compared between ceramic materials with comparable hardness which corresponds to comparable investigated volume. The results allow to establish a ranking of material reliability.

In order to quantify the material resistance to brittle fracture, indentation toughness was determined on the basis of both Niihara[2] and Anstis[3] equations.

To characterize the microstructure, average grain size and grain size distribution were measured by the linear intercept method[4] on Electron Channeling Contrast Images (ECCI) and by Electron BackScattered Diffraction (EBSD), respectively.

For a further characterization of the crystallographic phases, X-Ray Diffraction (XRD) spectra were acquired on all commercial materials. To verify at microscopic scale, the results have been compared with data acquired by Transmission Electron Microscopy.

Raman spectra were acquired on the same commercial materials in normal and confocal mode in order to confirm the crystallographic phases already identified by XRD and TEM. In comparison to TEM, results of Raman spectroscopy are more statistically representative of the macroscopic material.

Acknowledgement
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Mechanical and electrical properties of liquid phase sintered porous SiC using Al_2O_3-Y_2O_3-SiO_2 as sintering additives

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Keywords: porous SiC, flexural strength, apparent porosity, electrical resistivity

The porous SiC ceramics with specific pore characteristics has been widely used because of its attractive thermo-mechanical properties as well as chemical resistivity in various environmentally related industries. In this study, porous SiC ceramics with various pore characteristics were fabricated by a liquid phase sintering using SiO_2-Al_2O_3-Y_2O_3 sintering additives at the temperature below 1600 °C under argon atmosphere. The average pore size and porosity of fabricated porous SiC were varied depending on the starting SiC particle size as well as the amount of sintering additives used. It was found that the fracture strengths of liquid phase sintered porous SiC with the same porosity were decreased with increasing the pore size. With increasing the amount of sintering aid from 15 to 25%, the porosity and pore size of SiC porous body was decreased, but the fracture strength of porous SiC was increased. The electrical resistivity of liquid phase sintered porous SiC using Al_2O_3-Y_2O_3-SiO_2 was as high as 10^7 Ωcm, which was not closely dependent on the pore size as well as the porosity of the porous SiC.

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Graphene nanoplatelet/3 mol% yttria doped zirconia composites with high electrical conductivity

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Keywords: graphene nanoplatelets, 3YTZP, microstructure, electrical conductivity

The exceptional electrical properties of carbon nanostructures, such as carbon nanotubes (CNT) or graphene, have motivated a great interest in incorporating these nanostructures as second phase in a ceramic matrix, in order to enhance the functionalities of the final composite. An alternative cost-effective option in comparison with CNT or monolayer graphene is the use of other 2D carbon nanomaterials, such as graphene nanoplatelets (GNP) or graphene nanosheets (GNS). Although remarkable electrical conductivities have been reported for GNP/ceramic composites, just a few works approaching the electrical characterization of these materials have been published[1,2].

In this work, the microstructure and the electrical properties of 3 mol% yttria-doped zirconia (3YTZP) processed with up to 20 vol.% graphene nanoplatelets (GNPs) have been studied. Wet powder processing in isopropanol and electric pulsed discharge sintering were used to prepare the composites. The structural integrity of the GNPs was not damaged during the process, as confirmed by Raman spectroscopy. As a consequence of the uniaxial applied pressure during sintering, a preferential orientation of the GNPs in the direction perpendicular to the pressing axis was observed. This microstructural anisotropy resulted in an electrical anisotropy, since the electrical conductivity measured along the direction perpendicular to the pressing axis was significantly higher than the one measured along the parallel direction. Electrical conductivity of the composites along both directions was obtained in a wide temperature range. The relationships between GNP content, GNP dimensions, microstructure and electrical conductivity, as well as the conduction mechanisms of the composites, have been analysed and discussed.

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Structure, mechanical characteristics and stability of (Ti,Nb)-Al-C MAX-phases-based composites in hydrogen and oxidizing atmosphere

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Keywords: structure, mechanical characteristics and stability of (Ti,Nb)-Al-C MAX-phases-based composites in hydrogen and oxidizing atmosphere

The developed materials are promising for interconnects of hydrogen fuel cells, damping material in machine building, in nuclear industry, for pantographs or sliding bearings, etc. The dense MAX-phases-based materials of Ti,Nb–Al–C systems prepared by hot pressing at 30 MPa are stable in hydrogen and oxidizing environments at 600 °C, are about twice lighter ($\rho = 4.27$ g/cm^3) and more stable in air (for 1000 h) than Cr-containing “Crofer” steels. The addition of Nb leads to the formation of about 10 times thinner surface oxidized layer and thus to the material stability increase. The most resistant among the studied materials in air at 600 °C for 1000 h turned out to be Ti_2AlC-based (73 wt.% of Ti_2AlC according to Rietveld refinement). The SEM study of it matrix revealed the near $Ti_{2,3}AlCO_{0,2}$ composition and the presence of elongated near $Ti_{3,6}AlC_{1.9}O_{0,6}$ grains. Somewhat less stable was preliminarily oxidized at 1200 °C (for 2 h) Ti_3AlC_2 (89 wt%). The Ti_3AlC_2-based materials at room temperature demonstrated 4.6–5.8 GPa microhardness at 5 N load, 500–570 MPa bending and 700–1300 MPa compression strengths, 10.2±0.4 MPa·√m fracture toughness and $2.7 \cdot 10^6$ Sm/m electrical conductivity at 20 °C. The bending strength of Ti_3AlC_2-based material in air at 20 °C was 535 MPa, after keeping at 600 °C in air and hydrogen it decreased to 490 and 500 MPa, respectively. For $(Ti,Nb)_3AlC_2$ –based materials the bending strength at 20 °C in air was 480 MPa and increased by 10% after heating at 600 °C both in air and in hydrogen. The estimated damping coefficient and stability to radiation of the MAX-phases were as well high.

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Mechanical properties of mixtures of 12Ce-ZrO_2 and 3Y-ZrO_2 and atom probe tomography of solute distribution

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Keywords: 12Ce-ZrO_2, 3Y-ZrO_2, atom probe tomography, mechanical properties, K_{IC}, LDT

3Y-ZrO_2 has attracted much attention in restorative dentistry because of its biocompatibility, aesthetical appearance, and excellent mechanical properties such as hardness, strength, and fracture toughness. However, it suffers of low temperature degradation (LTD), which consists in the spontaneous surface tetragonal-monoclinic transformation under the presence of moisture, which is detrimental since it induces surface microcracking and grain pullout. There is then interest in using ceria as a dopant for stabilizing the tetragonal phase of zirconia in concentrations higher than about 10% molar since it makes zirconia much more resistant to LTD and tougher than 3Y-ZrO_2, but Ce-ZrO_2 ceramics have lower hardness and strength than 3Y-ZrO_2. In this work mixtures of powders of 12Ce-ZrO_2 and 3Y-ZrO_2 in different proportions have been studied with the objective to find out a suitable combination of hardness and indentation fracture toughness for the mixture. The best compromise in mechanical properties and resistance to LTD were obtained in the mixture with 85 wt% 12Ce-ZrO_2-15 wt.% 3Y-ZrO_2, which was analysed by atom probe tomography after sintering at 1450 and 1600 °C. It is shown that the solid solution inside the grains is not homogenous and that there is strong segregation of Al, Ce and Y to the grain boundaries. Segregation to grain boundaries is quantified for all these elements, being stronger in the specimens sintered at 1600 °C. The mechanical properties and resistance to LTD have also been studied in more detail in the 85/15 mixture. In particular, the strength has been determined and analysed under the presence of surface micro-notches induced by pulsed laser ablation.

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Fatigue of three advanced SiC/SiC ceramic matrix composites at 1200 °C in air and in steam*

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Keywords: ceramic-matrix composites (CMCs), fatigue, high-temperature properties, mechanical properties, fractography

Silicon carbide/silicon carbide ceramic matrix composites (CMCs) are among leading candidate materials for use in advanced aeronautics and space applications, such as turbine engine components, hypersonic flight vehicles, and spacecraft re-entry thermal protection systems. In these applications the composites will be subjected to cyclic loadings under high temperature and varying environmental factors. Therefore a thorough understanding of fatigue performance of SiC/SiC composites in service environments is critical to design and life prediction for these materials. High-temperature mechanical properties and tension-tension fatigue behaviour of three advanced SiC/SiC composites are discussed. The effects of steam on high-temperature fatigue performance of the CMCs are evaluated. The three composites consist of a SiC matrix reinforced with laminated, woven SiC (Hi-Nicalon™) fibres. Composite 1 was processed by chemical vapour infiltration (CVI) of SiC into the Hi-Nicalon™ fibre preforms. Before the infiltration, the preforms were coated with boron nitride fibre coating (~0.25 μm thick) to decrease bonding between the fibres and the matrix. Composite 2 had an oxidation inhibited matrix consisting of alternating layers of silicon carbide and boron carbide and was also processed by CVI. Prior to infiltration, the fibre preforms had pyrolytic carbon fibre coating (~0.40 μm thick) with boron carbide overlay (~1.0 μm thick) applied. Composite 3 had a melt-infiltrated (MI) matrix consolidated by combining CVI-SiC with SiC particulate slurry and molten silicon (Si) infiltration. The fibre preforms were first coated with BN by CVI. Then a CVI SiC coating of initial matrix was applied to rigidize the preforms. This step was followed by slurry infiltration of SiC particulates and infiltration of molten Si to fill in the remaining porosity. The tensile stress-strain behaviour of the three CMCs was investigated and the tensile properties measured at 1200 °C. The tension-tension fatigue behaviour of the three SiC/SiC CMCs was investigated at 1200 °C in laboratory air and in steam. The tests were performed at 1.0 Hz with a stress ratio of minimum to maximum stress of $R = 0.05$. Maximum stress ranged from 80 to 160 MPa in air and from 60 to 140 MPa in steam. Fatigue run-out was defined as 2×10^5 cycles. Presence of steam significantly degraded the fatigue performance of the CVI SiC/SiC composite 1 and of the MI SiC/SiC composite 3, but had little influence on the fatigue performance of the SiC/SiC composite 2 with the oxidation inhibited matrix. All specimens that achieved fatigue run-out were tested in tension to failure to characterize the retained tensile properties. Composite microstructure, as well as damage and failure mechanisms were investigated.

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*The views expressed are those of the authors and do not reflect the official policy or position of the United States Air Force, Department of Defense or the U.S. Government.

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Development of environmental barrier coatings for SiC/SiC ceramic matrix composites

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Keywords: EBC; CMC; SiC/SiC, corrosion stability

Advanced ceramic matric composites (CMCs), in particular silicon carbide fiber reinforced silicon carbide matrix composites (SiC/SiC), are increasingly used in the aerospace industry for manufacturing of hot components due to their excellent properties compared to super alloys. In the aero engine, a part of the combustion gas is water vapor resulting from the burning of hydrocarbon fuels in air. The water vapor will corrode the CMC components, resulting in their final failure. To protect the SiC/SiC components from corrosion, environmental barrier coatings (EBC) have been developed to increase their durability in combustion environments.

Based on detailed understanding, several multilayer coating systems with high corrosion stability were fabricated and tested successfully. For the deposition process the atmosphere plasma spray process (APS) was used.

In this study the oxidation and corrosion behavior of the SiC/ SiC material with different EBC systems were investigated. Diffusion processes or reaction at the CMC / coating interface led to microstructural or chemical change with consequence of crack formation and failure of the EBC what is discussed in this presentation.

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Influence of humidity and temperature on the fatigue behavior of silicon nitride and zirconia ceramics

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Keywords: fatigue, corrosion, contact damage, silicon nitride, zirconia

In power engineering applications and chemical facilities there is a high demand for components e.g. springs which are resistant against high temperatures as well as corrosion. They also have to provide a reliable and maintenance-free usage without change of their technical properties. In this regard, ceramic materials may expand the application range of springs in comparison to metals, as they are furthermore electrically isolating and nonmagnetic. However, the time-dependent mechanical strength at static or cyclic loading in corrosive media and high temperatures has to be taken into consideration to evaluate the system reliability. Addressing this aspect, it is focused on the fatigue behavior of silicon nitride and zirconia ceramics. Both materials are characterized by high strength and fracture toughness and are therefore the first choice for manufacturing of ceramic springs. Although ceramic springs have been processed for many years already, there are low experiences with the corrosive, fatigue and relaxation behaviors at high temperatures. Hence, experimental investigations and numerical simulations have been applied in this study to determine characteristic mechanical values and to describe the microstructural responses which depend on dynamic loading and environmental conditions.

The results after cyclic 4-point-bending tests show that the resistance against fatigue clearly diminishes in water. Increasing the temperature to 1000 °C furthermore enables to emphasize on the influence of high temperatures on the change of strength. Against the background to use silicon nitride and zirconia for springs, the uniaxial state of stress at cyclic 4-point-bending was also varied to a torsional loading for particular samples with bone-shaped geometry. Of special interest is additionally the wear resistance of the ceramics surfaces at cyclic contact loading with spherical shape. The analyses of fractured surfaces after cyclic bending, torsion and frictionally induced wear were conducted via SEM to investigate the activated damage mechanisms. Also, the transformation of the metastable tetragonal to stable monoclinic phase of zirconia ceramics was investigated via Raman-spectroscopy.

Eventually, material laws have been established on the basis of the experimental data to numerically calculate the stress distribution of given spring geometries. This approach is purposeful to reliably predict the live time and to adjust the design of ceramic springs to the specific loading conditions.

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$CaZrO_3$-MgO multiphase ceramics obtained from natural and pure raw materials

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Keywords: multiphase ceramics, $CaZrO_3$-MgO based ceramics, reaction sintering, structural ceramics

Recent trends in materials engineering favour composite materials as opposed to single phase ones. The most known multiphase ceramics for severe environments are refractories, which are responsible for the success of essential industries connected to high temperature processing, such as glass and cement production, thermoelectric power stations and foundries. Complex compositions in ternary or quaternary systems such as ZrO_2-MgO-CaO, Al_2O_3-SiO_2-MgO-CaO or Al_2O_3-SiO_2-MgO-ZrO_2 are usual.

The successful design of multiphase ceramics requires an integrated approach which takes into account the equilibrium phase constitution and how the properties of the constituent phases affect the global behaviour of the material.

This work is a part of a wider project focused to the development of new multiphase oxide ceramics for structural applications of high responsibility with compositions inspired by those of refractories. The ternary system ZrO_2-MgO-CaO has been chosen due to the high temperature of its eutectic point, 1982 ºC. Fine grained and dense ZrO_2-$CaZrO_3$-MgO materials of high purity and with different levels and nature of impurities have been developed and characterise in order to evaluate the capability of multiphase materials in this system for advanced structural applications. The influence of composition and temperature on the microstructural and mechanical characterisation is described. In addition, the wear resistance of the materials is analysed.

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Microstructures and properties of bulk $Al_2O_3/Y_3Al_5O_{12}$ eutectic ceramics prepared by different methods

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Directionally solidified $Al_2O_3/Y_3Al_5O_{12}$ ceramic has been received extensive attentions as a promising candidate for high or ultra-high temperature structural material due to its excellent performances from room temperature to near its melting point. Its outstanding properties are mainly originated from the unique “Chinese script” microstructure, consisting of three-dimensionally and continuously entangled single crystal phases without either grain boundaries or amorphous interfacial phases. However, there is a crucial challenge to fabricate large-size bulk eutectic ceramics with fine eutectic microstructure due to the limitations of their typical preparation methods.

In this work, large-size highly-dense $Al_2O_3/Y_3Al_5O_{12}$ bulk eutectic ceramics were prepared by both traditional hot pressed sintering and rapid sintering methods such as induction heating and spark plasma sintering methods. Starting powders were the pulverized eutectic particles prepared by optical floating zone method. The sintering densification and microstructure evolution of the $Al_2O_3/Y_3Al_5O_{12}$ eutectics were studied. Moreover, the mechanical and thermal properties of as-prepared bulk materials are characterized and discussed. The results show that the initial eutectic particle size and the sintering methods impressively affect the sintering behavior and the eutectic structures of $Al_2O_3/Y_3Al_5O_{12}$ bulk materials. And most important of all, the sintered bulk samples show analogous mechanical properties compared with directionally solidified eutectic material. Therefore, this work provides feasible ways to process large bulk eutectic ceramics for its potential applications.

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Surface and volume crystallization in glasses from the system BaO-SrO-ZnO-SiO_2

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Keywords: crystallization, thermal expansion, nucleation, transmission electron microscopy

Glasses and glass-ceramics containing high concentrations of alkaline earth oxides are widely known as high thermal expansion materials for sealing applications. However, in the system BaO-SrO-ZnO-SiO_2, a recently found phase with the formula $Ba_{1-x}Sr_xZn_2Si_2O_7$ exhibits very low or even negative thermal expansion. This phase can be precipitated in high concentrations from suitable glasses. Unfortunately, such glasses show solely surface crystallization, which makes it impossible to prepare large sized samples. For this purpose, volume crystallization has to be achieved. In order to trigger the formation of volume crystals, different additives such as ZrO_2, SnO_2, Au, and Pt are introduced, and their performance as nucleation agents is analyzed within the scope of this study. To examine the crystallization behavior, various methods are combined, which are differential scanning calorimetry, X-ray diffraction, UV-vis-spectroscopy, scanning electron microscopy, and analytical high resolution scanning transmission electron microscopy.

It will be shown that the used additives affect the crystallization behavior in different ways, which is, amongst others, caused by the different size of the particles acting as nucleation centers, ranging from above 1 µm to below 10 nm, depending on the used additive and the applied heat treatment.

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Aligned porosity SiOC ceramics

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Keywords: porous ceramics, aligned porosity

A simple and inexpensive technique was developed to form porous SiOC monoliths having aligned but also gradient porosity. Preceramic polymer blends were mixed with a catalyst, followed by curing via directional heating the molds, and pyrolysis. SEM, tomography (CT), BET and water immersion porosimetry were used to characterize the structural properties of the porous materials. The resulting bodies have axially oriented channels (average diameter in between 0.59–1.25 mm) and open porosity up to 85 vol% with high specific surface area (121.9 m^2/g).

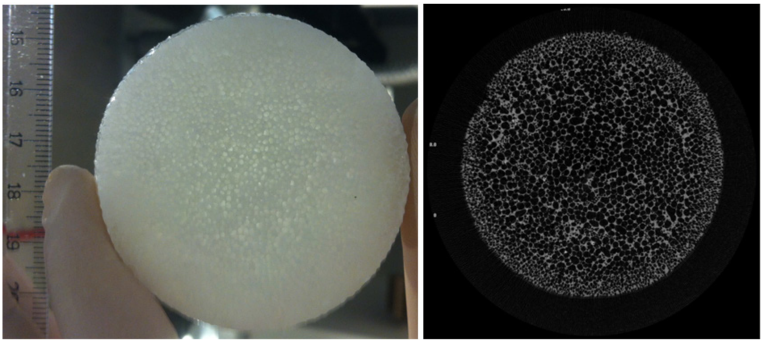

Fig. 1. Aligned porosity samples, (left image) cured thermoset, and (right image) tomography image of the pyrolyzed sample

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Effect of SiC on the oxidation resistance of carbon fibre reinforced ZrB_2/SiC composites

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Ultra-High-Temperature-Ceramics (UHTCs) are a novel class of refractory materials characterized by melting points exceeding 3000 °C and very good thermo-mechanical properties.[1] Among UHTCs, ZrB_2/SiC composites have been investigated as potential candidates for the fabrication of reusable Thermal Protection Systems (TPS) for aerospace applications due to their good oxidation resistance.[2] However, their low fracture toughness and thermal shock resistance remain major obstacles to their implementation.[3,4]

For this purpose, continuous carbon fibres (~45 vol.%) were used as reinforcement in order to increase their damage tolerance and thermal shock resistance.[5] The resulting materials were labeled "UHTCMCs" (Ultra High Temperature Ceramic Matrix Composites).

In this work, the oxidation resistance of carbon fibre reinforced ZrB_2/SiC composites was investigated. Composites with SiC amounts ranging from 5–20 vol.% were fabricated by slurry infiltration and hot pressing at 1900 °C and 40 MPa. Oxidation tests were carried out on cut specimen ($2 \times 2.5 \times 12$ mm^3) in a bottom-up loading furnace at 1500 °C and 1650 °C. The resulting microstructures were analysed by SEM-EDS and X-ray diffraction analysis.

Results show that the formation of a viscous borosilicate glass phase is essential for the protection of carbon fibres from oxidation; low amounts of SiC do not provide enough protection against fibre degradation, while excessive formation of SiO_2 is not beneficial for oxidation resistance. The best compromise was found for the composition with 15% of SiC which was characterized by the lowest degree of oxidation and weight loss.

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Fabrication and characterization of nacre-inspired metal infused ceramics

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Keywords: brick-and-mortar, alumina, BMG, structural materials, bioinspired, freeze casting, presureless infiltration

The goal of this work is to increase the strength and toughness of bioinspired ceramic materials, modelled on the brick-and-mortar structure of nacre. Past theoretical studies (Begley, et al. 2012) have suggested that a metallic mortar, as opposed to a polymer, would lead to significantly improved properties in a nacre-like material as long as the strength of the mortar does not exceed the ceramic bricks. Based on these results, a freeze-cast ceramic scaffold was infiltrated with a metal. This work used freeze casting because it is a relatively simple technique to replicate the hierarchical structure of nacre. One challenge for producing a ceramic/metal composite is that metals typically do not wet ceramics. This introduces the need for high pressure to overcome capillary forces during infiltration. To resolve this issue, a Zr-based bulk metallic glass (BMG) ($Zr_{46}Cu_{30.14}Ag_{8.36}Al_8Be_{7.5}$) was used as the metallic mortar because it reacts with the surface of the alumina to create an interfacial layer the metal readily wets. This study focuses on how the mechanical properties of the hybrid ceramic materials changes with respect to the infiltration temperature and ceramic content in order to find the optimal processing conditions to create an effective brick-and-mortar architecture. The results illustrate a trade-off between the fracture toughness and the flexural strength of the resulting materials. Samples with higher ceramic content and higher infiltration temperature have lower flexural strength, but higher fracture toughness. One cause of this behaviour is the increasing infiltration temperature decreases the glassiness of the BMG phase, which leads to an increase of thickness of the brittle intermetallic phase.

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Fly ash based-cordierite containing mullite geopolymer composite

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Keywords: geopolymer composite, compressive strength, modulus of rupture, thermal property

Attempt to improve thermal properties of the fly ash based-geopolymer was performed by compositing with cordierite containing mullite in the 20–60 wt% replacement range. A number of characterization and property testing were carefully executed. The XRD showed existence of cordierite, mullite, quartz, cancrinite and lazurite in all the geopolymer composites. Upon heating the geopolymer composite, lazurite phase became more intensed and at 800 °C, cordierite had reacted and changed to diopside. Derivative thermal gravimetric analysis (DTG) and dilatometer test results showed that the geopolymer composite (60% cordeirite replacement) had a much smaller weight loss, and thus a smaller shrinkage, than the based geopomer (control), producing a less internal stress. Improvement of the compressive strength and the superior strength retention ability after the thermal exposure at 400 °C was found in the geopolymer composite especailly those with 20–40 wt%. Further heating to 600 °C, all geopolymers showed insignificant difference in the compressive strength. Fire resistance was improved with increasing the cordierite contents. This research showed that compressive strength and thermal properties of fly ash based geopolymer could be improved by compositing with cordierite containing mullite in the selected amounts.

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Tuning ceramic microstructures using capillary suspensions with incorporated nanoparticles

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Keywords: porous materials, open porosity, structure formation, hierarchical structure, mechanical strength, nanoparticles, sintering, capillary suspensions, high temperature applications, filtration, catalysis

Capillary suspensions can be used as stable precursors to create porous ceramics with a high open-porosity. Capillary suspensions are solid-liquid-liquid systems with a small amount of an immiscible secondary fluid added to a suspension. A strong particle network forms due to capillary forces, which changes the material strength from fluid-like or weakly elastic to strong gel-like behavior.[1] The particle network connected through capillary bridges is much stronger than those created by van der Waals forces; it does not collapse during debinding or sintering, and therefore can serve as precursor for sintered materials with high open-porosity.[2]

We utilize the secondary fluid to deposit ceramic nanoparticles specifically in the contact regions of the microparticles. Therefore, we have advanced control over the resulting microstructure. We show an increased mechanical stability and a lower sintering temperature for the sintered bodies by adding 2–40 vol% nanoparticles to the secondary phase. Moreover, the resulting pores are smoother and give rise to a higher permeability. Thus, we are able to control the sintering of the neck regions and pore shape, which allows us to specifically tune the final ceramic properties. These nanoparticles can also be from a dissimilar material.

Through this approach, we can use nanoparticle-laden secondary liquids as a temperature stable “bonding agent” for catalytically active particles, e.g. zeolites, to generate hierarchically structured porous bodies. The capillary-induced particle network creates macroporosity and microporosity is supplied by the coarse particles. The sintering activated neck formation of the ceramic nanoparticles “glues” the coarse particles together and supplies mechanical stability while preserving the inherent porosity in the catalytic particles. The strength and porosity can be controlled by combining the particle size dependency with nanoparticle type and sintering temperature. Hence, we can create hierarchically structured porous bodies with high specific surface area for high-temperature catalysis applications.

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A study on the feasibility of $Zr_{n+1}AlC_n$ and $Zr_{n+1}SiC_n$ MAX phases for future fission environments

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After Fukushima’s nuclear disaster there has been a growing interest in introducing new safety concepts for future fission reactors. One approach is to develop Accident Tolerant Fuels (ATF) that can withstand the harsh environment within a fission reactor for at least 10 hours in a Loss-of-Coolant-Accident (LOCA). MAX phases are potential candidates for use in ATF as cladding. The system that has been targeted is $Zr_{n+1}AlC_n$. Zr offers compatibility with the zircaloy cladding, Al offers resistance to corrosion and oxidation, while C limits nuclear transmutation. In addition, $ZrSi_2$ has been recently proposed as another candidate for ATF, which suggests that $Zr_{n+1}SiC_n$ MAX phases could be potentially used in ATF. However, there are some concerns about corrosion resistance due to the presence of Si and SiO_2 solubility under normal pressurized water reactor (PWR) operating conditions as well as accident scenarios.

This work examines stabilization of $Zr_{n+1}AlC_n$ MAX phases by partial substitutions in the quaternary systems $(Zr,M')_{n+1}AC_n$ and $Zr_{n+1}(A, A')C_n$ where A = Al, Si. Synthesis and sintering of MAX phases will be discussed as well as oxidation resistance, corrosion resistance in PWR conditions and thermal properties.

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Design and characterization of substoichiometric zirconium carbides for Gen-IV Very High Temperature Reactors (VHTRs)

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Zirconium carbide is considered as an attractive structural material for new generation reactors operating at high temperature, due to its promising properties, including high melting point, high hardness, good wear and corrosion resistance, high thermal conductivity at high temperature, high thermal-chemical stability, as well as low cross section capture for neutrons and superior resistance to radiation damage. Besides, zirconium carbide is a typical non-stoichiometric compound with a high carbon vacancy concentration. Using First-principle calculations, the structural characteristics and stability of non-stoichiometric zirconium carbide have been identified. Accordingly, advanced zirconium carbides have been designed by tuning the carbon vacancy characteristics. Then non-stoichiometric $ZrC_{0.86}$, $ZrC_{0.78}$, $ZrC_{0.55}$, and $ZrC_{0.49}$ were synthesized by PVD method. The microstructure, and mechanical properties of the as-synthesized coatings were investigated. Finally, the irradiation damage tolerance against Au ions were performed to evaluate the feasibility of the advanced zirconium carbides in Very High Temperature Reactors.

Poster presentations

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Effects of additive amount and mechanical alloying duration on the microstructural and mechanical properties of ZrB_2 ceramics prepared via pressureless sintering

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Keywords: zirconium diboride, mechanical alloying, co sintering aid, pressureless sintering

Amongst various transition metal borides, zirconium diboride (ZrB_2) has attracted considerable interest due to its superior properties such as high melting point, low density, high hardness, high elastic modulus, low thermal expansion coefficient, high electrical and thermal conductivity, high wear, corrosion and thermal shock resistance, good oxidation resistance, excellent chemical inertness and durability.[1] ZrB_2 has been used in cutting tools, crucibles and dies for molten metals, thermocouple sheaths, ballistic armours, wear resistant coatings, electrodischarge machining electrodes, particulate reinforced composites, integrated circuits, leading edges and nosecaps for hypersonic atmospheric re-entry, rocket nozzle inserts and high temperature nuclear reactors.[1,2] However, consolidation problems, weak fracture toughness, flexural strength and intrinsic brittle character of ZrB_2 usually restrict its extensive applications as a structural material. The densification of ZrB_2 requires extremely high sintering temperatures and long dwell times because of a rather-low self-diffusion coefficient caused by the predominant covalent bonding. Such extreme processing conditions induce excessive grain growth, internal stresses and microcracks which are detrimental to mechanical properties. Besides, densification of ZrB_2 is feasible at lower temperatures with the use of sinter additives such as Fe, Ni, Cr, Co, Mo and Cu or some silicides, oxides, etc.[2]

On the basis of the reported literature, pressureless sintering of ZrB_2 with Co metallic additive is not a well-discussed topic. This study presents the microstructural and mechanical properties of ZrB_2 ceramics prepared by using a combined method of mechanical alloying (MA), cold pressing and pressureless sintering. The effects of Co addition (0, 5, 10 and 20 wt.%) and mechanical alloying duration (0, 3, 6 and 9 h) on the properties of ZrB_2 ceramics were investigated. MA experiments were carried out in a Spex™ 8000D Mixer/Mill and milled powders were subsequently compacted to cylindrical preforms by uniaxial pressing at 400 MPa. The green compacts were sintered in a controlled atmosphere at 1550 ºC for 1 h. Phase and microstructural characterizations of the mechanically alloyed (MA'd) and sintered samples were performed by X-ray diffractometer (XRD), optical microscope (OM) and scanning electron microscope/energy dispersive spectrometer (SEM/EDS). Density measurements were conducted using Archimedes method. Vickers hardness, elastic modulus and fracture toughness of the sintered samples were measured using Indentation technique.

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Study of microstructure and functional properties of layered $BaTiO_3$–ferrite–$BaTiO_3$ magnetoelectric composites obtained by SPS method

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Multiferroic trilayer $BaTiO_3$–$Co_{0.8}Zn_{0.2}Fe_2O_4$–$BaTiO_3$ (BT–CZF–BT) and $BaTiO_3$–$CoFe_2O_4$–$BaTiO_3$ (BT–CF–BT) composites are synthesized by Spark Plasma Sintering method. The investigation of the cross-sectional view of the trilayer composites using scanning electron microscopy shows a clear interface between the different layers. Microstructural SEM analysis (fracture) of the layered composites consolidated by SPS indicates the presence of two distinct phases: grey area corresponding to the ferroelectric phase (BT), while dark regions correspond to the magnetic phase (CF/CZF). It can be observed that by SPS consolidation was obtained good quality dense composite ceramics with (2–2) interconnectivity and a good separation of the two phases, with neat and clean interface without porosity and limited interdiffusion at interface. Furthermore, the dependence of dielectric properties on the frequency and temperature has been examined. In the dielectric constant versus temperature plots, a dielectric anomaly is observed near the ferroelectric to paraelectric phase transition of the BT, which shifts towards high temperature side as frequency increases for all the samples, demonstrating relaxor like behavior. In addition, broad peaks are also noticed in the loss tangent versus temperature plots in the same temperature range. Study of ferroelectric (P(E), dc-tunability and pyroelectric effect) properties have been investigated and discussed in details. The evolution of temperature and of the pyroelectric current for the layer BT-CZF/CF-BT ceramic samples for determination of pyroelectric coefficient on heating and cooling rate, respectively was described. The influence of the magnetic layer (CZF/CF) thickness and dc magnetic field on the magnetoelectric coefficient (α_E) of the layer composites is studied.

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Preparation and characterization of aligned alumina scaffolds using Bi-directional freeze casting

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Keywords: freeze casting, alumina, highly aligned structure, dual tempreture gradients

Freeze casting or ice templating, is a novel method to fabricate highly porous ceramic materials. Despite its well-documented advantages, the lack of a precise way to control the hierarchical structure of the porous network is considered a major limitation[1]. Understanding the freezing mechanism to fabricate reproducible highly aligned structure materials using freeze casting is important to apply these porous materials to biological and industrial applications[2]. In this work, alumina ceramic slurries were freeze casted under dual temperature gradients. A special mould using a polymer wedge with different slope angles was used to modulate the temperature field. The effects of different processing parameters (cooling rate, mould slope angle, solid loading and binder concentration) on lamellar orientation were studied. The results showed that freezing under dual temperature gradients produced highly aligned ceramic scaffolds. Increasing both the cooling rate and the mould slope angle increase the size of the highly aligned ordered ceramic domain. Using different alumina solid loadings in the initial suspension had a minimum effect on the aligned lamellar structure. Increasing the binder

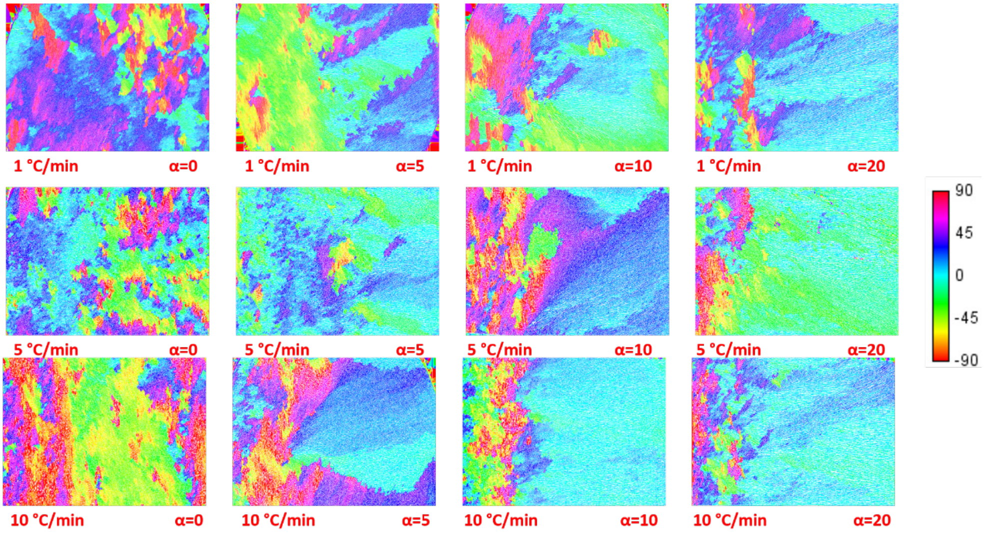

Fig. 1. Light microscope images show the alignment of lamellar structure of ceramic samples produced at different cooling rates (1, 5 and 10 °C/min) and using different copper moulds with various slope angles (α = 0°, 5°, 10° and 20°). The colour gradient represents different angles of lamellar alignment, the colour bar at the right side of the images

concentration affected ice crystal's growth in an aligned direction. Therefore, freeze casting technique under dual temperature gradients could be used as a viable method to fabricate highly aligned porous materials. By controlling the microstructural features, it is possible to produce biomimetic materials with potentially superior mechanical properties.

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Yttrium silicate used as environmental barrier coating: relation between microstructure and protection efficiency

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Future generations of parts of turbines will be replaced by Ceramic Matrix Composites (CMCs). Generally these CMCs consist of ceramic matrices reinforced fibers, both in silicon carbide. However, at elevated temperatures and under severe atmospheres, the silica protective scale over silicon carbide volatilize as hydroxides species and the resulting recession of silicon carbide may cause the loss of the composite's mechanical properties.

To protect CMCs, EBCs are put in place. The most stable EBCs are often rare-earth silicates.[1] This investigation is focused on yttrium silicate EBCs. To deposit EBCs, each process generates a different microstructure, by varying the duration of sintering, for example, or by varying the particle size distribution of the powder. These differences in microstructure will have an important influence on the ionic conductivity inside the coating as well as the recession rate of EBCs.[2] The challenge of this investigation is to measure the ionic conductivity of yttrium silicates (mono and di) and to quantify their rate of recession. Ionic conductivity has been revealed by employing complex impedance spectroscopy. The use of this technique allows determining the ionic conductivity of the ceramic at different temperatures in various environments dry or wet. Moreover, the contribution of the bulk and the grain boundaries can be separated. For different microstructures (nanostructured or micron), the grain surface and grain boundaries surface will be different therefore, inducing changes in the ionic conductivity also. A similar issue occurs in the case of volatilization at the EBC surface. For example, reactions of volatilization should take place in the less crystallized zones as grains boundaries. Further, model layered composite (EBC/Si/EBC) are made and submitted to moist air at high temperature, to compare the efficiency of the EBC to limit the diffusion of oxidizing species with the previous measured ionic conductivity. More than the role of microstructure, its efficiency is related with the grain growth rate in function of ageing.

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Wear behavior and mechanical properties of SiC/GPLs composites with different counterparts

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Keywords: wear, friction coefficient, hardness, toughness

Wear behavior and mechanical properties of composites with silicon carbide matrix with addition from 0.5 to 6 wt.% of GPLs filler were investigated and compared to the monolithic silicon carbide material. All experimental materials, containing 0.5 wt.% of boron and 3.5 wt.% GPLs as sintering additive plus 0 wt.% (reference sample) – 6 wt.% GPLs as reinforcing phase, were hot pressed at 2100 °C for 1 h under 25 MPa in argon flow. The wear behavior was observed by means of the ball-on-flat technique with a both silicon carbide and tungsten carbide – cobalt balls used as the tribological counterpart at room temperature ~25 °C, in dry sliding at different loads (5, 30 and 50N). Addition of such amounts of GPLs did not lower the coefficient of friction. Wear rates values showed strong dependence on the applied load, at both tribological pairs. Tenfold increase of normal load (from 5 to 50 N), results wear rate increase of two orders of magnitude. Friction coefficients decrease with an increase of the applied load. The influence of the GPLs addition on bending strength, fracture toughness and related fracture characteristics was investigated. Both the bending strength and fracture toughness increased with increasing of GPLs additives. The fracture toughness was enhanced due to the activated toughening mechanisms mainly in the form of crack bridging and crack branching, while the crack deflection was limited.

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Novel ceramic composites reinforced with ZrO_2 nanofibers

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Keywords: Si_3N_4, ZrO_2 nanofibers, electrospinning, SPS, mechanical properties

Silicon nitride (Si_3N_4) based ceramics exhibit a remarkable combination of mechanical properties: good wear, oxidation and corrosive resistance, excellent thermal shock resistance and not at least high hardness, however, currently their poor fracture toughness is a significant disadvantage which is a limitation factor for its widespread application. In case of Si_3N_4 many reinforcing phases have been studied successfully, for example, it was reinforced with various ceramics particles and carbon structures, such as nanotubes and graphene. The different carbon structures could show very good opportunity to improve the fracture toughness[1]; however, the main drawback of these non–oxide secondary phases is their mechanical properties degradation at elevated temperatures under air. To avoid this degradation, one of the potential reinforcing phase is the ZrO_2. Therefore, in this work we are investigating an alternative route to develop a SPS sintered Si_3N_4 ceramic composites with high fracture toughness and strength reinforced by self-made electrospun 3 mol% Y_2O_3 partially stabilized ZrO_2 nanofibers, which could be suitable to use the composites at high temperature beside in air atmosphere, as well.

We obtained significant fracture toughness and flexural strengths improvements in ZrO_2 fiber reinforced Si_3N_4 composites. The sample loaded by 15 wt% ZrO_2 fibers had 10.05± 0.7 MPa $m^{1/2}$ fracture toughness and 543±19 MPa flexural strength, which means 105% and 115% improvements respectively, regarding to the reference sample. Thus, the incorporation of fiber into the Si_3N_4 composite is effective way to increase the fracture resistance and avoided the catastrophic fracture behaviour since ZrO_2 fiber is able to improved mechanical properties of the composites in a complex way, such as phase transformation toughening and fiber toughening mechanisms.

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Spark plasma sintering of alumina ceramics

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Keywords: spark plasma sintering, ceramics, alumina

In recent decades, the high-speed compaction technology known as Spark Plasma Sintering (SPS) has become a frequent practice in powder engineering.[1] One of the key features of SPS technology that distinguishes it from other consolidation technologies is its high control precision of sintering parameters. Optimization of SPS modes allows to obtain almost any oxide ceramics with density close to 100% and grain growth factor below 2.[2] At the same time, ultrafine-grained structure of sinter materials ensures high strength properties. On the other hand nano powders, surfactants, and ultrasonic-mixing processing allow to obtain even distribution of the dispersed particles in the base material and therefore reduce their volume fraction without decreasing of the mechanical strength. From this perspective, it looks very promising to combine innovative approaches to obtaining powder composite systems and SPS technology to produce Al_2O_3-based ceramics, which is the goal of the present work.

It is crucial to note that unless a continuous net of grain boundaries is formed, coarsening of grain is impeded. A net of grain boundaries is considered to be formed at relative density of $\rho \sim 90\%$. From this point an intense grain growth is observed.[3] In this context, in order to obtain materials with maximum density and minimum grain size it is required to optimize temperature and isothermal time after the material passes through $\rho \sim 90\%$. At high sintering temperature, boundary migration speed is generally high, boundaries may «come off the pores» leaving them in the grain volume. In this case, pores dissolution rate as well as contraction will be controlled by volume diffusion rather than grain boundary diffusion. Dense materials are therefore hard to obtain. To eliminate the come-off effect, boundary migration speed shall be slowed down. It can be achieved through reducing the sintering temperature after reaching the 90%-density point. This approach is known as «Two Step Sintering», «Multi Step Sintering», «Rate Control Sintering».

Lowering the temperature at the second sintering stage helps to reduce grain growth rate while maintaining pores dissolution rate at a reasonable level. materials in order to obtain lightweight ceramics Al_2O_3/ZrO_2 with enhanced strength properties. Optimization of SPS modes helps to produce ceramics with grain size of less than 400 nm, microhardness $H_V = 24$ GPa, and crack resistance $K_{IC} = 4.2$ MPa·m$^{1/2}$.

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Alumina/zirconia composites toughened by the addition of graphene flakes

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The effect of graphene flakes on the mechanical properties of the composite containing 20 wt. % Al_2O_3 and 80 wt. % ZrO_2 (stab. 3 mol% Y_2O_3) was studied. To obtain samples a commercial ceramic powder produced by Tosoh (Japan) and graphene oxide (GO) made in Institute of Electronic Materials Technology (Poland) were used. The obtained composites based on an aqueous (GO) mixtures of both components. After drying, they were sintered under a uniaxial pressure (HP furnace). The composites contained by weight from 0 to 3% of GO. It was found that as a function of the GO: fracture toughness has a maximum for 0.02% GO (42% increase compared to GO free matrix), strength decreases, the Young's modulus and Vickers hardness remain constant up to 0.5% GO, and then decrease.

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Electrical and magnetic properties of SiC ceramics with addition of Ti and NbC

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Keywords: silicon carbide, hot-press, electrical conductivity

In this work silicon carbide based composites were prepared by hot-press method. 30, 40 and 50 mass% of of Ti and NbC were used as sintering additives. Their molar ratio was kept at 1:1.8 (Ti:NbC). Samples were sintered by two step sintering to avoid the squeezing out the melted titanium above 1668 °C. Composites were sintered at 1650 °C for 3 h and subsequently at 1850 °C for 1 h under mechanical pressure of 30 MPa in Ar atmosphere. Composite with 50% of Ti-NbC phase showed the electrical conductivity of 240 $S \cdot mm^{-1}$, which is three times order higher than in reference SiC. SEM analysis showed that there are agglomerates of SiC grain and agglomerates of (Ti, Nb)C solid solution in the sample. Only a thin layer of secondary phase is located between SiC grains. XRD pattern confirmed the formation of (Ti, Nb)C solid solution in the SiC matrix. Magnetic measurements showed that the sample with 50 mass% Ti-NbC is clearly ferromagnetic at 2K while the behavior of samples with 30 and

40 mass% of Ti-NbC is changing from ferromagnetic to diamagnetic at higher fields (up to 7T). At room temperature samples with 30 and 40 mass% of Ti-NbC are diamagnetic and the sample with 50 mass% of Ti-NbC is paramagnetic.

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Characterization of thermal barriers coatings of Y-TZP/AL_2O_3/SiC composite obtained by suspension plasma spraying

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Keywords: thermal barrier coatings, suspension plasma spraying, composite, self-healing

Thermal barrier coatings (TBCs) are used for protection of metals and ceramic components against corrosion, erosion and high temperature. The most common composition is based in yttria-stabilised zirconia (Y-TZP) because this material exhibits excellent mechanical and thermal properties. Nevertheless, continued use in extreme temperatures and aggressive conditions favours the appearance of cracks and the quick wear of the zircona layer. Hence, these TBCs must be improved in order to increase their lifetime under aggressive conditions. For that reason, the design of new TBCs with a self-healing functionality, which allows to increase the TBCs lifetime, could be an alternative challenge.

There are few ceramic materials with this ability, being silicon carbide (SiC) the most studied one. Nevertheless, SiC particles tend to decompose and oxidise inside a plasma torch losing their healing ability. The preservation of this ability is essential, thus, a new strategy has been followed in the present work in order to avoid the decomposition of the SiC. This strategy consists of employing a suspension as feedstock instead of powders. In this way, the solid material receives less energy during deposition due to solvent evaporation. Furthermore, the addition of a third compound (Al_2O_3), which helps to melt the matrix mixture, can make a further contribution to the protection of the SiC particles in the plasma torch.

In accordance with the proposed strategy, an aqueous-based suspension of SiC, Y-TZP and Al_2O_3 was prepared and deposited by suspension plasma spraying (SPS). The deposition was performed onto substrates of stainless steel, employing different solid contents and stand-off distances with the purpose of assessing coatings microstructure. The obtained coatings were microstructurally analysed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX), while the different crystalline phases were determined by X-ray diffraction (XRD). The characterisation reveals the presence of unmelted SiC particles dispersed in a partially melted matrix of Al_2O_3/Y-TZP, confirming that the SiC particles have not been oxidised during plasma spraying, preserving its potential self-healing ability. Besides, the effect of stand-of distances on the coatings porosity and adherence was also assessed.

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Adhesion assessment of bioactive coatings deposited by atmospheric plasma spraying

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Keywords: bioactive powders, atmospheric plasma spraying, bioactive coatings, coatings adhesion

Bioactive coatings are used in the field of medicine as coatings for orthopaedic implants made of bio-inert materials such as stainless steel, chromium/cobalt or titanium alloys with the aim of conferring biocompatibility and protecting them against the corrosion and the degradation promoted by biological fluids. Usually, these coatings can be deposited by different techniques such as enamelling, sol-gel or dipping. However, atmospheric plasma spraying (APS) is one of the most studied and used method for obtaining these coatings. While bioactive coatings have to accomplish several requirements (biocompatibility, porosity, rough surface, etc.), a good adhesion to the implant surface represents one of the most important challenges which is hardly reached.

Therefore, the aim of the present work is to prepare bioactive coatings by APS employing different spraying parameters and substrates in order to model the adhesion of the coatings and to determine the best parameters that allow to prepare coatings with good adhesion to the substrate. For that purpose, a statistical analysis was performed evaluating the adhesion in function of different variables, each one at two different levels, and correlating the adhesion with them. The variables chosen are the argon flow and the feedstock feed rates, the type of substrate and the presence of a bond coat. Furthermore, coatings were microstructurally characterised by scanning electron microscopy and their nature (amorphous or crystalline) was determined by X-ray diffraction.

The obtained results show significant differences in coatings adhesion in function of the variables tested, varying this mechanical property from 0.6 to 10 MPa. Moreover, the model and the correlations between variables obtained from the statistical analysis, confirm that the adhesion is strongly influenced by the presence of a bond coat as well as the plasma gases flow rate and the type of substrate. Besides, it can be appreciated that coatings with higher adhesion values show better microstructures.

Acknowledgements
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Creep behaviour of alumina reinforced composites sintered by spark plasma sintering

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Keywords: graphene-oxide, carbon nanofiber, alumina composites, creep resistance

Alumina (Al_2O_3) ceramic composites reinforced with either graphene oxide (GO) or carbon nanofibers (CNFs) were prepared using Spark Plasma Sintering. The effects of GO and CNFs on the microstructure and in consequence, on their mechanical properties, were investigated. The microstructure of the sintered materials have been characterized quantitatively prior to and after the creep experiments in order to determine the deformation mechanism.

Carbon materials, such as carbon fibers or carbon nanotubes (CNTs), or graphene, have been used in the last decades to improve the mechanical properties of a large variety of materials. Another way to improve the mechanical properties of alumina is by means of fibers as reinforcement in ceramic composites. Fiber/whiskers usually have diameters ranged from a micrometer to tens of micrometers and lengths from several micrometers till hundreds of micrometers, embedded inside a fine-grained ceramic matrix.[1]

The study of their plasticity can permit to go insight the intrinsic mechanisms of matter flow and phase arrangement under loading conditions. This basic information is crucial to feedback and improve the processing conditions for an optimized composite.

High-temperature creep behavior of graphene-oxide reinforced alumina composites and carbon nanofiber reinforced ones prepared by spark plasma sintering have been studied at temperatures as high as 1200 ºC and above. The results show that the microstructure is quite stable during creep and consistent with grain boundary sliding as the deformation mechanism. The graphene-oxide-reinforced alumina composite is systematically more creep resistant than the carbon nanofiber one, although the creep resistance diminishes when temperature increases. In this context, graphene oxide and carbon nanofibers offer similar advantages in very high-temperature applications of alumina composites.

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Low volumetric heat capacity insulation coating by room-temperature operating spray coating process

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Keywords: insulation, low volumetric heat capacity, spray coating

Insulation coating with both low thermal conductivity and low volumetric specific heat is useful for heat loss reduction of engine combustion chamber without any sacrifice in other engine performances.[1] In comparison with conventional dense - high volumetric specific heat insulation coating, the low volumetric specific heat coating can reduce surface temperature of insulation coat on combustion chamber wall rapidly, according with the fluctuating temperature of in-cylinder gas. To realize low volumetric specific heat, microstructure of the coat should be porous. Also, the coat should have high enough durability – adhesion strength, hardness, and chemical inertness for real operating condition, justly with low thermal conductivity. In this work, we fabricated porous ceramic insulation film with thickness of ~100um, porosity of 35~42%, adhesion strength of 20~28MPa, thermal conductivity of less than 0.5W/mK without thermal damage of metal substrate by novel ceramic spray coating. The processing, microstructure, thermal properties, and mechanical properties of the films were analyzed.

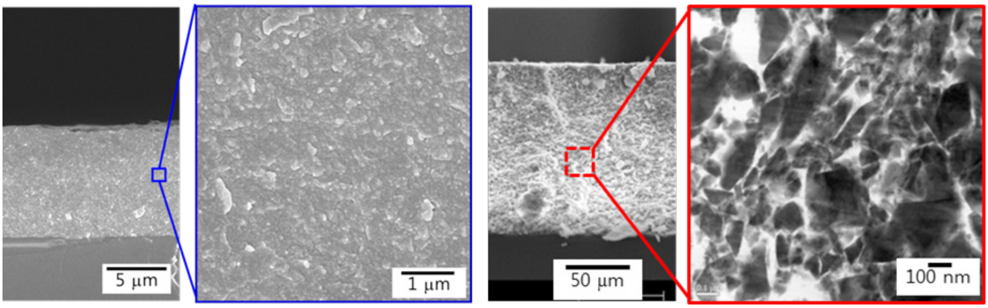

Fig. 1. Microstructure of dense and porous insulation film fabricated by room-temperature operating ceramic spray coating process

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Improvement of densification uniformity in carbon/silicon carbide composites by chemical vapor infiltration

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Ceramic matrix composites (CMCs) have attracted lots of attentions due to their increased fracture toughness, elongation and thermal shock resistance, which results in wide applications under extreme environmental conditions. The silicon carbide-based CMCs can be commercially produced by silicon infiltration, precursor infiltration pyrolysis (PIP), chemical vapor infiltration (CVI) and their combined (or repeated) processes. The CVI process is carried out by chemical deposition of reactive gaseous species into porous fiber preforms. As a carbon fiber preform is exposed to a mixture of hydrogen and methyl-trichlorosilane (MTS) at elevated temperature around 1000 degree Celsius, silicon carbide is deposited in between the carbon fibers by decomposition of MTS. After CVI process, pores still exist partially in the preform. Distribution of the remained pores varies with the infiltration depth of precursor gas that is related to the gas flow and the temperature distribution of the preform. Improvement of densification uniformity of the preform is the main purpose of this work. The optimum condition for densification was predicted with CFD simulation and the resultant microstructure of CMC was demonstrated.

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Ceramic materials for high efficiency advanced microturbines

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Gas microturbines are considered as a small size generation technology with a simplified plant exercise and maintenance and a reduced environmental impact; commercial success of the technology is however hindered by a limited efficiency compared to other small size technology as internal combustion generation plants. The increase of electrical and overall efficiency would allow to extent also the field of application for the microturbines with a possible application also in residential and tertiary sectors where the electrical and thermal demands change in time and are highly weather conditions dependant. Production of advanced microturbines, with efficiency comparable to internal combustion engines, is strictly related to the possibility to manufacture some parts of the machine with materials showing a satisfactory mechanical and oxidation resistance to more severe exercise conditions; in particular high temperature resistant materials, as ceramic type, are required.

Preferable materials for high efficiency microturbines are, up to now, silicon nitrides whose increased resistance can be obtained by sintering with particular additives or by protection

with coatings in order to improve high temperature corrosion resistance. During recent years RSE performed a characterisation activity of commercial and under development silicon nitride materials that can be used for manufacturing advanced microturbines. Four point bending mechanical strength tests have been performed at ambient and high temperatures up to 1200 °C for yttrium and rare earth metal added silicon nitrides; results of mechanical tests and material exposition in burner rig at 1200 °C confirm rare earth metal added silicon nitride as preferable to yttrium added ones, unless some yttrium silicon nitride later can be satisfactory for application in rotor and casing of high efficiency microturbines with limited increase of gas inlet temperature (TIT).

The relevant loss of material observed in burner rig tests, for any tested silicon nitride suggests that, also the most resistant material requires a protective coating application. Base on this result a first trial of ceramic materials coated by other ceramics have been prepared and tested, among tested combinations of materials a promising solution appears to be the application of ytterbium disilicates on silicon nitride. A good resistance in exposition to severe conditions has been observed for it, but further studies for optimisation of coating process and tests for the characterisation of the overall system are still required before than actual application on a prototype microrotor component.

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Development of geopolymer composites reinforced with fiber felts

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Keywords: geopolymer, composite, fibers felt, RTM

Geopolymers are synthetic inorganic alumino-silicate materials generally formed by reaction of an aluminosilicate with an alkali (Na,K) silicate solution. The reaction occurs at room temperature, so geopolymer can be considered as a type of bi-component inorganic resin.

Considering their inorganic structure, geopolymer composites have better thermal properties than organic resins, which typically decompose by oxidation starting from ~400 °C.

In collaboration with Trucker Subforniture s.r.l., geopolymer based composites reinforced with different kinds of felt, have been developed as alternative to GFRP and CFRP, for applications where a high thermal resistance is required.

Different kind of fibers were considered as reinforcement; using felts based on recycled fibers it is possible to keep the cost lower than that of virgin fibers, in particular for carbon and basalt fibers. Geopolymer composites were developed using RTM and infusion technology. In order to have a good infiltration of the felts, the rheology of a potassium based geopolymer resin was optimized in terms of water and alkalinity.

Density, mechanical properties and thermal stability of the different composites were tested.

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Characterization of slip casting of ceramic Hollow Sphere slurries and casting properties for ceramic processing applications

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Keywords: Hollow Sphere, ceramic slurry, slip casting, closed cell foams

Light weight ceramic foams and composites are in focused attention in ceramic industries, due to their high energy absorption, outstanding thermal properties, and light weight. They have a significant potential for application in a wide range of industries, such as refractories, light weight structural ceramics, metal casting parts, gas sensors, gas- and molten metal filtration, implants, adsorbing structures, catalyst carriers, heat-insulation materials. The use of Hollow Spheres (HSs) to build such ceramic foams is advantageous, as the cell sizes can be easily controlled by the diameters of the HSs.

In the literature, to fabricate such kind of composites, several manufacturing process were used, for instance sacrificial cores[1], high temperature binders[2], and dry compressing technology[3].

The goal of this research is to manufacture HS ceramic composites and coatings with slip casting method. The slip casting method gives one the ability to increase packing densities with avoiding the fracture of the HSs during manufacturing. Moreover, slip casting technique can be automated easily. The main limit of this technique is the size of the used HSs, as gravitational forces play more significant role in colloidal systems, as the used particles' size are increased.

In this study, I have chosen fine sized, commercially available mullite HSs, with an average diameter of 90 µm, the distribution of their sizes was lognormal with the standard deviation value of 0.35. The slurry was built on with the use of various amount of HSs, dispersant, and distilled water. Flow curves, sedimentation curves were plotted, and it has been proved, that there exists a technological window, where the slurry is stable enough to use in slip casting, and in coating technologies. Slip casted specimens with cylindrical shape were prepared, and fired at different temperatures in the range 1000 to 1400 °C. The shrinkage behaviour strongly depended on the firing temperature. The output densities were in the range 26 to 47% of mullite's density. The feasibility of producing ceramic closed cell foams with slip casting method starting with HSs has been demonstrated.

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Layered functionally graded alumina ceramic composites

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Keywords: alumina, graphene, functionally graded, composite

Multi-layered ceramic composites with alternation of grain sizes in layers have been produced by adding thin inter-layers of graphenated alumina nanofibers (GAIN) between layers of pure alumina. The composite was mounted layer by layer directly in the graphite mold, using filter to precipitate alumina nanopowder and GAIN layers from corresponding suspensions. The 20 mm diameter samples were consolidated by Spark Plasma Sintering (SPS) technology at 1350 °C in nitrogen atmosphere under 50 MPa pressure. The effect of inter-layers on microstructure and mechanical properties of alumina has been studied. SEM analysis of microstructure reveals distinct grain size reduction in the areas surrounding GAIN layers. Vickers hardness, fracture toughness and nanoindentation tests have been performed.

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Electrophoretic deposition of dispersion of ZrB_2 and SiC powders on woven carbon fibers for the processing of novel UHTCMCs

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In the present work, the deposition of Zirconium diboride (ZrB_2) or/and Silicon carbide (SiC), on carbon fibers via electrophoretic deposition (EPD) is studied. The final purpose is the fabrication of novel ultra-high-temperature ceramics matrix composites (UHTCMCs) for aerospace featuring optimized fiber/matrix interfaces. Ceramic coatings are required for the optimization of the fiber/matrix bonding, oxidation protection, and prevention of fiber-matrix interfacial degradation at high temperatures. Ethanol –based ceramic suspensions of ZrB_2 or/

and SiC powders have been studied in order to determine the optimal solid concentration and dispersant amount. Several deposition experiments were carried out to optimize voltage and deposition time. An incremental approach was adopted, starting from deposition onto individual bundles, then unidirectional carbon fabrics, and finally 2D carbon fabrics. The unidirectional coated woven carbon fibers were further infiltrated with a ceramic slurry, overlayed, and consolidated by hot pressing, to obtain $30 \times 30 \times 5$ mm^3 pellets. The microstructure of the pellet was examined by scanning electron microscopy and optical microscopy. Flexural strength and fracture toughness were measured on machined bars at room temperature, reaching values of 280 MPa and 14 MPa*m$^{1/2}$, respectively. The structure obtained by the combination of these techniques is typical of novel UHTCMC materials that can potentially couple the high oxidation resistance of UHTCs to the damage-tolerance of CMCs, provided that a suitably tailored matrix/fiber interface can be obtained.

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Mechanical properties and wear damage of silicon carbide composites with carbon nanotubes

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Keywords: SiC, CNT, nanoindentation, mechanical properties, tribology, electrical conductivity

Five types of composites based on silicon carbide were prepared and studied. SiC/CNT powder precursors were produced by CCVD method and compacted by hot pressing (1850 °C/Ar/60 min/40 MPa).

Mechanical properties such a hardness and elastic modulus of the composites were investigated by nanoindentation using Berkovich indenter tip (applied load 500 mN). Hardness of the composites as a whole was also evaluated by the macro-indentation method with Vickers diamond tip under the load of 1 kg (9.81 N). Indentation fracture toughness (K_{IC}) was calculated from the lengths of the radial cracks produced in the material under the load of 10 kg (98.1 N) using the Anstis formula. The microstructure and chemical composition of the resulting materials were studied by SEM/EDX. The electric conductivity as function of fraction of additives was determined. Tribological properties have been characterized by the ball-on-disc method at the ambient temperature and dry wear conditions at the 5 N load, 500 m sliding distance with the static partner made from SiC.

Resulting materials were relatively hard $HV_1 = 24$ GPa and with presence of CNT moderate decrease down to $HV_1 = 17\text{-}19$ GPa. Similarly, the fracture toughness decrease with presence of CNT from 7 MPa.m$^{1/2}$ down to 4 MPa.m$^{1/2}$. Nanoindentation shown that hardness H_{IT} of monolithic sample was around 26 GPa and with increasing amounts of CNT decrease down to the roughly same value 21GPa. The samples with CNT had similar modulus of elasticity (E_{IT} = 337-348 GPa) and for monolith sample E_{IT} = 434 GPa. Electrical conductivity was determined by the four point probe method and the measured values increases with amount of CNT (1.76 S/m for monolith, 420.2 S/m for 2.5% CNT, up to 2873.6 S/m for 10% CNT). Created wear track was observed using scanning electron microscopy and main wear mechanisms were cracking and oxidation. Area of the wear track cross-section was measured using 3D optical profiler and the wear loss volume was calculated according to the international standard ISO 20808.

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Influence of post-hip treatment on the optical and microstructural properties of $MgAl_2O_4$ spinel

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Keywords: ceramic, transparent, spinel, pressureless, HIP

Magnesium aluminate spinel ($MgAl_2O_4$) ceramic exhibits a high potential for application in which a combination of optical and mechanical properties is needed: an isotropic propagation of the light due to a cubic structure, a wide range of transmission, low density and high toughness.[1]

Conventional transparent armour is commonly a multi-layered system of glass and polymer, which provides ballistic protection and optical transparency. Found in the civil and military fields as windows of vehicles, face shields or lenses, a transparent armour has to be thick to face armour piercing bullets and multi-impacts, which implies a substantial increase of weight, volume and a loss of optical quality.[2] With higher mechanical properties than glass, polycrystalline ceramic could be an alternative as the front face. In addition, its use is expected to lead to a significant lightweighting since it favours the global efficiency through the fragmentation of the projectile and the decrease of the penetration at the impact.[3]

In order to elaborate transparent ceramic, a procedure was established where the introduction of defects is minimised. Indeed, transparency involves an absence of scattering centres such as pores and secondary phases, which may cause a loss of optical quality. Therefore, high purity of the raw powder and full density of the sintered sample are required.

Commercial spinel $MgAl_2O_4$ powder was directly poured into a die and compacted. Then, the obtained samples were pressureless sintered under vacuum without sintering aids. Finally, a post-treatment by hot isostatic pressing was applied to reach full density and thus to obtain transparent spinel by the elimination of the residual porosity. The study is focused on the influence of the post-HIP parameters on the microstructural and optical properties. Promising result was obtained on spinel ceramic with a thickness of 2 mm and a diameter of 21 mm, which exhibits an in-line transmission higher than 82% in the visible and near-infrared wavelengths domains (94% of the theoretical value) and a heterogeneous microstructure with two populations of grain size (25 ± 8 µm and 130 ± 50 µm).

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Graphene – ceramic composites with 3YTZP matrix

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Keywords: 3YTZP, GNP, processing, SPS, electrical conductivity.

Ceramic composites with carbon nanostructures (carbon nanotubes, graphene…) constitute an interesting research topic due to the expected reinforcement effect of the ceramic matrix and especially due to the fact that significant values of electrical conductivity can be achieved. Yttria tetragonal zirconia polycrystalline (3YTZP) ceramic makes an interesting matrix for these composites since it exhibits quite high fracture toughness due to the tetragonal to monoclinic transformation toughening effect during crack propagation.[1] It can also conduct electricity at high temperatures by ionic conduction. Graphene has exceptional electrical, thermal and mechanical properties, including extremely high electron mobility at room temperature and a very high Young's modulus.[2] However, due to its high surface area, graphene tends to form agglomerates, so it is very difficult to obtain individual graphene sheets. For its use in composites, graphene is commonly in the form of graphene nanoplatelets (GNP) and thinner graphene nanosheets or few layered graphene (FLG), both composed by pile up of several graphene sheets.

In this work, processing of graphene/3YTZP composites with different number of graphene sheets (i.e. differing in planar dimension and thickness) has been approached by wet powder techniques, paying special attention to dispersion of the graphene nanostructures into the ceramic matrix to minimize or avoid their agglomeration. Uniaxial pressure sintering with a pulsed electric discharge furnace (spark plasma sintering, SPS) provided composites with a high degree of microstructural anisotropy. The effect of processing conditions and graphene dimensions on the microstructure, hardness, crack propagation and electrical conductivity of the composites has been evaluated.

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Effect on the mechanical properties of Ce-YTZP/Al_2O_3 nanocomposites for dentistry use

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Keywords: dental ceramic materials, microwave sintering, mechanical properties, microstructure

Ceramic materials are commonly used in restorative dentistry, because they have an esthetics closer to the natural tooth and do not produce allergic reactions or rejection. The most popular ceramic material in this field is zirconia-based materials. Therefore, the purpose of the present study is to investigate zirconia doped with ceria and toughened with alumina. This material is less common than zirconia doped with yttria, and it has not already been researched in detail. Hence, it can be a good topic since is estimated that 240 million people in the Western World have lost at least one tooth. Most of these patients benefit greatly from dental implants.

The samples, that have been studied, are Ce-YTZP/Al_2O_3 nanocomposites and have the following proportion: 65%vol 10Ce-ZrO_2 + 35%vol Al_2O_3. They were sintered using a non-conventional method, microwave technology, in order to enhance the mechanical properties and at the same time to reduce production costs and processing times[1].

Both the starting and sintered material have been evaluated. Regarding the raw material, grain size, phase constitution and X-ray diffraction have been assessed. The mechanical properties, final density and microstructure of the sintered sample have also been studied.

Another aim of this investigation is to compare the studied ceramic material with YTZP, a commercial zirconia currently used in dental reconstructions. Moreover, the effects of the alumina particles dispersed in the zirconia matrix have also been investigated.

Acknowledgements

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Rheological principles of development hetero-modulus and hetero-viscous ceramic matrix composites with extreme dynamic strength

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Keywords: ceramics, composites, diamond-like, elasticity, hetero-modulus, nanostructure, rheology, strength, viscosity

Materials with different crystalline and morphological compositions have different chemical, physical, mechanical and rheological properties, including wear protection, melting temperature, module of elasticity and viscosity.[1–4] Examining the material structures and behaviors of different ceramic bodies and CMCs under high speed collisions in several years the authors have understood the advantages of hetero-modulus and hetero-viscous complex material systems to absorb and dissipate the kinetic energy of objects during high speed collisions. Applying the rheo-mechanical principles the authors successfully developed a new family of hetero-modulus and hetero-viscous alumina matrix composite materials with extreme mechanical properties including dynamic strength. These new corundum-matrix composite materials reinforced with Si_2ON_2, Si_3N_4, SiAlON and AlN submicron and nanoparticles have excellent dynamic strength during collisions with high density metallic bodies with speeds about 1000 m/sec or more. At the same time in the alumina matrix composites can be observed a phase transformation of submicron and nanoparticles of alpha and beta silicone-nitride crystals into cubic c-Si_3N_4 diamond-like particles can be observed, when the high speed collision processes are taken place in vacuum or oxygen-free atmosphere.

Using the rheological principles and the energy engorgement by fractures, heating and melting of components the authors successfully developed several new hetero-modulus, hetero-viscous and hetero-plastic complex materials. These materials generally are based on ceramic matrixes and components having different melting temperatures and modules of elasticity from low values like carbon and light metals (Mg, Al, Ti, Si) up to very high values like boride, nitride and carbide ceramics. Analytical methods applied in this research were scanning electron microscopy, X-ray diffractions and energy dispersive spectrometry. Digital image analysis was applied to microscopy results to enhance the results of transformations.

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Effect of different steel binders on microstructural and mechanical properties of NbC-Fe cemented carbides prepared from fine NbC powder

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Keywords: fine NbC powder, cemented carbide, binder, tool steel, cubic carbide

WC-Co cemented carbides are materials with wide applications as tools due to their excellent mechanical properties like hardness and toughness. Due to the proven toxic nature of Co and WO3 in WC-Co cemented carbide, researches have been taking place during the last decades to substitute them with non- toxic materials. Reports show that NbC matrix cemented carbide can be a good candidate due to the non-toxic and not water soluble characteristic of Nb_2O_5.[1] Moreover, studies have shown improved elevated temperature mechanical and tribological properties of these materials.[2,3] The aim of this study was to analyze the effect of binder phase on the mechanical and microstructural properties of NbC-Fe base cemented carbides. Meanwhile the effect of adding TaC, VC, and Mo2C cubic carbides as particle growth inhibitors was also studied. For this mean, two grades of 316 L stainless steel and DIN 1.3207 high speed tool steel were selected as binder. Fine NbC powder (d50 = 0.8 μm) was mixed with 12 wt% of each grade and gas pressure assisted sintered for 1 h at 1460 °C. Microstructural and elemental mapping of the sintered parts were performed by scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). Mechanical properties, including Vickers hardness and indentation toughness were also assessed.

Results indicated that the binder phase can influence the mechanical and microstructural properties of the NbC-Fe base cemented carbide. Microstructural investigations showed a higher NbC particle growth rate with stainless steel as the binder. It was also evident that the addition of cubic carbides can greatly limit the NbC particle growth rate. Mechanical properties measurements indicated higher hardness values for the sample with high speed tool steel as binder. Moreover it could be observed that the addition of cubic carbides can greatly influence the mechanical properties due to the reduced NbC particle size inside the sample. A maximum hardness of 15.4 ± 0.8 GPa was measured for the sample with high speed tool steel as the binder and cubic carbides as particle growth inhibitors. A low fracture toughness of 2.6 ± 0.15 MPa.m1/2 was achieved for the same sample. It was evident from the microstructural investigations that the low fracture toughness is related to high density of pores inside the sample.

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Influence of particle arrangement during electrophoretic deposition to properties of alumina and zirconia ceramics

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Keywords: electrophoretic deposition, alumina, zirconia

Electrophoretic deposition is shaping method enabling preparation of ceramic material from stable suspension of ceramic particles by means of direct electric current.[1–3] The aim of the work was to identify an effect of the electric current magnitude on the particle arrangement, final microstructure and resulting mechanical properties. The alumina and zirconia layers were prepared by electrophoretic deposition from stable suspensions of alumina and zirconia ceramic powders having different particle size distribution functions. The stable alumina and zirconia suspension were prepared by dispersing of powders in isopropanol and stabilized with monochloracetic acid.[4,5] Recently, it was found that the real time dependence of particle deposition differs from the theoretical prediction for given electrical conditions.[6] By precise measurement of kinetics of the electrophoretic deposition the current electrophoretic mobility of the particles and corresponding amount of particles taking part in the deposition process were found. It was found that with decreasing the electrical current the electrophoretic mobility was increased but in contrast the amount of particles taking part in the deposition process was decreased. Also the green and fired densities of deposits depend on the electric current used for the electrophoretic deposition. At lower electric currents just the particles having high electrophoretic mobility and thus having high radiuses were deposited. The increasing velocity of particles under higher electrical currents also led to the deterioration of particle arrangement in the electrode and thus to the increasing of the pore sizes lowering final densities of deposits. These microstructural changes reflected in the hardness decrease of about

300HV5 in the case of alumina. The optimized process of the electrophoretic deposition of alumina and zirconia using isopropanolic suspensions stabilized by monochlor acetic acid allowed preparation of the laminate consisting of strongly bonded layers of certain thicknesses.

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Influence of machining and crack healing on the strength of a commercial silicon carbide ceramic

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Failure of brittle materials starts in general from defects which exist in the volume or on the surface of the specimens. Surface flaws, which are more dangerous than volume flaws, can be introduced by machining. They decrease the strength of specimens and components. This investigation compares two different ways to avoid surface defects and, as a consequence, increase the strength.

For the investigation disc shaped silicon carbide samples were machined with different machining conditions. As expected, it could be shown that a better (gentler) machining increases the strength. In order to heal the surface defects a sample of specimens was heat treated and then tested with the B3B-test. Microstructural investigations (SEM, FIB) reveal the formation of a thin glassy layer which heals the cracks on the surface if these are not too large.

It was observed that a better machining as well as annealing (depending on machining conditions and healing temperature, respectively) leads to a significant increase of strength (up to 250%) in the same amount.

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Safety performance evaluation of silicon carbide ceramics for accident tolerance fuel in hydrothermal exposure conditions

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Keywords: SiC, nuclear fuel, PBAT, TRISO, ATF

The recent events at the Fukushima Daiichi nuclear power plant in Japan highlighted the need for added safeguard, including fuels with enhanced accident tolerance that can delay or even prevent severe accidents. In this sense, the use of particle-based accident tolerant (PBAT) fuels is an alternative strategy for overcoming this issue by multiple silicon carbide (SiC) barriers such as SiC layer in TRISO and the dense SiC matrix of the ceramic capsules. The performance on high temperature oxidation of PBAT fuel is one of important factors for plant safety of nuclear reactors. In this work, safety performance evaluation of SiC ceramics for accident tolerance fuel (ATF) in hydrothermal exposure condition was performed at 1200 and1700 °C for ~25hr. PBAT fuel and monolithic SiC ceramics was fabricated by hot-pressing and normal pressureless sintering, respectively. After 25hr hydrothermal oxidation, some TRISO kernel in PBAT fuel were exposed and inner surface portion of PBAT fuel shows pore channel by permeated liquid phase through the grain boundary and junction. The high temperature oxidation resistance of SiC ceramics was dependent on the chemistry inside the grain structure, the additive composition and the additive content. More importantly, suppression of liquid phase formation by reaction between SiO_2 and junction part is ans essential factor for oxidation resistance performance of SiC ceramics. Detail data for oxidation behavior of SiC ceramic under hydrothermal exposure conditions will be presented.

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Measurement of residual stress caused by gallium-ion implantation from FIBing in alumina

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Keywords: focused ion beam, gallium ion implantation, residual stress, alumina, fracture toughness

Toughness measurements of the individual microstructural components of alumina, i.e. grains and grain boundaries, are indispensable to a full understanding of the mechanical properties of the bulk material. One method for making such measurements is to test microcantilever beams manufactured using focused ion beams (FIB) and including a notch at the chosen microstructural feature. However, residual stress caused by Ga-ion implantation at the notch root during FIBing is thought to influence the results in alumina, though to a lesser extent in some other ceramics.[1] To clarify the extent of this effect, the present study measures the implantation stresses in single crystal alumina and silicon by applying a combination of various methods such as beam curvature measurements in a dual-beam FIB. The effect of FIB accelerating voltage is also investigated. The implications of the results for microcantilever toughness measurements are described.

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Control of sintering of NiO/GDC porous ceramics by mechanical treatment of raw materials

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Keywords: NiO/GDC, mechanical treatment, sintering, control

Solid oxide electrolysis cells (SOEC) have a layered structure of dense solid electrolyte and porous electrode. Gadrinium doped ceria (GDC) is a typical solid electrolyte having good ionic conductivity and high relative density. Porous composites of GDC and Ni, which is converted from NiO, are generally used because the electrode requires ionic and electron conductivity. In order to fabricate the layered structure, it is necessary to sinter layered powder compacts at the same time. However, difference in the sintering shrinkage behavior of the powder compact layers resulted in deformation and fracture of the products after sintering. In this work, sintering shrinkage behavior of NiO/GDC porous ceramics was controlled by restricting contact between NiO particles using the GDC coated NiO composite particles. The composite particles were prepared by mechanical treatment technique. A powder mixture prepared by ball-milling was used as a reference. SEM images of the powder mixture prepared by mechanical treatment showed that smaller GDC particles existed on a larger NiO particle. In addition, specific surface area of the composite particles was smaller than that before mechanical treatment, resulting from jointing of GDC particles on NiO particles. Microstructural observation of powder compacts indicated that NiO particles are successfully separated by GDC particles when the NiO/GDC composite particles were used. Sintering shrinkage of the powder compact of the mixture particles prepared by ball-milling was started at 800 °C, which is almost the same as that of a powder compact of raw NiO particles. This indicated that initial sintering of the powder compact using ball-milled powder was dominated by sintering of NiO. On the other hand, sintering starting temperature and sinter-

ing shrinkage behavior of the powder compact using the composite particles agreed with those of raw GDC particles. This result indicated that GDC particles in the powder compact using the NiO/GDC composite particles restricted contact NiO particles, and they controlled the sintering behavior of NiO/GDC porous ceramics. Furthermore, the dominant sintering mechanism was also confirmed by apparent activation energy calculated by Arrhenius plots based on MSC theory. Consequently, it was shown that mechanical treatment of raw materials to make use of composite particles was effective in control of sintering of NiO/GDC porous ceramics.

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Effect of residual stress in FRP stage on liquid silicon infiltrated C/C-SiC composites

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Keywords: residual stress, LSI, composites

Fiber reinforced ceramic matrix composite materials are most promising materials in aerospace and high temperature environmental application because of its high thermal and structural stability. In this study, LSI (Liquid silicon infiltration) process was applied to fabricate ceramic matrix composite. Generally, porous C/C preform is prepared from FRP material by carbonizing and transversal cracks are formed that acts as a path for liquid silicon infiltration. Various residual stress in FRP material were introduced by fiber volume fraction control and measured by drilling method. During carbonization step, most of obtained cracks were transversal segment cracks in low residual stressed FRP specimen. However, not only segment cracks but also fiber and matrix interfacial cracks were occurred in high residual stress introduced specimen. The relation between residual stress in FRP material and carbonized composites was investigated with finite element analysis. Higher residual stress in FRP induced fiber matrix debonding and it caused silicon infiltration into debonded crack during LSI process that weaken reinforced carbon fiber. For evaluation of residual stress effect in LSIed composite, density, porosity and mechanical properties were investigated including SEM observation for microstructure.

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CMAS and hot corrosion resistance behavior of functionally graded Al_2O_3/CYSZ thermal barrier coatings

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Keywords: hot corrosion, CMAS, Al_2O_3, CYSZ, thermal barrier coating, functionally graded, thermal cycling performance

Hot corrosion salts and CMAS powders are main destructive factors in thermal barrier coatings. Low quality fuel that is used as energy producer in combustors releases hot corrosion molten salts on gas turbine engine parts.[1] CMAS powders that are taken from air shorten maintenance time of TBCs.[2]

In this study, alumina/CYSZ powders were produced by APS with functionally graded design as TBC materials. Functionally graded eight layered specimen showed better properties on thermal cycle, adhesion and thermal shock resistance in the previous study. Therefore, functionally graded eight layered TBC specimen was chosen to evaluate hot corrosion and CMAS attack resistance at high temperature conditions. Hot corrosion and CMAS powders were used together during 1 hr. heating and cooling at the same time, moreover, specimens were cycled with 1 min. heating and 1 min. air cooling under static heat source CO_2 laser. Microstructure and XRD were evaluated to understand effects of hot corrosion and CMAS attack on TBCs.

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Effect of graphene platelets addition on microstructure and mechanical properties of boron carbide ceramic composites

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Keywords: boron carbide, graphene platelets, microstructure, mechanical properties, wear behaviour

Boron carbide is an interesting material because of its excellent hardness, low density, high melting point ~2450 °C, and good chemical and wear resistance. For applications of B_4C materials under demanding working conditions, an improvement of reliability, tribological behaviour, and mechanical properties is required. The unique structural, electrical, mechanical and thermal properties of graphene combined with its low density make it an ideal candidate as reinforcement in ceramic matrix. In this work, the influence of the graphene platelets addition on the microstructure development, mechanical (hardness, bending strength, fracture toughness, Elastic modulus), tribological properties (coefficient of friction, wear rate, wear mechanisms), and electrical conductivity of B_4C/ GPLs composites has been investigated. SEM, TEM, and FIB microscopy have been used for microstructural analyses, characterization of fracture origins, fractography, and toughening mechanisms. To analyse the worn surfaces and wear behaviour after tribological tests, the cross sections using focus ion beam have been prepared. Almost fully dense boron carbide composites (with grain size in the range of 2–4.5 µm) with GPLs addition up to 6 wt. % were prepared by hot pressing at 2100 °C/1 h. During the sintering, only GPLs have been used as sintering additives. Multilayer GPLs were well distributed in B_4C matrix, located at the B_4C/B_4C grain boundaries. The hardness and Young's modulus of prepared ceramics significantly decreased from 30.3 to 18.2 GPa and from 411 to 271 GPa with the higher amount of GPLs, respectively. The highest fracture toughness of 4.48 $MPa.m^{1/2}$ was achieved at 6 wt. % of GPLs addition, which was ~50% higher than the K_{IC} value of reference material. The toughening mechanisms in all B_4C/GPLs composites were similar in the form of crack deflection, crack branching, crack bridging, and graphene sheet pull-out, only the frequency of their occurrence during crack propagation and their effectiveness in the toughening process are different. A significant improvement of electrical conductivity around two orders of magnitude up to ~1500 S/m was noticed. The coefficient of friction for composites were similar (0.5–0.6), however the wear rate significantly decreased ~77% in the case of B_4C+6 wt.% GPLs when compared to reference material at a load of 5 N, and ~60% at a load of 50 N. The main wear mechanisms were in the form of abrasion and tribochemical reactions.

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Obtaining of nano composites via alum-thermal and nitrogen processes in the SiC-Si_3N_4-ALN-AL_2O_3-$SiO_{2.}$ system

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Keywords: alum-thermal process, nitrogen medium, SiAlON, composites

SiALON-s are solid metal oxide solutions in nitrides. Area of their presence is considered in four-component system - Si_3N_4-ALN-AL_2O_3-$SiO_{2.}$

In the present paper SiALON-containing nano-composite was obtained through alum-thermal process on the base of kaolin and aluminum nano-powder in the nitrogen medium, by the reactive baking method. The advantage of this method is that compounds, which are newly formed thanks to interaction going on at thermal treatment: Si_3N_4, Si, AlN are active, which contributes to SiALON formation at relatively low temperature, at 1250–1300 °C. It is evident that inculcation of α - Al_2O_3 and ALN in crystal skeleton of ß-Si_3N_4 is easier since at this temperature interval crystal skeleton of Si_3N_4 is still in the process of formation.

It should also be stated that strength and wear resistance of SiALONs increase in their presence in silicium carbamide and corundum-containing composites.

The paper offers processes of formation of SiC-SiAlON and Al_2O_3-SiAlON composites and their physical and technical properties.

Phase composition of the composites was studied by X-ray diffraction method, while the structure was studied by the use of optic and electron microscope. Obtained materials are used in protecting jackets of thermo couples used for melted metal temperature measuring (18–20 measuring) and for constructions used for placing objects in factory furnaces.

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Surface modification of titanium with silicon nitride

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Keywords: silicon nitride, titanium, coating, diffusion, hardness

Titanium (Ti) and titanium alloys have been used in biomedical and aerospace industry due to their combination of properties such as high corrosion resistance, high specific strength and relativity low density. However, relatively low wear resistance limits the potential applications of these engineering alloys. Therefore, in this study, the surface of titanium (Grade 2) is coated with silicon nitride via three different techniques to obtain hard surface coating layer. Initially, the surface of titanium is coated with a slurry containing Silicon Nitride (Si_3N_4) powder using drop casting method and heat treatment for diffusion bonding is conducted under high purity Argon atmosphere. In the second method, Ti surface is nitrided under high purity nitrogen gas which is followed by pack siliconization process to obtain *in-situ* Si_3N_4 layer. In the last technique, Si_3N_4 layer is formed by applying pack siliconization and nitriding as primary and final steps, respectively. The temperature for diffusion bonding, nitriding and siliconization processes are maintained above α/β transition of titanium. The type and formation of different phases in the diffusion layer between Ti and Si_3N_4 is examined by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The change in hardness through thickness is measured by Micro hardness Testing.

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Effect of carbon content on fluoride adsorption of bone char

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Keywords: bone char, carbon content, fluoride removal

Bone char is obtained by calcination of bone from food industries under anaerobic condition. Bone consists of nano-scaled hydroxyapatite (HA) particle and fibrous collagen, and translates well- crystalline HA and carbonized collagen by calcination. One of the usage of bone char is as adsorbent of fluoride in polluted water such as ground water. Catching fluoride by bone char have been considered ion-exchange and/or dissolve-precipitation[1,2] of HA in it. In this study, effect of carbon content in bone char on adsorption property was investigated.

Bone char was prepared from chicken wing by calcination at 500 °C[3] for various periods. Crystallinity of HA was analysed by powder X-ray diffraction (XRD), and did not observed remarkable change by calcination at this temperature. Carbon content was calculated by weight change on combustion of carbon content that measured by thermal gravimetric-differential thermal analyzer (TG-DTA). From result of TG-DTA analysis, carbon amount did not change by calcination for 6 to 24 hours. Removal (adsorption) amount of fluoride was estimated by mixing an aqueous solution containing 10 mg/L of fluoride ion and various amounts of bone char for 24 hours. After treatment, residual content of fluoride in the aqueous phase was analyzed by ion selective electrode (ISE). From result of the determination, removal amount and equilibrium concentration of fluoride was calculated. From results of fluoride removal, removal amount of fluoride of bone char calcinated for 24 hours was remarkably decreased. From these results, removal property of bone char seems to affect by not carbon amount but chemical characteristics of carbon such as crystallinity or polymerization. Characterization of carbon in the bone char from viewpoint of material science is expected novel information for improvement of removal property of it.

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Assembly of transparent polycrystalline ER:YAG ceramics by SPS

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Keywords: assembling SPS ceramics

Today, transparent polycrystalline ceramics are widely used: they find applications in various fields like electronics, biology or optical systems. Our subject is the laser developed at the ISL is a Solid State Heat-Capacity Laser (SSHCL[1]): in that case, the gain medium is an Erbium-doped YAG single crystal (Er:YAG) exhibiting an emission at 1.6 µm so-called «eye-safe». The main improvements expected for such laser systems concern its maximum power of solicitation and its lasing time, both limited by an accumulation of heat in the laser cavity during use.[1] Ways to solve these issues are intensively explored through the replacement of single crystal by polycrystalline ceramics. This approach relies on i) their tunable fine microstructure allowing to reach better thermomechanical properties than the single crystals and ii) the possibilities that offers powder metallurgy in terms of controlled doping profile, which leads to a better distribution of heat in the material, and low production costs thanks to fast synthesis and low matter waste compared to single crystals synthesis.

In order to integrate the polycrystalline ceramic in a SSHC laser, one must focus on two aspects: i) make a ceramic with dimensions compatible with ISL SSHCL cavity, and ii) the development of doping gradient ceramics, allowing a better distribution of heat in the solid medium.

For satisfying these two conditions, SPS process is considered to be a promising way since it allows to both to fully densify ceramics and to assemble dense ceramics together. This approach was considered to produce a large piece of ceramic with a suitable profile doping. Attention focused on the optimisation of surface preparation and SPS processing parameters to reach high transmittance and avoid any defect at the interface. Further investigations are currently carried out by SEM to qualify the interface between the two pieces.

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Thermal durability test of suspension precursor plasma sprayed lanthanum-gadolinium zirconate/YSZ tBC

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Keywords: thermal barrier coating, plasma spray coating, thermal durability

Heat insulation by ceramic coatings are indispensable for protecting nickel based alloy material of hot gas parts in the gas turbine. When fuel is burned with compressed air, temperatures are known to rise up to 1500 °C, therefore, thermal resistant ceramics such as low thermally conductible materials are needed to endure severe hot temperature. On the other hand, high mechanical properties against wear and damages are also required for thermal barrier coatings. Therefore, multi-layers consisting of low thermally conductible material and YSZ layers are maybe a solution to protect the sub-alloy at both high temperature condition and wear resistant condition. In this study (La, Gd)$_2$Zr$_2$O$_7$/YSZ thermal barrier coatings are deposited by suspension precursor plasma spray(SPPS) on the bondcoat/Ni superalloys to insulate high temperature effectively by pyrochlore-fluorite structure and resist against wear and damage owing to YSZ material. The compositions of multi-layered coatings from La$_2$O$_3$, Gd$_2$O$_3$

and Y_2O_3 doped ZrO_2 and the thickness of each layer are controlled by processing parameters during SPPS. Thermal cycling tests are conducted at 1275 °C for 1hr until interface delamination occurs during repetitive cycling. Thermal fatigue tests are also conducted to test thermal durability under 1350 °C of top part and 900 °C or room temperature of bottom part. The cycles are conducted to 1,100 cycles. Ball indentation tests are conducted before and after thermal fatigue test. Tungsten carbide ball with a radius of 3.18 mm is used for obtaining indentation load-displacement curves. Relative hardness and stiffness changes will be discussed from load-displacement curves. The results indicates that the $(La,Gd)_2Zr_2O_7$/YSZ multi-layers have good thermal durability and desirable for high damage resistance than commercial YSZ material.

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Reaction-bonded silicon carbide for fusion applications

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Keywords: fusion, melt infiltration, silicon carbide, micromechanics

Silicon carbide has potential applications in the breeder blanket of fusion reactors, where its chemical inertness, low neutron cross-section, radiation tolerance, and low activation are especially useful. The main challenge currently facing existing forms of "nuclear grade" SiC is processing them reliably on a large enough scale for making components with minimal joining. Reaction-bonding is a commercial processing technique capable of making large components reliably and precisely to near net shapes. Early work suggested that residual stress between SiC and silicon phases caused by irradiation swelling leads to microcracking and failure.[1]

Novel forms of RBSC have been processed with low-activation silicides and fine grain structure aimed at reducing residual stresses in RBSC caused by radiation-induced swelling. These are investigated using micromechanical techniques, ion implantation, and Raman microscopy.

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Preparation of reaction-bonded Si-C-N porous ceramics by foaming

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Preparation of the reaction-bonded Si-C-N porous ceramics was investigated using foaming and nitriding. Porous Si-C-N ceramics were sintered at 1500–1650 °C under nitrogen atmosphere by silicon carbide and silicon powders as the main raw materials, FS60 as vesicant, Y_2O_3 as sintering additive, and HT as foaming agents. The influence of the different sizes Si powders (d<74μm, 1# and d<9μm, 2#)and sintering temperatures were studied. The phases, microstructure and mechanical property were characterized by XRD, SEM, TEM and compressive strength tests. The results demonstrated that the porous Si-C-N ceramics were successfully obtained with porosity from 47% to 70%, compressive strength from 6.5 MPa to 37.5 MPa, and multi-level vias (pore size from 1 μm to 1000 μm). 1# sample used Si powders (d<74μm) as porosity ceramics was optimized.

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Microstructure and properties of pressureless sintered graphene nanoplatelet/3YTZP zirconia composites

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Keywords: graphenenanoplatelets, 3YTZP, pressureless sintering, microstructure, electrical conductivity

Incorporation of carbon nanostructures as reinforcement phase for ceramics has been an attractive topic in the recent decades. More recently, two-dimensional nanosized carbon materials, such as graphene nanoplatelets (GNP), multilayered graphene (MLG) or few layer graphene (FLG) have emerged as an alternative to carbon nanotubes or carbon nanofibers, since remarkable properties have been reported for ceramic composites incorporating these 2D nanomaterials[1,2]. Typically, these composites are prepared by a colloidal or wet powder mixing procedure and a pressure assisted sintering technique, being the most common used techniques hot pressing (HP) and spark plasma sintering (SPS). However, despite the potential interest of the pressureless sintering (PLS) of these composites, the published studies up to date are scarce.

The aim of this work is the fabrication and study of 3YTZP composites reinforced with GNPs. Composite powder was prepared by wet powder mixing and pressureless sintered in argon flow at temperatures between 1200–1500 ºC.The effects of GNP content and processing conditions on the densification, microstructure, hardness and electrical conductivity of the composites were analysed and discussed.

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Organically-modified ceramic membranes for solvent nanofiltration

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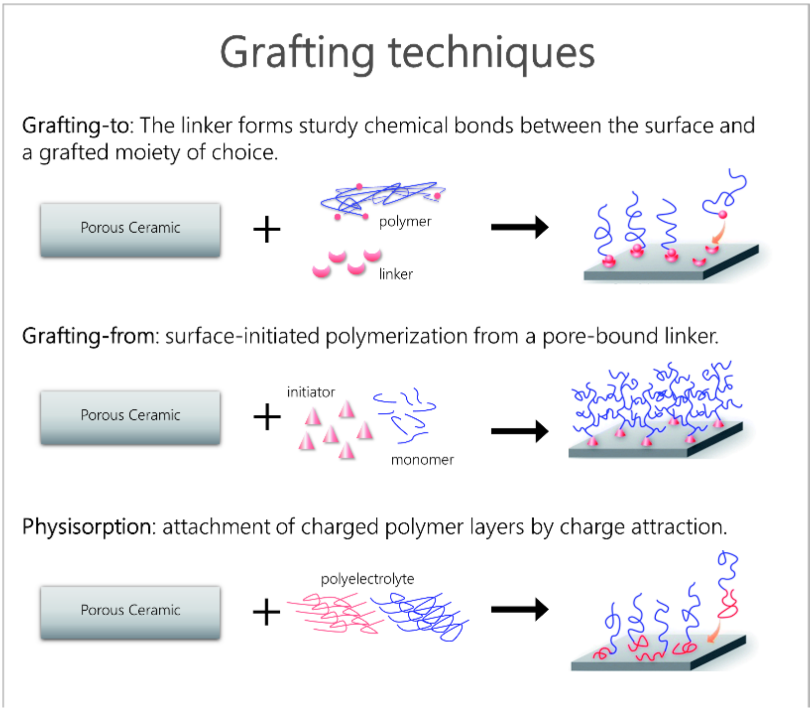
Highlights

1. An overview of different grafting techniques will be presented.
2. A variety of polymers can be attached onto the pore surface of ceramic membranes.

Separation of solvents by membranes is a potential key enabling technique for many chemical processes. State-of-the art polymeric or ceramic membranes do not always meet stability and/or selectivity demands at process-relevant conditions like separation/purification of harsh organic solvents and operations at high temperatures or pressures. In order to fulfil these operational requirements a concept is developed, based on mesoporous (pore size 5–10 nm) ceramic membranes, as a non-swelling and non-compactable, rigid material, acting as a support, on which polymer materials are immobilized; i.e. covalently or electrostatically bonded. In this way the pore size and surface chemistry of membranes can be adjusted for any specific separation application by varying the composition/structure of the polymer.

This functionalization of ceramic membranes is viable through grafting. Grafting is a process in which a specific organic substance is chemically bonded to an inorganic substrate. The OH-groups of the oxide ceramic surface will react with the hydrolysable groups of the to-be grafted organic moiety to produce a stable bond, resulting in a permanent modification of ceramic membranes.

An overview will be presented of the different grafting techniques, summarized in Fig. 1. Some performance results will be given as well.



Grafting techniques

Grafting-to: The linker forms sturdy chemical bonds between the surface and a grafted moiety of choice.

Grafting-from: surface-initiated polymerization from a pore-bound linker.

Physisorption: attachment of charged polymer layers by charge attraction.

Fig. 1. Three ways of grafting

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Spark plasma sintering of alumina ceramic reinforced with WC-Co

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Keywords: alumina, tungsten carbide cobalt, spark plasma sintering, mechanical properties, cutting tools

Alumina (Al_2O_3) and cemented tungsten carbide cobalt (WC-Co) are ceramic materials successfully used for metal cutting tools because they provide good strength, hardness and durability. Al_2O_3 has poor toughness and WC-Co do not allow high speed cutting and can easily deform due to heat generated while cutting. Hence, the combination of Al_2O_3 and WC-Co becomes a matter of interest. However, the combination of Al_2O_3 and WC-Co has not been extensively studied and not clearly understood. As a result, the mixture of Al_2O_3 matrix with WC-Co reinforcement was sintered and its mechanical properties investigated in this report. The composites of 85–95 wt% Al_2O_3 and particle reinforcement containing varying ratios of WC-Co were prepared by conventional powder processing and the powder mixtures were sintered using spark plasma sintering between 1400 and 1600 °C in an argon atmosphere. Physical and mechanical properties of the composites, such as density, hardness and fracture toughness including microstructure were investigated. It was found that the composites of 98–99.9% relative density were achieved after sintering at 1600 °C for the WC-12Co composites. The prepared Al_2O_3/WC-Co composites provided both hardness and fracture toughness between 17–18 GPa and 5–8 MPa.$m^{0.5}$ respectively, which are still appropriate for cutting tool applications.

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Novel silicon oxycarbide-carbon nanofiber materials with high electrical and thermal properties

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Keywords: silicon oxicarbide, ceramic composite, Spark Plasma Sintering, electrical conductivity, thermal conductivity

Dense bulk silicon oxycarbide-carbon nanofiber (SiOC-CNF) composites have been obtained by Spark Plasma Sintering (SPS) without the degradation of the carbon reinforcement. SiOC-CNF mixtures with an increasing CNF content ranging from 0.5% to 10% are used. The application of this non-conventional sintering route which simultaneously applies high electric current and uniaxial pressure allows obtaining extremely fast heating rates reducing both sintering temperature and holding times and as consequence dense composites whit novel properties are obtained. The density of the SiOC-CNF derived materials is similar independently of the CNF content and it is near 2.2 g/cm^3 in all the cases. The electrical conductivity is increased by five orders of magnitude (up to $1\times10^{+2}$ S/m) and the thermal conductivity also increases by 40% (up to 2.0 W/mK) when compared to SiOC. These changes must be related with the formation nanodomains of β-SiC and carbon within the glassy matrix as consequence of the sintering conditions and the carbon reinforcement.

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Transport phenomena through grafted ceramics for OSN

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Unlike their polymeric counterparts, ceramic membranes benefit from a rigid architecture which does not swell in the presence of organic solvents. However, their hydrophilic surfaces makes them ill-suited to organic solvent nanofiltration. Grafting short chains of PDMS not only shrinks the pore to the desired size but also renders them suitable for organic solvent nanofiltration (OSN). These membranes exhibit particular transport phenomena due to the localized swelling of the PDMS. The degree of swelling is solvent-dependent, which impacts both the permeability and retention of the membrane.[1]

We have examined how solvent mixtures permeate and solutes are retained across PDMS-grafted gamma-alumina selective layers supported on alpha-alumina. Four types of membranes were fabricated: two initial pore sizes of alumina, 5 nm and 9 nm, each grafted with two sizes of PDMS, either a degree of polymerization n = 10 or n = 20. A range of solvents and their mixtures were tested, from ethanol to toluene, in a cross-flow setup from pressures 10 to 40 bar. Characterization by permporometry and contact angle, as well as retention and permeability measurements indicated a membrane well suited to OSN applications. Parameters such as the size of the initial pore, swollen pore and solute are inputs to a modified Spiegler Kedem model to predict the performance of these grafted ceramic membranes for OSN. By allowing the diffusion (but not convection) of solutes through the swollen graft, we find that predictions obtained through the Spiegler Kedem model agree with the experimental data.[1]

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Microstructure and mechanical properties of *in-situ* (Ti,W)C particles reinforcing iron

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Keywords: transition metal carbides, metal matrix composite, mechanical properties, nanoindentation

MC carbides are well known hard phases that are used to give strength, wear and corrosion resistance to steels or steel matrix composites. In steel, MC carbides are commonly present as small (micron-sized) particles. The most important and commercially used MC carbide particles are WC and TiC. The development of cubic (Ti,W)C solid solutions, possible in this system with up to 50%W, might further improve the mechanical performance of these reinforcing particles, potentially overcoming some of the application limits of TiC or Ti(CN)-based cermets. Recent advances in processing carbides have offered a way of producing such materials; however, no comprehensive investigation of this system has yet been carried out and there is still a significant lack of knowledge about their intrinsic mechanical behaviour.

Results will be presented from an investigation of the subject, which comprises two main thrusts: (i) to synthesize *in situ* (Ti,W)C particles reinforced iron matrix where the tungsten exchange in the monocarbide TiC phase can be tailored and (ii) to evaluate the mechanical properties of hard particles by conducting small scale mechanical tests directly on particles within the microstructure. In particular, high purity and homogeneous $(Ti_xW_{1-x})C$ particles have been grown *in-situ* during solidification within an iron matrix by arc-melting. Mechanical properties (elastic modulus and hardness) of $(Ti_xW_{1-x})C$ particles, exposed on the polished surface of the iron matrix, are probed by nanoindentation testing. The variation of composite microstructure and carbide morphology as well as that of the elastic modulus and hardness of the particles is then quantified as a function of the Ti/W ratio.

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Gigantic grain growth in boron carbide ceramics during spark plasma sintering

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In the ceramic fields, research on ultra-high-temperature ceramics is a hot topic nowadays. Boron carbide deserves a particular attention since it is one of the hardest material in the Nature.

Sintering of boron carbide has been an overwhelming task until recently, due to the very low diffusion coefficients and the extremely high temperatures required to this end. In this regard, spark plasma sintering has revealed as a crucial technique for fully-dense preparation of fine-grained boron carbide ceramics.

The study of the mechanical and microstructural properties is now available. This presentation is concentrated on the grain growth kinetics at very high temperatures, typically over 1800 ºC, during SPS sintering. It will be shown that grain growth does not follow the classical laws because growth kinetics is drastically affected by the presence of the electrical field as well as singular microstructural evolution of boron carbide grains.

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Effect of zirconia surface treatments on friction coefficient and surface properties

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Keywords: zirconia, surface treatment, roughness, friction coefficient

Zirconia is a widely used ceramic material in biomedical field, mainly because of its high mechanical properties and biocompatibility. However, zirconia is chemically inert and it does not allow to naturally form a direct bond with bone[1]. It has been already shown that surface roughness plays an important role in cell response[2]. Thus, several treatments such as sand-blasting, etching and laser irradiation were used to enhance the biological performance of zirconia surface[1]. Among these, laser technology has been extensively used as there is no risk for surface contamination, like in the case of blasting and etching treatments, and also there is no change in the bulk properties of the material[1,3].

The aim of this study was to investigate the surface modification of Yttria-tetragonal zirconia polycristals (3Y-TZP) using different treatments, such as sandblasting, etching and laser irradiation by a Nd:YAG. Sandblasting treatment was performed with 100-µm alumina particles and etching treatment was accomplished using hydrofluoric acid.

To determine both the static and dynamic coefficient of friction a reciprocating pin-on-plate tribometer (Bruker-UMT-2, USA) was used. The plates (4×16×x20) were bones that were cut from a femur of bovine. The pins were the studied materials. The bone plates were mounted in an acrylic electrochemical cell attached to the tribometer. The bones were always hydrated with a Phosphate Buffered Saline (PBS) fluid. The tribological parameters were 150 N normal load, at a frequency of 1Hz, and the total stroke length 5 mm.

The surfaces were inspected by Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS). Roughness was measured using a surface profilometer (Surftest SJ 201, Mitutoyo, Tokyo, Japan). Wettability characteristics were also evaluated. Results suggest that the investigated surface treatments have a great influence on friction behavior of zirconia 3Y-TZP. Also, it is shown that the wettability characteristics of the zirconia 3Y-TZP can be improved by laser surface treatment.

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Effect of freezing temperature on microstructure and mechanical properties of porous Si_3N_4 ceramics produced by freeze casting

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Keywords: freeze casting, freezing temperature, porous silicon nitride, unidirectional porosity

Porous silicon nitride ceramics have been widely used in industrial applications, such as high-temperature gas filters and separation membranes because of its excellent mechanical properties at both room and elevated temperatures, good oxidation resistance, good thermal shock resistance, thermal–chemical corrosion resistance as well as lightweight structural materials[1–4]. For practical applications, these properties are related to the pore structure (shape, morphology, orientation, porosity, etc.). The porous ceramics from freeze casting do not have ultra-high porosity and have large interconnection and dense ceramic networks that are necessary to enhance its mechanical properties. In addition, freeze casting is able to easily control the pore morphology, porosity, microstructure as well as the mechanical properties of porous ceramics by adjusting the concentration of ceramic slurry, vehicle phase, freezing rate and freezing temperature[3] such as –18, –198[3], –10, –60 °C[6] and sintering conditions[2,7]. However, as we know, the reports on the microstructural control and mechanical properties of porous silicon nitride ceramics fabricated by freeze casting are very scarce. The purpose of this study is to illustrate the influence of freezing temperature on the microstructure and mechanical properties of porous Si3N4 ceramics produced by freeze casting[8].

In this research, porous silicon nitride ceramics were fabricated by freeze-casting process at different freezing temperatures to obtain different pore morphology. The microstructure and mechanical strength of porous Si_3N_4 were investigated[3]. Slurries were prepared by mixing distilled water. The suspensions consist of solid loading 35vol%. Slurries were ball-milled for 24 h and de-aired by stirring in a vacuum desiccator. The resultant slurries were then poured into molds immersed in liquid nitrogen (–196 °C) and freezer (–5 °C). Immediately after casting, the ice crystals grow unidirectionally. After the frozen samples were completely dried under special sublimation cycles for 3 days, the green compacts were placed in a graphite crucible with a silicon nitride-based powder bed and sintered in a graphite resistance furnace at 1650 °C for 4 h. Samples were kept in furnace to get cool down. The densities of the samples were calculated from the dimensions and weight of the samples.

Crystalline phases of the sintered porous Si3N4 ceramics were characterized by X-ray diffraction (XRD). Quantitative analysis of αand β-Si3N4 phase content was determined by comparing the peak intensity ratios[9]. The microstructure of the cross section was observed by scanning electron microscopy (SEM). Flexural strength measured in air at room temperature. Although both samples have same density and α and β-Si_3N_4 phase content and porosity percentage, they have different flexural strength. Freezing samples in freezer contains large pores interconnected with dendritic microstructure, but freezing samples in liquid nitrogen has fine pores interconnected with columnal microstructure. Pore shape and size and wall thickness are effective on flexural Strength, in away that freezing samples in liquid nitrogen and freezer has strength of 81.74 and 39.92MPa, respectively.

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Reactivity of dicalcium phosphate dihydrate with various fluoride compounds

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Keywords: calcium phosphate, fluoride, soil pollution

Remediation of soil by fluoride compound is important environmental issue because of fluoride in the polluted soil affect health impact to surrounding ground water for drinking water. Mineralization and stabilization of fluoride in the polluted soil is one of the candidates. In previous study, we have appeared that transform reaction of dicalcium phosphate dihydrate (DCPD) is applicable to stabilization of fluoride in the polluted soil[1] for long term over 2 years[2]. However, stabilization amount of fluoride by addition DCPD was different on various sites. We have assumed that this difference of reactivity of DCPD with fluoride in the polluted soil depend on chemical formation of fluoride such as mobile (soluble), residual (insoluble) and exchangeable, etc.

In this study, reactivity of DCPD with various fluoride compounds in an aqueous solution. We selected calcium fluoride as residual fluoride content in the polluted soil. Calcium fluoride used in this study was sludge from wastewater treatment on the assumption of polluted soil in industrial sites. In previous study, it was appeared that DCPD do not react fluoride ion directly but form nano-scaled precursor on surface of the DCPD particles. To improve reactivity of the DCPD, DCPD was pre-treated and induced the nano-scaled precursor[1] on it. The DCPD was mixed with the calcium fluoride and ultra-pure water, and reacted for 24 hours at room temperature. After reaction, fluoride concentration in the solution was analysed by ion selective electrode and ion meter. By using the DCPD, fluoride release from dissolution of the calcium fluoride was successfully inhibited. From result of powder X-ray diffraction analysis of obtained solid phase, it was appeared that the calcium fluoride was transformed to stable flouraptite (FAp) by reaction of the DCPD with fluoride ion from calcium fluoride in gradually. From these result, addition of DCPD is applicable to immobilize and transform stable fluoride residual in the polluted soil to form of stable mineral, FAp.

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High temperature erosion behavior of max phase (Ti_3SiC_2) reinforced nickel composites

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Keywords: MAX phases, Ti_3SiC_2, erosion, oxidation, composites

MAX phases have attracted considerable attention in recent years due to their unique set of properties that may enable them to bridge the gap between metals and ceramics. Ti_3SiC_2 is one of the most promising MAX phases for elevated temperature applications due to its low density, high temperature strength, and relatively high oxidation resistance below 1100 °C. These properties, along with the inherent toughness and damage tolerance endowed by the intrinsic nanolaminate structures present in MAX phases makes Ti_3SiC_2 an ideal reinforcement for high temperature metals and alloys, such as Ni. In this study, 10 vol. % of Ti_3SiC_2 MAX phase particulates are used to reinforce a Ni matrix composite (Ni-MAX). The erosion behavior of Ni-MAX is evaluated at room temperature (RT) and at high temperature (~1000 °C) using 50 µm Al_2O_3 particles as the erodent media. Particle impingement angles are varied from 30° to 90°. Erosion scars are analysed using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), x-ray diffraction (XRD), and focused ion beam (FIB) subsurface cross-sectioning in order to assess erosion mechanisms, damage modes, and possible chemical reactions. Erosion performance and behavior of Ni-MAX composites is compared with that of pure Ni in order to gauge the effectiveness of utilizing MAX phase reinforcements for enhanced erosion resistance at RT and ~1000 °C.

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Irradiation of ceramics based on titanium, zirconium, and hafnium nitrides with high-energy xenon ions

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Keywords: titanium nitride, zirconium nitride, hafnium nitride, ceramics, oxidative constructing, irradiation

The purpose of this work is to assess the structural and morphological changes produced in Ti, Zr, and Hf nitrides by irradiation with high-energy xenon ions. Titanium was nitrided at 1700 °C, and zirconium and hafnium at 2000 °C for 60 min. The starting materials used were ribbons 60 mm in length and 3.0 × 0.5 mm in cross section. Samples of the Ti, Zr, and Hf nitrides were irradiated with 167-MeV $^{+24}Xe^{136}$ ions to a fluence of 5.3×10^{14} cm^{-2} at a temperature of 20–25 °C for a total of ten days. The use of xenon ions with this energy, which are not radioactive, makes it possible to simulate the formation of uranium fission fragments.

Irradiation produced no changes in the phase composition and lattice parameter of the nitrides.

Irradiation of titanium and hafnium nitrides leads to the formation of nano- and micropores in the surface layer of the samples. The surface layer of zirconium nitride samples contains nanopores both before and after irradiation. The presence of pores in the unirradiated ZrN_x samples probably ensures the possibility of structural relaxation without further pore formation under irradiation. The pore size characteristic of irradiated ZrN_x is greater than that of the unirradiated material. High-resolution TEM of the irradiated ZrN_x samples revealed local crystal structure distortions unrelated to dislocations and attributable to the impact of high-energy xenon ions.

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Comparison of the properties of un-seeded and seeded alumina powders

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Keywords: α-Al_2O_3, Sol-gel, seeding

Alumina (Al_2O_3) is a widely used structural ceramic due to its high compression strength, hardness, chemical stability and wear resistance. Sol-gel is an effective way to obtain alumina powders with high purity at low temperatures.[1–4] From our previous studies, it was found out that sol-gel derived alumina powders used as a component of a composite material (alumina-hydroxyapatite) did not show sufficient mechanical strength.[3] Therefore, in this study it was aimed to enhance the compression strength of alumina by applying the seeding approach.[1,2,4] α-Al_2O_3 seeding enables to control the nucleation and growth mechanism of alumina grains during hydrolysis and peptization process.[1,2,4] Aluminium isopropoxide (AIP, ($Al(OC_3H_7)$), Aldrich $\geq$ 98%), the starting material, was hydrolysed at 90 °C by employing a heating mantle with magnetic stirrer. At this point, a novel principle was followed; the seeding agent, α-Al_2O_3 (Merck, 0.063–0.2 mm), was mixed with the starting precursor and added together to the distilled water to be hydrolysed. In this way, it was tried to create protentional nucleation areas in the boehmite (AlOOH) sol. In order to compare the effect of seeding on the properties of sol-gel derived alumina powders, un-seeded and wt.10% of AIP seeded samples were prepared. 40 ml HCl (Merck, 37%) was used as peptizer agent to accelerate the hydrolysis reactions. After hydrolysis and peptization steps, partially opaque boehmite solution was obtained. Un-seeded and seeded samples were gelated at 110 °C for 6 h and then heat treated at 1600 °C for 2 h with a 10 °C/min heating and cooling rate. Finally, irregular shaped alumina powders were produced and these powders were ground manually utilizing a mortar and pestle. Cylindrical pellets were formed from the ground powders by using a hydraulic press and stainless steel moulds. The pellets were sintered at 1600 °C for 1 h. XRD, FTIR, SEM-EDS analyses were carried out for the powder samples while bulk density, % apparent porosity and compression strength determinations were performed for the sintered pellets.

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Characterization of tungsten boride – tungsten disilicide composites fabricated by mechanical alloying and pressureless sinterıng

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Keywords: tungsten boride, tungsten silicide, composite, mechanical alloying, pressureless sintering

Tungsten boride (WB) has a potential for industrial applications at extreme environmental conditions amongst transition metal borides due to exhibiting interesting properties such as high melting point, high hardness, high abrasion resistance, chemical inertness, magnetic and electrical properties and good thermal shock resistance.[1–3] Tungsten disilicide (WSi_2) can be a good candidate as a reinforcement material thanks to its abrasive/adhesive wear resistance and oxidation resistance.[4,5]

In this study, WB composites with various amounts of WSi_2 addition were produced by high energy ball milling, cold pressing and pressureless sintering. Ball milling experiments were conducted in ethanol and Ar atmosphere using WC-Co vial and balls at different durations. Phase and microstructural characterizations of the sintered samples were performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Archimedes and pycnometer density measurements were carried out. Microhardness and wear resistance tests of the sintered samples were also conducted. Moreover, oxidation resistance studies were employed via thermogravimetric analyzer (TGA).

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Grain refining in Al_2O_3-Ni nanocomposites prepared via pressureless or field assisted sintering

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Keywords: nanostructured alumina, Ni inclusions

The aim of the present work is to (get a better knowledge) elaborate on the grain refining process by incorporation of Ni nanoinclusions into alumina nanoparticles and subsequent densification employing either pressureless or field-assisted sintering.[1] Hybrid Al_2O_3-Ni nanoparticles were prepared through an innovative wet-chemical route utilizing a hyper-branched polymer (poly(ethylene)imine) as template material to synthesize the boehmite powder and combine it with Ni ions. Various treatments were followed to receive a deagglomerated γ-alumina/Ni powder. DTA/Tg and dilatometric studies were carried out. Pressureless sintering was performed in the high temperature range of 1500–1650 °C under various atmospheres: air, argon and nitrogen. Field assisted sintering (FAST) was completed under uniaxial pressure of 50 MPa in the temperature range of 1150–1350 °C for 2–15 min investigating various heating-up regimes. Density and microscopic studies of the average grain size were performed. It has been shown that the examined specimens were densified with varying rate depending on the densification parameters and that the presence of Ni inclusions was effective in preventing densification. Pressureless sintering in argon atmosphere at 1650 °C led to a relative density of 90% but the mean grain size appeared large with their distribution lying in the range of 4–20 μm. FAST densification resulted in relative density in the range of 96–98% after sintering at 1350 °C for 4 min, but the grain size was in the order of 3–4 μm. Nanometric grains of an average diameter of 500 nm formed as a result of sintering at 1200 °C for 2 min, but the relative density was about 70%. Consolidation of powders in the temperature range of 1200–1300 °C caused an abrupt grain size growth but elongation of the consolidation time did not lead to higher densification. Discussion of the observed behaviour is provided.

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Synthesis and characterization of selected Al_2O_3-YSZ composites for the application in CMAS resistant thermal barrier coating systems

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Keywords: thermal barrier coating, CMAS, ATZ, alumina toughened zirconia, composite, sol-gel

Today's state of the art topcoat material in thermal barrier coatings (TBCs) for airplane gas turbines is 7-8 wt.% yttria stabilized zirconia (7YSZ) which shows two main limitations regarding the application's conditions. Firstly the long-term operation temperature is limited to ~1200 °C. Above that accelerated sintering and destructive phase transformations can be observed. Specifically spoken the metastable tetragonal t'-phase decomposes into a phase equilibrium of cubic and tetragonal ZrO_2 phases (c + t). During thermal cycles the reversible phase transformation in between t-ZrO_2 and monoclinic ZrO2 (m) leads to stress-induced spallation of the topcoat. The second limitation arises in dusty environments where molten silica-rich CMAS particles (amorphous Ca-Mg-Al-Si-slags) infiltrate the 7YSZ topcoat and decompose the t'-phase by chemical reactions. Moreover rapid densification can be observed which lowers the thermal conductivity and induces topcoat spallation during thermal cycles. One possible solution to overcome the given limitations would be the use of Al_2O_3-YSZ composites (ATZ). By adding α-Al_2O_3 to YSZ the t'-phase can be stabilized chemically and mechanically thus allowing higher operation temperatures. Furthermore an Al2O3 reservoir switches the chemical CMAS composition to faster crystallisable phases which may hinder a complete infiltration of the topcoat.

ATZ-composites have been wet-chemically synthesized with 1, 10, 20 and 30 wt.% of α-Al_2O_3. The yttria content in YSZ was fixed to 9.7 mol.% which lead to the crystallization of t'-phase even by slow cooling. Fully-dense specimen have been prepared and essential characterizations regarding their thermo-physical properties, phase stabilities and CMAS corrosion have been carried out. The sintering rate of ATZ with higher α-Al_2O_3 content is lowered and maximum densification delayed to higher temperatures. At the same time the thermal conductivity increases and the CTE decreases as expected. Thermal cycling in between 800 °C and 1250 °C shows no measurable volume changes for the ATZ composites but for the 9.7YSZ indicating a higher stability of the t'-phase in ATZ composites. CMAS corrosion tests show well-crystallized CMAS and anorthite on ATZ surfaces and glassy CMAS on 9.7YSZ surfaces. Moreover XRD results showed less t'-decomposition after CMAS corrosion in ATZ composites.

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Nano-sized SiC rich composite coatings produced by noble gas ion mixing

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Keywords: SiC, nano coating, ion mixing, corrosion

Silicon carbide (SiC) is a material that has attracted considerable interest for a long time, particularly due to its high temperature strength, thermal shock resistance, good thermal conductivity and its inertness to exposure in corrosive environments. In thin film form, SiC is used for micro/nano-electromechanical system (M/NEMS) operating in harsh-environments e.g. automotive and aerospace applications such combustion processes or gas turbine control. Different methods can be used for producing SiC thin films eg.: physical and chemical vapour deposition. However these methods need elevated temperature which might be disadvantageous by certain substrates. Ion bombardment might be also used to overcome the high activation barrier of the compound formation since it creates far from equilibrium conditions, where the apparent activation barrier might be much lower.

Recently we have demonstrated that focused ion beam method (FIB) by using Ga^+ ions can be applied to produce some nanometers thick SiC layer at room temperature.[1] We have also presented that the produced layer shows an excellent chemical resistance against polysilicon etchants.[2] By applying the FIB method the irradiated area is very small, 200*200 μm. However for suitable protective SiC coatings much larger area is required. Replacing the expensive and less-efficient FIB method is advisable by other IBM method: e.g. noble gas ion irradiation.

In the present work a C(20nm)/Si(20nm) multilayer system was irradiated with Ar^+ and Xe^+ ions at room temperature applying energy and fluence ranges of 40-120 keV and 1-6x10^{16} ion/cm^2, respectively. The layer thickness and in-depth distribution of SiC was determined by Auger electron spectroscopy depth profiling. The thickness of the SiC rich region was only some nanometer and it could be tailored by changing the ion irradiation conditions. The corrosion resistance of the layers was measured by potentiodynamic corrosion test in 4M KOH solution. The decreasing corrosion exchange currents showed that the corrosion resistance of the layers was order of magnitude better than that of pure silicon; by selecting the irradiation parameters carefully the chemical resistance can be tailored.

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Erosive wear of slip cast ceramics

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Keywords: alumina-zirconia, composite ceramics, solid particle erosion, slip casting, surface roughness

The objective of this investigation was to improve the tribological properties, particularly the solid particle erosion resistance, of slip cast alumina with the addition of small amount of zirconia nanoparticles. Two groups of suspensions, with solid loading of 70 wt.%, were prepared: the first one contained 100% of Al_2O_3 powder, while the second one contained 99 wt.% of Al_2O_3 and 1 wt.% of ZrO_2 powder. Suspensions were homogenized in a planetary ball mill and green bodies were formed in prepared plaster moulds. The optimal amount of used commercial dispersant and homogenization parameters were determined and previously reported.[1] As a result of two different suspensions, two types of green bodies and, subsequently, sintered samples were produced: monolithic Al_2O_3 and composite Al_2O_3-ZrO_2 ceramics.

Sintered samples were subjected to the solid particle erosion in order to discover whether the addition of zirconia nanoparticles improves the erosion resistance of alumina. Solid particle erosion can be defined as a degradation of material caused by repeated impacts of small solid particles.[2] Silicon carbide was used as an erodent under different impact angles (30° and 90°). According to literature, the lower impact angle (30°) corresponds with abrasive erosion, while the higher one (90°) correlates to impact erosion.[2] Wear mechanisms were analysed by comparing the surface roughness parameters (R_a, R_z, R_{max}) before and after erosion. It is assumed that higher surface roughness after the test indicates lower erosion resistance.[3]

After the erosion test, all surface roughness parameters increased for both samples. Obtained results confirmed that this type of slip cast ceramics is more sensitive to impact than to abrasive erosion, because all surface roughness parameters were higher for the higher impact angle (90°), for both samples. This investigation also confirmed the hypothesis that tribological properties of alumina can be improved with the addition of the small amount of zirconia nanoparticles: all surface roughness parameters were higher for monolithic alumina than for composite alumina-zirconia, for both impact angles.

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Influence of yttria stabilized zirconia nanoparticles on the setting time of submicrometer-sized Portland cement

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Keywords: average particle size, setting time, hydration process, Portland cement

The objective of this research was to determine the effect of the addition of Yttria stabilized Zirconia in t 'phase nanoparticles, on the setting time of the composite Portland cement paste (CPC 40) with submicronic average particle size. The CPC 40 was subjected to a milling process in a planetary ball mill to obtain the submicrometric size, and the Yttria stabilized Zirconia in its t' tetragonal phase was obtained by sol-gel and spray drying synthesis process. After thermal treatment at 600 °C the obtained spherical aggregates were subjected to a grinding process to obtain a nanometric particle size. Pastes were prepared with different combinations and the setting time was evaluated using the Vicat apparatus according to the ASTM C 187-11E1 and ASTM C 191-01 standards, comparing the results with the control cement and submicronic cement without addition. The decrease in the average particle size APS of the CPC 40 from 13.6 to 0.83 microns, has a very important effect as an accelerator in the CPC 40 hydration process, reducing the initial setting time by up to 88% and increasing the requirement of Water up to 49% to obtain the normal consistency (penetration of the Vicat needle of 10 mm). For the different cement pastes, the temperature evolution during the setting time process was evaluated, and the hardened pastes were characterized by Scanning Electron Microscopy SEM. The effect of the nanometric particles of Yttria stabilized Zirconia on the submicron CPC 40 cement, on the one hand, increases the water requirement as it decreases the penetration of the Vicat needle in the normal consistency test, and on the other, increases the initial setting time by 300% for an optimal addition of nanoparticles of 0.5%.

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Fabrication of oriented h-Bn/epoxy resin composites by applying a low magnetic field using multi-layered-graphene-coated platelets

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Keywords: h-BN, orientation, mechanical treatment

Hexagonal boron nitride (h-BN) has intrinsically high thermal conductivity and electrical insulation, and the typical shapes of conventional h-BN particles are plate-like because *c* plane of h-BN was developed. The h-BN platelets have been dispersed in a resin to improve its thermal conductivity. Since thermal conductivity of direction perpendicular to *c*-axis of h-BN are much higher than that parallel to *c*-axis, the improvement of thermal conductivity of a resin has been reported by orientation of h-BN platelets with a high magnetic field using a super conducting magnet. In this work, oriented h-BN/epoxy resin composites were successfully fabricated by applying a low magnetic field using the multilayered-graphene-coated h-BN composite platelets. Two types of h-BN having different particle size were used as raw materials. Multilayer-graphene-coated h-BN platelets were prepared through mechanical treatment technique under the same condition. SEM images showed that the original morphology of the h-BN platelets remained after the mechanical treatment and small irregularities existed on their surface. Furthermore, signal of carbon appeared on the surface of the composite platelets in the elemental mapping of EDS, which showed that multilayered-graphene was successfully coated on the h-BN platelets. After mixing and deforming an epoxy resin, a curing agent and the composite platelets, they were poured into a mold and cured with and without the application of a low magnetic field of 0.5T. The XRD peak intensity of (100) of h-BN epoxy resin composites prepared with a magnetic field was larger than that prepared without a magnetic field, which indicated that *c*-axis of the composite particles are oriented in a direction normal to the applied magnetic field. Such orientation of h-BN resulted from the large anisotropy of magnetic susceptibility of multilayered-graphene coated on the h-BN platelets. The peak intensity of (002) with a magnetic field increased with an increase in the volume fraction of h-BN. Use of coarser h-BN platelets caused the better orientation even at the same volume fraction compared with use of finer platelets. These mean that lower viscosity of h-BN/epoxy resin mixtures due to the lower volume fraction and/or the coarser particle size of the h-BN platelets resulted in the higher the orientation by applying a magnet field. Microstructural observation also showed that the high orientation of h-BN platelets in the h-BN/epoxy resin composites prepared in a low magnetic field. Consequently, oriented h-BN/epoxy resin composites was successfully fabricated by applying a low magnetic field using the multilayered-graphene-coated h-BN composite platelets, and degree of the orientation was controlled by the particle size of the composite platelets and the viscosity of h-BN/resin mixtures.

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Mechanical characterization of Y-TZP/Al_2O_3-NbC nanocomposites sintered by different techniques

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Keywords: nanocomposites, zirconia/alumina-niobium carbide, sintering, SPS, mechanical properties

Composites with zirconia matrix and addition of alumina and carbides have been studied for the improvement of mechanical properties, as fracture toughness and wear strength. However, carbide-containing materials need non-conventional sintering methods, due to their low sinterability and high reactivity with oxidizing atmospheres. In this work, there was produced a 3 mol % yttria-stabilized tetragonal zirconia polycrystal (3Y-TZP) matrix nanocomposite with 5 vol% of a nanometric Al_2O_3-NbC powder obtained by high-energy reactive milling. The incorporation of this powder in the matrix was done by the suspension mixing technique, in a ball mill. The resulting powder was characterized by X-ray diffraction, to verify the present phases, and conformed in cylindrical shape. The sintering of the nanocomposites was performed by two techniques: (a) conventional sintering, at the temperatures of 1400 °C, 1450 °C and 1500 °C for 2 h, using graphite powder as sacrifice material, to prevent carbide oxidation, and (b) non-conventional sintering, by Spark Plasma Sintering (SPS) technique, for 15 minutes, at vacuum, under the pressure of 80 MPa, at the temperatures of 1300 °C, 1350 °C and 1400°C. The characterization of the sintered nanocomposites was done by apparent density measurement and X-ray diffraction. The mechanical properties of the sintered nanocomposites were evaluated by Vickers microhardness measurements, nanohardness and Young's modulus determination by nanoindentation and calculation of fracture toughness using the indentation technique. The results showed that, by the proposed method, there was possible to produce 3Y-TZP/Al_2O_3-NbC nanocomposites with high density by both sintering techniques (>97% TD in conventional sintering and >98% in SPS), with good dispersion of the Al_2O_3 and NbC phases on the 3Y-TZP matrix, keeping NbC structure without its decomposition. The hardness and fracture toughness these nanocomposites were also improved with relation to 3Y-TZP without addition of Al_2O_3-NbC, attaining 13.2 GPa and 8.6 MPa.$m^{1/2}$, for the samples sintered conventionally, and 12.7 GPa and 8.0 MPa.$m^{1/2}$, for the samples sintered by SPS, respectively.

Acknowledgements

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Advanced oxidation of dyes with ceramic-based electrodes

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Keywords: pollutants, electrooxidation, ceramic electrodes

Traditional treatments are not successful in dealing with emergent contaminants in recycled industrial wastewaters as recent standards includes a larger number of substances with lower discharge limits. In consequence, alternative methods are needed to separate or destroy contaminants such as dyes, antibiotics, hormones, etc.[1]

Advanced oxidation allows the mineralization of organic contaminants without addition of reactants, because it generates hydroxyl radicals by means of electrodes[2]. These radicals can degrade the organic molecules to H_2O and CO_2. However, chemically resistant electrodes are needed. Expensive metals show good electrochemical behaviour (Ti, Pd), but ceramic electrodes can balance the cost with the performance.

A cheaper alternative to more expensive ceramics (ITO, BDD) has been tested. Concretely, a Sb-doped tin oxide electrode which has been optimized for electrooxidation of dyes. Sintering and doping have been done in the same thermal treatment. Dopant level and sintering conditions have been adjusted to balance low resistivity with enough mechanical resistance to easily manipulate the electrodes. In addition, sintering temperatures have been maintained as near as possible to the traditional ceramic firing interval (1050–1250 ºC).

Results showed that a fraction of the dopant is lost during the sintering, being higher at T > 1150 ºC (up to 20% of initial proportion), and the samples just densify (volumetric contraction < 1%). However, the resistivity reaches values low enough for the electrode function (lower than 1 Ω·cm), with little influence of the sintering temperature.

The electrodes were tested in the oxidation of RB5 dye. Results showed that the electrodes partially degraded the dye, but sintering temperature and current intensity influences their performance. The oxidation rate was higher for the electrode sintered at intermediate temperature (1200 ºC) and oxidation of the chromophoric groups was achieved because treated water lost the colour. However, the mineralization of the RB5 was not complete, as organic groups were detected in the UV absorption spectra of treated water.

In conclusion, the developed electrodes can eliminate the dye, but additional modifications are in study in order to achieve its full mineralization.

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Morphology dependency of powder flowability of dicalcium phosphate dihydrate

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Keywords: powder flowability, dicalcium phosphate dihydrate (DCPD), morphology

Controlling the shape of functional material is one of the important themes; their size and surface condition (such as specific surface area and ratio of the crystal face) change their chemical reactivity. When one chooses a functional material as an environmental material, chemical reactivity and responsibility are necessary factors; moreover, some physical properties are strongly required at field trial. On the other hands, dicalcium phosphate dihydrate (DCPD; CaHPO4·2H2O) is researched as the environmental treatment material for removing fluoride ions. DCPD crystals change to stable material fluoroapatite (FAp; Ca10 (PO4)6 F2) and immobilizing fluoride ions from some fields (waste water management, soil purification).[1] And the morphology of DCPD crystals is controllable by adding other ions during aqueous synthesis, changing the initial pH value and concentrations of calcium and phosphate ion. The morphology of DCPD crystals is changeable from tabular structure to petaloid structure by preceding parameters.[2]

In this study, we compared the powder flowability between tabular and petaloid shaped DCPD. Preceding chemical reaction from DCPD to FAp, morphology was kept; therefore evaluation of powder flowability was important not only transit the DCPD powder from plant to field, during immobilization fluoride ion, but also after treatment (FAp sludge usability).[3] Powder flowability test was complied International Organization for Standardization and Japanese Industrial Standards. Particle size distribution was measured by laser diffraction particle size analyzer to calculate the uniformity of powder.

The compressibility ratio shows large different between petaloid (20.9) and tabular (40.2). The angle of repose result shows that petaloid (36.1°) was lower than tabular (43.5°). The collapse angle, spatula angle and uniformity of powder were comparable value (petaloid (23.4°, 35.9° and uniformity was 2.8), tabular (26.6°, 34.8° and uniformity was 3.3)). The analysis of Carr's flowability indices, petaloid shaped DCPD shows good fluidity but tabular shaped DCPD needs to devise a countermeasure against powder bridging. Moreover, analysis of Carr's floodability indices, each sample needs rotary sealing.

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Boron carbide/graphene platelets ceramics with improved fracture toughness, functional and tribological properties

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Keywords: boron carbide, graphene platelets, microstructure, fracture toughness, conductivity, tribology

Boron carbide/graphene platelet (B_4C/GPLs) composites have been prepared with the addition of different weight percent of GPLs by hot-press processing technology at 2100 °C in argon. The influence of the GPLs addition on microstructure development, fracture toughness, electrical conductivity and tribological properties was investigated. The microstructure was studied by SEM, TEM, HRTEM, XRD and Raman spectroscopy. SEVNB method was used for fracture toughness and four-point Van der Pauw method for electrical conductivity measurement. Almost fully dense B_4C/GPLs composites have been prepared with lower wt.% of GPLs additives with relatively homogeneously distributed platelets in the matrix. With increasing amount of GPLs additives, the fracture toughness increased due to the activated toughening mechanisms in the form of crack deflection, crack bridging, crack branching and graphene sheet pull-out. The highest fracture toughness of 4.48 MPa.m$^{1/2}$ was achieved at 6 wt.% of GPLs addition, which was ~50% higher than the K_{IC} value of reference material. The electrical conductivity increased with GPLs addition with percolation threshold between 2–2.5 wt.% of GPLs and reached the maximum values at 4 wt.% GPLs addition. A significant improvement of electrical conductivity around two orders of magnitude up to 1526 S/m

in the perpendicular direction and to 872 S/m in parallel direction was noticed. The friction and wear behaviour of B_4C/GPLs composites have been investigated using the ball-on-flat technique with SiC ball under dry sliding conditions at room temperature. The coefficient of friction for composites were similar, however the wear rate significantly decreased ~77% in the case of B_4C+6 wt.% GPLs when compared to reference material at a load of 5 N, and ~60% at a load of 50 N. Wear resistance increased with increasing GPLs content in regards to the present graphene platelets, which during the wear test pulled-out from the matrix, exfoliated and created a wear protecting graphene-silicon based tribofilm. For revealing and observation of the wear damages under the worn surfaces, focused ion beam (FIB) technique was used for the preparation of the cross section of wear tracks.

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3D printed geopolymeric lattices: effect of processing parameters on the mechanical properties

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Keywords: geopolymers, direct ink writing, geopolymeric lattices, porous ceramics, robocasting

Geopolymers are iniorganic materials generally obtained through the reaction of aluminosilicates in highly alkaline solutions. These materials consolidate at low temperature and possess good mechanical, weather and fire resistance, which make them suitable for a wide variety of applications, such as structural materials, thermal insulation, and so on. Our group developed mixtures based on geopolymer for additive manufacturing of porous components via direct ink writing (DIW). We optimized the rheological properties in order to obtain suitable inks for the production of highly porous lattices. It should be noted that, as geopolymer mixtures are subjected to ongoing poly-condensation reactions, their viscosity changes with time in what ca be seen as a 4D printing process.

Different parameters can influence the mechanical properties of the printed components. We produced lattices with different porosities and evaluated their compressive strength. The influence of different consolidation (curing) and calcination treatments on the mechanical behaviour and on the microstructure of the components was also investigated.

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Corrosion resisting properties of pressureless sintered silicon carbide for the reactor of PFCs gas scrubber

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Keywords: SiC, pressureless sintering, corrosion weight loss, flexural strength

The PFCs used in the field of the semiconductor industry have very high GWP in the range of 6,500–23,900 and are being combusted over 1500 °C in scrubber system due to its chemically non-degradable property. However, the metal reactors in gas scrubber are easily corroded and damaged by HF gas generated from PFCs with high temperature, and the high cost for frequent replacement of the reactor is occurring. In this study, we fabricated porous honeycomb SiC with high strength and corrosion resistance for use in the reactor of gas scrubber through pressureless sintering process. The SiC dough for extrusion was prepared by mixing SiC powder with carbon resin, organic binder and DI water in optimum ratio. The prepared SiC dough was extruded into a honeycomb mould and was sintered at 2150 °C for 2hrs in flowing argon atmosphere. The sintered honeycomb SiC has channels density up to 500 CPSI (Channels Per Square Inch). To evaluate this honeycomb SiC, we prepared disc type SiC w/o sintering additives and sintered at 1950–2150 °C. The microstructure and phase were evaluated through SEM and XRD, respectively. The long-term corrosion resisting properties were also evaluated to confirm the feasibility for the reactor of gas scrubber using HF solution (conc. 50%) for 1 year. The corrosion weight loss and flexural strength (3-points) were measured before/after the long-term corrosion test, and the microstructural study was conducted through TEM analysis.

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2YSZ as alternative matrix for alumina toughened zirconia composites

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Keywords: alumina toughened zirconia, Y-TZP, mechanical properties, bioceramics, biocompatibility

Zirconia and alumina are well known bioceramics, used in the field of orthopedics,[1] since they show reduced wear rate and excellent biocompatibility. However, these ceramics presented some limitations: the brittleness of alumina and the ageing sensitivity of zirconia.

Zirconia oxide is characterized by the phase transformation with temperature, being necessary a stabilizer to maintain the desired tetragonal phase, with outstanding mechanical properties. Yttria is the most used stabilizer, replacing zirconia (Zr^{+4}) and forming oxygen vacancies.[2]

Alumina-Toughened Zirconia (ATZ) ceramics combines the hardness and wear resistance of alumina and the fracture toughness as well as flexural strength of zirconia,[3] widely used for those applications that require high mechanical properties such as hip arthroplasty.

In the present work, different aqueous suspensions of Alumina-Toughened Zirconia (ATZ) composites (20% Al_2O_3) with 2 and 3 mol% YSZ (synthesized by Innovnano using Emulsion detonation process) were prepared and characterized before a spray drying process; subsequent powder morphology was analyzed by scanning electron microscopy (SEM), chemical and crystal phase composition using X-ray fluorescence (XRF) and X-ray diffraction (XRD) respectively. Samples were prepared by uniaxial and cold isostatic pressing followed by low temperature (1400 ºC) conventional sintering achieving a densification level above 97%. The obtained ceramics pieces were subjected to mechanical test as hardness, fracture toughness and flexural strength resulting in a non-negligible improvement of properties for the compositions with 2 mol% YSZ, up to 5 $MPa.m^{1/2}$ and 1400 MPa of fracture toughness and flexural strength respectively.

In order to confirm an eventually degradation as consequence of ageing effect, more typically for 2YSZ samples were submitted to an accelerate ageing test in an autoclave (134 ºC, 2 bar) without appreciable loss of mechanical properties even after 96 h.

The biocompatibility of these composites was also tested. MG63 cells were seeded on the sintered samples and MTT and alkaline phosphatase activity assays were performed. The cell proliferation increased significantly from day 1 to day 4 in both cases, being remarkable that lower yttria content (802YSZ20A sample) presents higher cell viability in comparison with 803YSZ20A.

The use of 2YSZ instead of 3YSZ as ATZ composite matrix results in an improvement of the mechanical properties, as well as of biocompatibility without being strongly affected by the ageing process.

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Fabrication of oxide ceramic fibers by needle-less electrospinning

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Keywords: electrospinning, nanospider, electrospun nanofibers, alumina, metal oxide catalysts, oxide ceramics

Ceramic fibers can be effectively produced by electrospinning and post-electrospinning process.[1,2] In this study the term "needle-less" electrospinning means the free surface electrospinning technique developed by ELMARCO and realized in "Nanospider^{TM}" instrument. It was used for preparation of fine oxide ceramic fibers on the example of α-Al_2O_3 fibers with diameters of 0.5–1.5 µm described in this work.

The fabrication process consists of three basic steps: i) preparation of spinning solution, ii) electrospinning of the prepared solution and collection of the composite fibers, iii) calcination of the composite precursor fibers. The electrospun fibers were prepared from polyacrylonitrile/N,N-dimethylformamide (PAN/DMF) polymer solution and $Al(NO_3)_3.9H_2O$ in ratio 1/10/1. Thereafter, the precursor fibers were calcined in the furnace at 900, 1100, and 1200 °C with a heating rate of 5 °C/min in air. The formation of crystalline phases, surface morphology and diameters of metastable and final alumina fibers were characterized using thermogravimetric analysis, X-ray diffraction analysis, scanning electron microscopy and transmission electron microscopy. The precursor PAN/$Al(NO_3)_3$ fibers were amorphous. The thermal treatment of precursor fibers leads to the polymer decomposition/oxidation, decomposition of $Al(NO_3)_3$ with next phase transition from γ-Al_2O_3 to α-Al2O3. The fine porous microfibers composed of pure α-Al_2O_3 phase were prepared after calcination at 1200 °C. The same method can be used for preparing ZnO, SnO_2, TiO_2, ZrO_2, CuO and other oxide ceramic materials.

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Characterization of joined single-end type RBSC radiant tube

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The aim of this study is to develop single-end type RBSC tube which was focused on joining of tube and cap. As it has many merits like high thermal efficiency and low pollutant emission, RBSC radiant tube will be used gradually for heat treat applications. SiC powders were mixed with thermo-set polymers in a chamber at low temperature. Pouring it into the casting mold, tube was formed by centrifugal casting and cap was formed by thermo-set molding method. The formed bodies were heat treated in order to transform polymers to carbon in Ar purging atmosphere. After joining the tubes with caps using a SiC bonding material, infiltrated by molten Si at 1500 °C in vacuum. It was studied effects of joining paste composition on bonding strength and microstructure of joint layer. The bonding strength were measured, and the microstructures of joint layer and fracture position were observed using microscopy.

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Effect of sintering atmosphere on the crystal texture and coefficiant of thermal expansion in cordierite ceramic honeycomb

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Keywords: cordierite, honeycomb, crystal structure, texture, CTE

Cordierite ($Mg_2Al_3Si_5O_{18}$) ceramic have a very low coefficient of thermal expansion (~1ppm/^{o}C). Hence its honeycomb ceramics have been used as the substrates in DOC (diesel oxidation catalyst), SCR (selective catalytic reduction), and DPF (diesel particulate filters) for diesel engines. The CTE of cordierite honeycomb can be lowered further to < 1ppm/^{o}C by means of enhancing the degree of crystal texture of the cordierite honeycomb and controlling the proportion of the crystal phases between the low symmetry cordierite (SG *Cccm*) and the high symmetry indialite (SG *P6/mcc*) phases. The extrusion process adopted for shaping the honeycomb substrate increases the degree of crystal texture. Sintering temperature is one of the important parameters affecting the texture and the crystal phase proportions between the cordierite and indialite phases.

In this study the effect of sintering atmosphere on the phase proportions between the low symmetry (orthorhombic) and high symmetry (hexagonal) phases. The evolution of crystal textures were investigated in the honeycomb sintered under the two different sintering atmo-

spheres, highly and weakly oxidizing environments. The textured degree and crystal phase formation were analyzed by using Rietveld refinement method (Full-prof software) for the XRD patterns of the sintered sample.

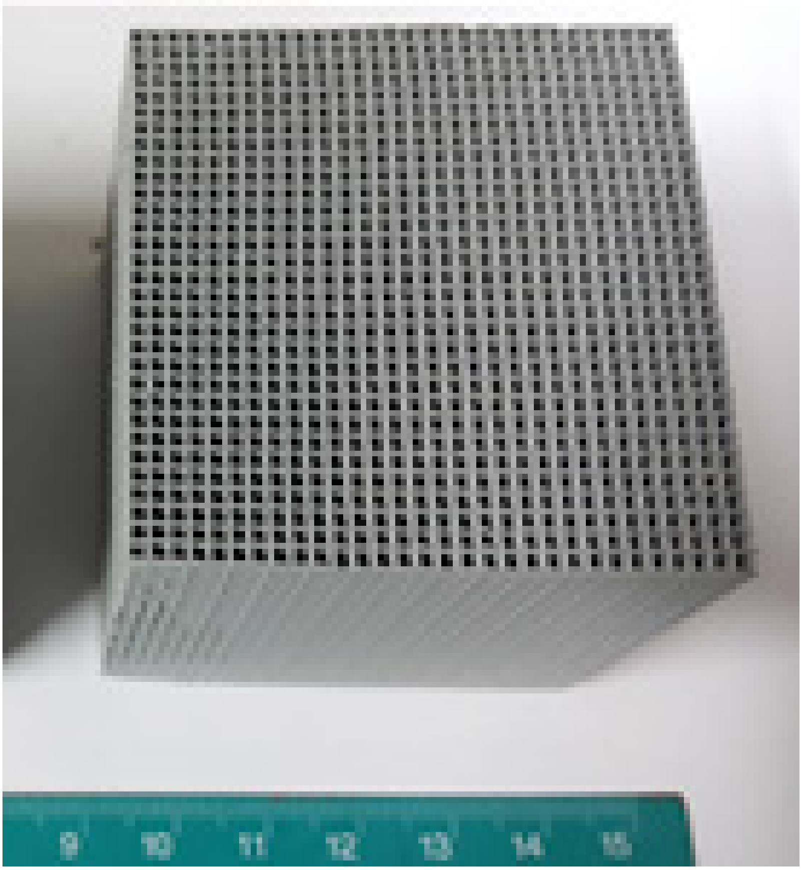

Fig. 1. Extruded cordierite preforms

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Microstructure effects on low and high field dielectric properties of (Ba,Sr)TiO_3 based porous solid solutions_

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Properties of a ceramic system can be improved using porosity and make the material proper for being used as high-frequency ultrasonic transducers or for tunable applications. The purpose of this study was to prepare and to discuss the role of porosity on functional properties in $Ba_{0.60}Sr_{0.40}TiO_3$ (BST) ceramics with different degrees of porosity. Preparation followed the mixed oxide method by solid-state reaction at a sintering temperature of 1450 °C for 2h. The BST ceramics with various porosities have been obtained by addition of lamellar graphite in concentration of 10, 20 and 35vol.%.

The phase purity of BST ceramics was checked by XRD analysis. The SEM investigations showed that with addition of graphite as pore forming the samples present a fracture mode transformation from intragranular fracture to an intergranular fracture and a decreasing of grain size of BST. Furthermore, as BST grain size becomes smaller, the volume of grain boundary increases and the crack prefers spreading along grain boundary to splitting the strengthened grain. Modifications of the grain size and of the grain boundaries volume were also observed and discussed.

The effect of addition of carbon black as pore forming agent on the dielectric response at low and high electric field was investigated and discussed. Impedance spectroscopy study was carried out in the frequency range of (10^1–10^6) Hz at temperatures between (25–200) °C. The temperature dependence of permittivity at a fixed frequency $f = 100$ kHz revealed a trend corresponding to the paraelectric phase, with a Curie temperature far from room temperature, irrespective of the porosity volume. The porosity level does not modify the temperature corresponding to the permittivity maximum. However, since porosity influences by reducing the ferroelectric phase volume, a depression with the same value of permittivity is noticed in all the temperature range.

Microstructural, morphological and dielectric investigations at low and high field have been performed and data were compared with other literature studies. The experimental results have been shown that the dielectric permittivity of the BST ceramics with different degrees of porosity decreases with increasing the porosity, from a few thousands down to a few hundreds, and present a trend of depression with temperature increasing, as required by wireless applications, without losing the high tunability.

A strong nonlinearity was observed for all the ceramics, with a tendency toward saturation for high fields. The relative tunability in BST porous structures preserved similar values as in the dense ceramics, irrespective of the porosity level.

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Removal of fluoride ion in the environments by using calcium phosphate-carbonate hybrid

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Keywords: dicalcium phosphate dihydrate (DCPD), fluoride, calcium carbonate

Dicalcium phosphate dihydrate (DCPD; $CaHPO_4 \cdot 2H_2O$) react with fluoride and transforms stable mineral fluoroapatite (FAp; $Ca_{10}(PO_4)_6F_2$). This reaction is applicable to immobilize fluoride ions in the water environments[1]. However, this reaction release excess phosphate ion such as eq (1).

$$10CaHPO_4 \cdot 2H_2O + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 4HPO_4^{2-} + 6H^+ + 20H_2O \quad (1)$$

Previously, we reported that addition of calcium carbonate is effective to inhibit release of phosphate ion from the reaction by supply calcium ion from dissolve calcium carbonate[2].

In this research, we investigated application of the DCPD-calcium carbonate hybrid to treatment of fluoride in waste water. Various materials have applied for waste water treatment; however, removal amount is remarkably decreased to 2–3 mg/g when concentration of fluoride is lower value such as a few mg/L after treatment[3]. Removal amount of fluoride from reaction of DCPD was analyzed by batch experiment. From result of experiment, removal of fluoride was around 10–15 mg/g in widely fluoride concentrations. This value was 5 times of adsorption amount of conventional adsorption material such as bone char, or conventional precipitation method by using aluminum salts. From addition of chemicals decreased than conventional process, amounts of resulted sludge waste also decreased conventional method. This result was effective not only waste amount but also economic efficiency including transport and waste management in landfill.

Hybridization calcium carbonate in DCPD improved removal amounts of fluoride ion. Suitable condition was addition of calcium carbonate in 25 wt% of DCPD. Usage of DCPD-calcium carbonate in this ration, payment for chemicals for treatment of waste water was decreased to around 0.7 Euro/m^3 of waste water. This value was 5% of usage of bone char. From these results, it was concluded that usage of DCPD-calcium carbonate is quite applicable to treatment of fluoride in waste water.

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Improving the tribological performance of Si_3N_4 composites by a few-layer graphene addition

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Keywords: silicon nitride, composites, graphene, melamine, tribology

Despite the outstanding solid lubricant properties of graphite, so far only a very limited improvement in the tribological properties of ceramic composites could be achieved by addition of graphene nanoplatelets (GNPs) – particularly, concerning the reduction of the friction coefficient. We propose that the reason for this is the relatively low exfoliation degree of the GNPs. Several exfoliation methods have been employed for graphite, aiming for large quantities of thin GNPs with their structure kept as intact as possible. One of the simplest, yet most efficient methods is the exfoliation by mechanical milling. Here, we propose to employ a novel mechano-chemical method to enhance the exfoliation degree of graphene nanoplatelets during mechanical milling, but without chemically modifying the resulting graphene sheets.

By employing the as-prepared ultra-thin few layer graphene nanoplatelets (FL-GNPs) as filler material, the wear resistance of Si_3N_4 composites can be increased by about twenty times, the friction coefficient reduced do nearly its half, while the other mechanical properties are also preserved or improved.

Using confocal Raman microscopy, we were able to demonstrate the formation of a continuous FL- GNP tribo-film, already at 5wt% FL-GNP content, which is at the origin of the outstanding improvement of the tribological performance.

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Fabrication and characterization of novel silk / chitin hydrogel / nano diopside composite scaffolds for tissue engineering

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Keywords: chitin, nanodiopside, composite scaffold, tissue engineering

Tissue engineering has recently developed a growing field in the regeneration of tissues Biomaterials are required in tissue engineering techniques for the construction of scaffolds by which relevant cells can be attached, grown, and proliferated. Silk fibroin (SF) is a natural polymer produced by a variety of insects. Recently, silk cocoons from *Bombyx mori* have been used as an in-access material for tissue regeneration purposes.[1]

Chitin, which is known to be a biocompatible and biodegradable polysaccharide, is the most abundant polymer on earth after cellulose. It is fabricated from the shells of shrimp and squid pens. It has also been found that the chitin hydrogel could be prepared by using this solvent system. In recent studies, the calcium solvent system has been found to be a suitable solvent to dissolve the chitin in the mild conditions.[2]

Diopside ($CaMgSi_2O_6$) ceramics possess excellent *in vitro* apatite-formation ability, *in vivo* bioactivity, degradability and improved mechanical strength compared to hydroxyapatite.[3]

In continuation of our previous studies on the construction of composite scaffolds.[4–5] In this research, novel porous composite scaffolds consisting of silk, chitin, and MCM-41 were prepared using the freeze-drying method. The prepared nanocomposite scaffolds were characterized by SEM, XRD, BET, TGA and FT-IR techniques. In addition, swelling, degradation and biomineralization capability, cell viability and cell attachment of the composite scaffolds were evaluated.

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Improvement usability of environmental material by morphology changing

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Keywords: permeability, calcium phosphate, morphology

Dicalcium phosphate dihydrate (DCPD) has attracted attention as an environmental material for immobilizing fluoride ions from waste water and/or soil by selectively reaction to form stable material, fluoroapatite (FAp). In the previous reports, the morphology of DCPD can be controlled by setting following parameters; initial pH, concentration and coexisting of other ion under solution synthesis[1,2]. On the other reports, particle shape is kept during preceding chemical reaction; it is equal to say, DCPD particles act as a template of FAp particles[3]. For these reasons, usability of FAp sludge can be controllable by changing DCPD morphology.

In this study we compared the important physical properties for using as environmental material under waste water and soil treatment. We used four kinds DCPD particles synthesized under different conditions; two samples were petaloid shaped and the others were tabular shaped. Density and particle size distribution were measured and used them to evaluate permeability and sedimentation results; affecting reactivity in soil and operability of sludge after water treatment.

In the case of bulk density, the petaloid shaped particles stacked higher than the tabular particles and in the case of tap density, all samples became same value. The petaloid shaped DCPD was quicker in a sedimentation rate and higher tendency permeability than the tabular shaped DCPD. The sedimentation value of petaloid shaped DCPD was smaller than that of tabular shaped DCPD. For these results, petaloid shaped DCPD particles have higher operability than tabular shaped DCPD particles under waste water treatment due to good sedimentation rate (short time separation waste water and sludge) and value (low moisture content is equal to low weight, transit cost of the FAp sludge).

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Determination of arsenic in waste gypsum board by using antidote reaction

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Keywords: gypsum board, arsenic, recycling

Gypsum board is commonly used as a house building material and so presents in large quantities when buildings are demolished. Most waste gypsum board is sent to landfill sites. Therefore, recycle of then waste gypsum is desired because of a lack of landfill capacity. Recently, many attempts have been made to use waste gypsum board for ground improvement as a roadbed material, a sludge stabilizer or as fertilizer. However, there are difficulties in gypsum recycling related to entrained impurities such as arsenic because these impurities cause soil and groundwater pollution. On-site monitoring of arsenic content is essential for the recycling process of the waste gypsum. In order to determine impurity in gypsum, complicated pre-treatment using harmful agents requires to dissolve gypsum. We have reported simple pre-treatment method to dissolve gypsum using ion exchange resins[1]. However, it was difficult to estimate arsenic in a solution dissolved gypsum sample, because of strongly interference of phosphate in gypsum to molybdenum blue method used as conventional determination method for arsenic content.

In this study, we attempted to develop evaluation method for arsenic content in gypsum with 2,3-Dimercaptopropanol and 5-(3-Carboxy-4-nitrophenyl) disulfanyl-2-nitrobenzoic acid. 2,3-Dimercaptopropanol which is dithiol compound strongly bond with arsenic ion and widely used for therapeutic agent for arsenic poisoning. Concentration of 2,3-Dimercaptopropanol is able to jugged by discolouring by using 5-(3-Carboxy-4-nitrophenyl) disulfanyl-2-nitrobenzoic acid (DNTB) which is colour reagent for thiol compounds in phosphate buffer[2]. Under presence of arsenic, the colour reaction is strongly interfered.

Based on these findings, content is able to be determined without phosphate interference using colour reaction with 2,3-Dimercaptopropanol and DNTB.

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Thermodynamic approach for Si_3N_4-superalloy joints and microscopic characterization

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In this study, silicon nitride ceramics (Si_3N_4) were joined by using capacitor discharge technique with Inconel 718 superalloy interlayer and heat treated in order to determine possible reactions between these two materials. After capacitor discharge joining, some of the samples were heat treated at 1100 ^{o}C under air and the resulting interfacial microstructure was characterized by using transmission electron microscope (TEM) attached with high angle annular dark field scanning transmission electron microscope (STEM-HAADF) detector (Fishione) and energy dispersive x-ray spectrometer (EDS). According to STEM images (BSE), all of the joining samples were well bonded through the interlayer and cracks were not observed along the interlayer, interface and the ceramics. According to point TEM-EDS analysis, some of the new spherical phases formation having white-grey contrast was observed along metal interlayer and small amount of silicon (Si), nitrogen (N) and aluminium (Al) was detected at the interlayer of as-joined samples. For the heat treated samples at 1100 °C, the symmetrical reaction layer was observed at both side of the interlayer which is expanding towards the ceramic side. Furthermore, approximately 1 μm thick continuous another reaction layer next to this was also determined. According to TEM-EDS point-line scan analysis along the metallic interface and ceramic side, nickel (Ni), iron (Fe) and chromium (Cr) were detected at reaction layer next to the ceramic side, whereas mainly Cr, niobium (Nb), molybdenum (Mo), titanium (Ti) and Al were concentrated at the 1 μm thick reaction layer.

In order to obtain thermodynamically favorable phases and diffusion paths, the interface between two Si_3N_4/Inconel 718 material was analyzed using CALPHAD based simulations. Possible chemical reactions and the corresponding free energy changes between Si_3N_4/Inconel718 materials were calculated and their ternary phase diagrams were also evaluated. All of the CALPHAD based simulations were performed using the Thermo-Calc software taking all possible phases in the database TCN17 (TCS-Ni based superalloy database) into account.

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Fabrication and mechanical properties of textured Ti_3SiC_2 systems

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Keywords: MAX phase, grain orientation

Ti_3SiC_2 is a typical $M_{n+1}AX_n$ (MAX) phase ceramics and shows unique metallic-like and ceramic-like properties, such as good electrical, thermal conductivities and corrosion, oxidation, wear resistance. Recently, Hu et al. fabricated the textured Nb_4AlC_3 MAX phase ceramics by slip casting in a strong magnetic field followed by SPS, and indicated textured Nb_4AlC_3 show excellent mechanical properties[1]. In this study, we attempt to fabricate textured Ti_3SiC_2 with excellent mechanical properties.

Ti_3SiC_2 powder (KANTHAL) was dispersed in ethanol with 1.5 wt% Polyethyleneimine as a dispersant. Textured green body was prepared by slip casting in a rotating magnetic field of 12T. In addition, non-textured body was also prepared without the magnetic field as a reference. They were sintered 1350 °C under a pressure of 40 MPa by SPS. These samples were characterized by X-ray diffraction, scanning electron microscope. Relative density of samples was measured by Archimedes method. The flexural strength was measured by mechanical strength testing equipment using the three point bending test. The fracture toughness was measured by same equipment using SEVNB method. The dimensions of samples for the three bending test and fracture toughness were $2 \times 1.5 \times 18$ mm^3 and $2 \times 4 \times 18$ mm^3 with a notch of 0.5 mm depth and 0.1 mm width, respectively.

In the non-textured samples, each of grains was randomly oriented in SEM images. In contrast, oriented plate-like grains were observed in the textured sample. Furthermore, high dense structures were observed in these pictures. Relative density of samples was nearly 99%. The degrees of orientation were characterized by XRD patterns. In the top surface perpendicular to the magnetic field, the intensities of $(00l)$ peaks are very high. On the other hands, the intensities of other Ti_3SiC_2 peaks are very small. The Lotgering orientation factor was calculated in order to determine the degree of orientation. The degrees of orientation were 0.96 and 0.60 in the specimens prepared with and without an applied magnetic field, respectively. The bending strength of textured sample was 977.6 MPa and the fracture toughness was 7.29 MPa·m$^{1/2}$. These values of non-textured sample were 843.1 MPa and 6.57 MPa·m$^{1/2}$, respectively. The mechanical properties of Ti_3SiC_2 were enhanced by texturing.

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Tribological properties and nanoindentation of refractory carbides

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Keywords: refractory carbides, coefficient of friction, wear resistance, nanoindentation, fractography

Wear behavior, deformation, and damage of spark plasma sintered VC, NbC and ZrC refractory carbides have been investigated using nanoindentation, micro/macro – indentation tests, and tribology. Fractography was used for the characterization of deformation and damage mechanisms. Considerable indentation load – size effect was found in all systems with hardness values from 30–36 GPa to 13–17 GPa corresponding to the applied loads of 1 mN and 100 N, respectively. During nanoindentation, characteristic stress-drops were observed on hardness-displacement profiles of NbC and ZrC at depth region of 15–30 nm while this was not typical in VC. The highest coefficient of friction was measured for NbC with a value of 0.45 and the lowest for ZrC with an average value of 0.3. The specific wear rate of the NbC and VC was similar, approximately 3.10^{-6} mm^3/Nm, only the wear rate of ZrC was larger, approximately 2.10^{-5} mm^3/Nm.

According to the fractographic examination the wear of the NbC and VC is similar, similarly for the wear parameters, – the COFs and the wear rates. At a lower load of 5 N we found more plastic deformation induced microfracture. As the contact stress increased, at the load of 50 N, varieties of short cracks like partial cone cracks, lateral/shallow cracks, and radial cracks etc. are generated intergranularly or transgranularly by friction around the Hertzian contact zone. Such micro-cracks intersect each other and detach chunks of material. The detached material is crushed into fine particles by further tribological contact and evolved as wear debris. In NbC system the intergranular cracks dominate, while in VC there is a mixture of intergranular and transgranular damage. The ZrC system shows different wear behavior with no crack formation and with very limited grain boundary or transgranular fracture caused material removal. It seems that during the wear the material removal without crack formation dominates, with a sign of a significant plastic deformation of ZrC, which is surprising taking into consideration the hardness of the system.

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Organic – ceramic oxides hybrid material for blast effect mitigation

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The improvements of physical, chemical and thermomechanical properties of polymer composite materials has been a major research interest in the last few decades. Polymer nanocomposites represent a new class of materials alternative to conventional filled polymers. In this new class of material, nanosized inorganic filler (at least one dimension) are dispersed in polymer matrix offering tremendous improvement in performance properties of the polymer.

Nanoscale materials have been the subject of research interest in recent years because of their unique properties as compared to the bulk counterparts and their potential applications in a wide variety of areas such as information storage, electronics, sensors, structural components, catalysis, and defence, etc.

The main challenge in fabrication of these polymer nanocomposites for structural applications is uniform dispersion of nanoparticles in the polymer matrix. However, good dispersion for nanoparticles in polymer composite materials is extremely difficult to achieve, since nanoparticles tend to aggregate together during fabrication. The degree with which the nanoparticles can be homogeneously dispersed in the polymer matrix would significantly influence the thermal, mechanical and optoelectronic properties of the material. It has used several techniques for dispersing nanoparticles. There is an ever-increasing demand for development of processing of polymer nanocomposites for advanced structural applications. This paper is focused on polymeric – organo-clay respectively on polymeric – fly ash nanocomposites for lightweight and high strength and temperatures application devoted mainly for blast protection and mitigation of their effects.

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Metallization of C12A7:e⁻ ceramic for low ohmic resistance

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Keywords: metallization, contacting, electride, Calcium aluminate, resistance

The composition $12CaO \cdot 7Al_2O_3$ (C12A7) crystallizes in a positive charged cage structure ($[Ca_{24}Al_{28}O_{64}]^{4+}2O^{2-}$), wherein the cavities are occupied by O^{2-} ions. Sintering this C12A7 oxide in a reducing atmosphere results in the substitution of the O^{2-} ions by electrons, so that the C12A7:e⁻ ($[Ca_{24}Al_{28}O_{64}]^{4+}4e^-$) ceramic becomes a material with high electrical conductivity and low work function for emission of electrons. These properties make the material suitable as an electron emitter for operating at temperatures above 250 °C what is interesting for technological applications. Although the bulk material indicates these extraordinary properties, the surface of the ceramic has insulating properties. Therefore, a metallization film is needed to realize an electrical contact, which minimizes ohmic losses. In this study, three different metal pastes (Pt, Au and Cusil-ABA®) for contacting the surface are investigated and the reduction of the resistance during the firing process of the pastes was measured. The resistivity of the contacted C12A7:e^- was determined as a function of the temperature under inert atmosphere. The lowest resistivity of about 1 Ω cm was measured with the Ag-based braze (Cusil-ABA®), but resulted in cracking of the contacted ceramic after the firing process. Alternatively the contacting with Au achieved a specific resistance of 5.4 Ω cm (T = 800 °C), what allows the measurement of the work function of samples shaped as hollow cathodes.

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The influence of microstructure on thermal residual stress and fracture toughness of nickel aluminide-alumina composites – experiment and numerical model

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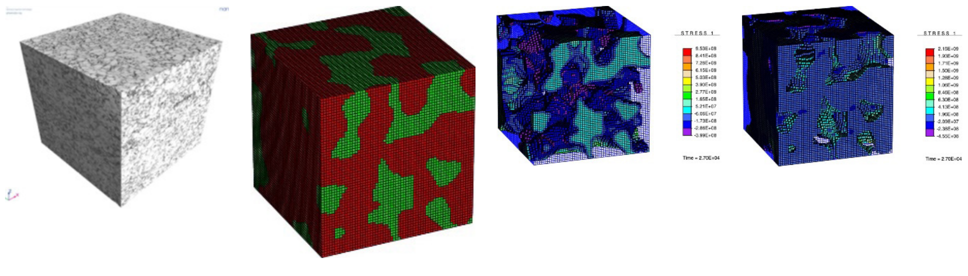
Keywords: thermal residual stress, neutron diffraction, metal matrix composite, numerical modelling

The NiAl–intermetallic based composites are potentially very attractive structural materials for aerospace and automotive applications due to high corrosion resistance, low specific weight and good strength properties at high temperatures However, the brittleness of NiAl limits its today's industrial use. In recent years a revival of research on improvement of NiAl toughness is observed and many technological approaches were proposed.[1]

The purpose of this paper is to explore the effect of alumina ceramic addition to NiAl using powder metallurgy route and to examine experimentally and numerically the effect of microstructure on the fracture toughness of NiAl/Al_2O_3 composite with processing-induced thermal residual stresses (TRS) being and additional factor taken into account. Powder mixtures with 30, 60 and 90 vol. % of Al_2O_3 and different NiAl particle size (5 vs. 45 microns) were sintered by hot pressing. In the FEM model of TRS real microstructure images from micro-CT were incorporated using the methodology developed in Basista et al.[2], (Fig. 1). The numerical results of TRS were compared with measurements by neutron diffraction method. The fracture toughness was determined in SEVNB test in four point bending.



a) b) c) d)

Fig. 1. MicroCT image of NiAl/Al2O3 composite (a), FE mesh (b) computed residual stresses for alumina (c) and NiAl (d) phase

The scientific objective of this study, i.e. experimental exploration and predictive modelling of the influence of microstructure on the TRS and K_{Ic} was achieved and the obtained results clearly confirm this effect.

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Verification of the lifetime of zirconia-alumina composites predicted by using the constant stress rate test data

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Proof Testing is a common method used in verification of ceramic components working under loads. Assuming the existence of subcritical crack growth in a material, short-time loading is not sufficient. There is a possibility to test samples for longer times, if the service time is defined, but testing greater amounts of samples would be really inconvenient.

Second approach, used in this case, involves testing with the Constant Stress Rate method. It allows authors to estimate subcritical crack growth parameters, and thereby, lifetime predictions also for static loading. These type of tests were conducted for zirconia-alumina composites with 5, 15 and 35 vol. % of inclusions. In order to complete these results, Proof Testing was performed for chosen lifetimes and probabilities of survival.

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Effect of fiber volume fraction on directional thermal conductivity in liquid silicon infiltration composites

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Keywords: ceramic matrix composites (CMC), thermal conductivity, LSI (liquid silicon infiltration), fiber volume fraction, flexural strength

Ceramic matrix composites (CMC) were widely used for aerospace and high temperature environment application because of its high thermal and structural stability. Especially, many aerospace vehicles are protected from hot atmosphere during operation and this protective structure needs high thermal conductivity for heat transfer. In case of in-plane thermal conductivity could be increased by using high thermal conductive fiber, however transversal thermal conductivity improvement is very difficult. In this study, LSI (liquid silicon infiltration) process was applied to fabricate CMC and its fiber volume fraction was controlled to improve transversal thermal conductivity. The lower fiber volume fraction the higher thermal conductivity obtained because of high thermal conductivity of matrix such as Si and SiC. However low fiber volume fraction induced poor mechanical properties and high fiber volume fraction induced high residual stress that induced fiber/matrix debonding weakening reinforced fiber during LSI process. The optimum fiber volume fraction with preserving its mechanical and thermal property was deduced by investigating its thermal conductivity (LFA method), mechanical properties (flexural strength), density and microstructure (SEM).

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The effect of kaolin type on properties of metakolin-based geopolymer

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Keywords: geopolymer, kaolin, XRD

Geopolymers are noncrystal alumina silicate polymers that formed with the combination of reactive alumina silicate materials and silicate solutions.[1] The mechanism is constituted on the reaction of different SiO_2-Al_2O_3-Na_2O or K_2O and H_2O ratios. Metakaolin, fly ash, volcanic glass and perlite were used as reactive alumina silicate material. In this study metakaolin based geopolymer mechanism was investigated. Metakaolin was obtained with kaolins which had different physical and mineralogical properties. The physical and mineralogical properties of the kaolins was observed with XRF, XRD, STA, FTIR, SSA and particle size distribution methods.[2] Structural alteration of metakaolins which was obtained with sintering of kaolins 700 °C, 8 h was tested with XRD-FTIR-STA-SEM methods. Particle size distribution, pozzolanic activities, the change of Si/Al and aluminum coordination number was analyzed.

In this work, SiO_2/Al_2O_3: 4 mole, Na_2O /SiO_2: 0.35 mole, H_2O/Na_2O: 18 mole ratio was fixed and according to this situation recipes were prepared to get geopolymer granules. Geopolymer granules were pressed in order to give tile shape, physical and mineralogical analysis were made with this geopolymer tiles. The bending strength of tiles varied with the change of time 1 h, 1–3–7 days of waiting time. Also the tiles were kept in the water and mechanic strength change was observed. Humidity adsorption-desorption performance of the tiles were monitored. The variation between geopolymer structures were introduced with XRD, SEM-EDS, FTIR, surface area and apparent density tests/analysis.

In conclusion metakaolin structures are changed with the kaolins which has different chemical and physical properties. It was found that oxides such as Fe_2O_3 in the kaolin prevents metakaolin formation. Geopolymer properties are affected due to the quartz and hydromica in the structure come up %20 because metakaolin formation is influenced negatively. It was seen that particle size also changes the reaction speed. The variation around the Al affects the humidity control. As a result humidity control was succeeded with all recipes.

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Mechanical properties of alumina carbon refractories with *in-situ* synthesis of Si_3N_4-SiC composite whiskers

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Whiskers or fibers in carbon-contained refractories take effect of the excellent reinforcement and toughness. In this paper, the *in-situ* synthesized mechanics of Si_3N_4-SiC composite whiskers in carbon refractories and their influence on the mechanical properties were investigated. The results showed that the large scale of Si_3N_4-SiC composite whiskers would be generated at 1400 °C and the existence of rare earth La_2O_3 could improve the *in-situ* synthesis of Si_3N_4 whiskers. Meanwhile, their strength could also be increased by above 30% due to the deflection and bridging effect of Si_3N_4-SiC composite whiskers.

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Ultra-fast fabrication of oriented 3C-SiC wafers by halide CVD

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Keywords: 3C-SiC films, halide CVD, orientation, deposition rate (R_{dep}), growth mechanism

Φ80 mm-diameter, highly oriented 3C-SiC wafers were ultra-fast fabricated via halide chemical vapor deposition (CVD) using tetrachlorosilane ($SiCl_4$) and methane (CH_4) as precursors The effects of deposition temperature (T_{dep}) and total pressure (P_{tot}) on the orientations, microstructures and deposition rate (R_{dep}) were investigated. R_{dep} dramatically increased with increasing T_{dep} where maximum R_{dep} was 930 $\mu m \cdot h^{-1}$ at $T_{dep} = 1823$ K and $P_{tot} = 4$ kPa, leading to a maximum of 1.9 mm in thickness in 2 hours deposition. The <110>-oriented 3C-SiC was obtained at $T_{dep} > 1773$ K and $P_{tot} = 1$-4 kPa. Growth mechanism of <110>-oriented 3C-SiC has also been discussed under consideration of crystallographic planes, surface energy and surface morphology. The effects of molar ratio of C and Si precursors ($R_{C/Si}$) on composition, preferred orientation, microstructure and deposition rate (R_{dep}) were investigated. The de-

posits transformed from silicon-rich to stoichiometric 3C-SiC to carbon-rich with increasing $R_{C/Si}$. <110>-oriented stoichiometric 3C-SiC with lower density of defects were obtained at $R_{C/Si}$ in the range of 0.86 to 1.00, where the maximum R_{dep} was 883 µm/h at $R_{C/Si} = 1.00$, leading to a thickness of 1.7 mm in 2 hour deposition. Formation of ridge-like morphology has been discussed based on a twin plane propagation model.

T04: Electroceramics and optical materials

Invited lectures

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All inorganic granular extrinsic multiferroics: from nanomaterial engineering to magnetoelectric coupling

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Keywords: multiferroics, polyol process, Spark Plasma Sintering, nanostructured ceramics

Since the observation in 1888 of a magnetization M in a dielectric material moving into an electric field E and the reverse effect observed in 1905 of an electrical polarization P in a dielectric system moving into a magnetic field H, the research on magnetoelectric materials and devices grew up tremendously. At the 70s, both experiments and theory bring to a saturation point, the scientific community focusing only on single-phase magnetoelectric (ME) materials.[1] In the early 90s, the renaissance of scientific interest into magnetoelectricity took place thanks to the elaboration of multiferroic composites. Combining piezoelectric and magnetostrictive and/or ferroelectric and ferromagnetic nanomaterials in new fancy architectures, gave rise to the observation of higher ME effect at room temperature. Typically, ME coefficient reached 130 mV.cm^{-1}.Oe in granular $CoFe_2O_4/BaTiO_3$ composite[2] while it did not exceed 0.8 mV.cm^{-1}.Oe in Cr_2O_3 single-phase.[3] In this context, we developed an original material processing route to produce such composites, exacerbating the high value of the surface/volume ratio of the involved phases. In practice nanoparticulated composites $BaTiO_3$-$CoFe_2O_4$ (BTO-CFO) in different atomic ratio were prepared by combining polyol method[4] and spark plasma sintering[5]. High dense and ultrafine grained samples were obtained.[6] Their impedance response was measured in the 5 Hz–10 MHz frequency range, under 0–7.5 kOe magnetic applied fields, between 40 and 170 °C.[7] The best agreement to models for the resulting cole-cole plots was achieved by means of three parallel RC arrangements connected in series; by their RC values, these circuits are representative of grain boundaries. An association between each RC circuit and each interface, i.e., BTO-BTO, BTO-CFO, and CFO-CFO, was successfully proposed on the basis of the temperature and magnetic behaviour of the constituting phases.

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SPS derived $CaTiO_3$-based dielectric ceramics with high energy storage density

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Keywords: dielectric ceramics, energy storage, SPS

$CaTiO_3$ is a linear dielectric material with the high dielectric constant, low dielectric loss and a wide band gap, which is a potential candidate for high density energy storage applications. An energy density of 1.5 J/cm^3 was obtained in $CaTiO_3$ ceramics prepared by conventional sintering process, and the dielectric strength was 435 kV/cm. On the other hand, the intrinsic dielectric strength of $CaTiO_3$ was predicted to be as high as 4.2 MV/cm, therefore, much higher energy storage density could be expected. In the present work, the dielectric strength of the $CaTiO_3$ ceramics was remarkably enhanced to 910 kV/cm by spark plasma sintering (SPS), and the corresponding energy density was 6.7 J/cm^3, which was much higher than that prepared by conventional sintering process. This could be interpreted as the result of the lower electrical conductivity and higher thermal conductivity, associated with the finer microstructures in the SPS derived samples. Moreover, the post-breakdown features were motivated to investigate the breakdown process, it turned out that a micro breakdown channel was formed due to the localized high temperature during breakdown process, accompanied by the crack growth, re-crystallization and texture structure. It was suggested that thermal breakdown was predominant in the present ceramics. In addition, the breakdown channel of SPS sample was discontinuous while that was continuous for the sample by conventional sintering process, implying a higher dielectric strength in $CaTiO_3$ ceramics prepared by SPS from the view point of microscopic.

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3D nanoarchitectures for energy energy conversion – enhanced functionality through correlative microscopy

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Complex nano-architectures of various material combinations (e.g. Si-nanostructures such as wires (NW) and cones (NC), GaN nanostructures, transparent conductive oxides e.g. Al doped ZnO, coinage metal nanoparticles e.g. wires, spheres, graphene and other 2D materials) integrated on Si wafer platforms will be presented for light absorption, light emission and sensing applications.

In this context we will show nano-material choices for surface enhanced Raman spectroscopy (SERS) and chemically functionalized SiNWs, SiNCs, GaN NWs with distinct resonances for optical sensing or distinct electrical performance in electrical devices such as resistors.

Materials and device optimization will rely on advanced correlated electron microscopy and optical spectroscopy (CORMIC) containing electron beam induced current (EBIC) measurements, I-V characterization with and without illumination (with tunable power and wavelength) inside a scanning electron microscope (SEM), cathodo-, photo- luminescence as well as in-SEM micro-Raman spectroscopy.

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Compositional tuning of Ba-based ferroelectrics and relaxors

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A- and B-site substitution of barium titanate with homovalent or heterovalent dopants is at the basis of solid solutions that lately found increasing importance for dielectric, piezoelectric, energy storage and microwave applications. High dielectric permittivity – stable over a large temperature range – and large high-field piezoelectric coefficients are typically sought-for figures of merit. Yet, compositional tuning to attain specific properties has been largely based on macroscopic observations and very little is known about the fine material structure on the short range that is necessary to induce those properties. In relaxors, for instance, it is not yet clear whether their peculiar behaviour originates from random electric fields or simple dipolar interactions.

Raman spectroscopy, being sensitive to the material's short range structure, is a very attractive technique to study structure-property relationships in Ba-based ferroelectrics and relaxors. In this presentation, an overview will be given on this technique and on the information it can convey on these systems. It will be shown that the Raman method is complementary to diffraction and macroscopic property measurements, and can add decisive details to understanding the whole picture, especially if coupled with atomistic simulations. We will focus on both A- and B-site substituted $BaTiO_3$ (with Bi and Zr, respectively) and also A- and B-site co-doped systems (with Bi, Yb and Fe).

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Local structure analysis of electroceramics via aberration-corrected scanning transmission electron microscopy

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Keywords: relaxor ferroelectric, STEM

The quantification of local symmetry and structure, as opposed to global averaged structure, is important to the fundamental understanding of structure and properties in many complex oxides. This is particularly important in relaxor ferroelectrics, which contain “polar nanoregions” where local fluctuations in cation composition gives rise to inhomogeneities in local strain and polarization on the nanometer scale. Prior experimental studies have focused largely on x-ray and neutron diffuse-scattering and pair distribution function experiments to understand local inhomogeneities and short-range ordering. While these techniques have been invaluable in furthering our fundamental understanding of polar nanoregions and the nature of relaxor behavior, they provide a statistical average over a large sampling volume and, to date, do not provide correlations with local chemistry. With recent advances in quantitative aberration-corrected scanning transmission electron microscopy (STEM) that enable picometer-scale precision in atomic column positions[1] and the unprecedented spatial resolution and chemical sensitivity of energy-dispersive x-ray spectroscopy (EDS), we are poised to provide *direct* correlations between compositional disorder and local polarization in these complex ferroelectric materials as has been demonstrated recently in lanthanum strontium aluminum tantalate (LSAT).[2] The research discussed in this talk focuses on the application of these techniques to relaxor ferroelectrics, such as lead magnesium niobiate (PMN), to provide spatially resolved quantification of local structure on a unit-cell by unit-cell basis. The use of atom column indexing allows for direct measurement of local displacements within the A and B sub-lattice positions and their local chemistry as evident in local column intensities. Through image simulations we evaluate optimal experimental conditions for, and limitations of, STEM-based measurement for local structure analysis.

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Transparent ceramics and glasses containing $TM^+(RE^+)$ cations: spectroscopy, materials and applications

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Keywords: transparent, ceramics, spectroscopy, transition cations

Many applications (e.g. armor windows, missile noses, optical lenses, hot reactor inspection windows) request robust solid parts exhibiting high transmission in various portions of the NUV-FIR region ($\lambda = 0.1–20\ \mu m$) of the electromagnetic radiation (EMR) spectrum.

A quite large number of inorganic glasses and ceramic (single or polycrystalline) materials contain suitable mechanical, thermal and chemical (stability to environment attack) properties cobined with the required transparency. For other applications, besides transparency in certain spectral domains, controlled absorption of other range(s), or EMR emission at certain frequencies, is needed. For such applications the necessary components are obtained by doping the transparent materials mentioned above with suitable transition metal (TM^+) or rare-earth (RE^+) cations.

Such cations, when present as unwanted impurities, are deleterious to the functioning of many an optical component. In this lecture the way in which the presence of $TM^+(RE^+)$ cations modifies the spectral properties of transparent inorganic solid hosts is reviewed, based on data drawn both from the research of the author and the relevant literature.

First, a brief presentation of the theoretical instruments used for the interpretation of the spectral (optical and magnetical) data is given. Then, examples of the effect of $TM^+(RE^+)$ cations, when present as impurities, are presented. The largest part of the lecture is devoted to the description of selected applications made possible by the spectral features (absorption and emission) of these cations.

The merits of glassy and ceramic hosts, related to these applications, are compared, with a view of determining what can be done to increase the competitivity of the ceramics.

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Exploring relaxor-ferroelectric ceramics for electrocaloric cooling applications

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Keywords: electrocaloric, relaxors, multilayers, microstructure

Increasing needs of society for electricity, heating, or cooling have become a global priority, thus efficient ways of energy production, conversion, storage, and consumption are needed. A contribution to solutions to such problems may be the innovative use of ferroelectric or relaxor ferroelectric ceramic materials in dielectric cooling by exploiting the electrolaloric effect (ECE). The latter is defined as a reversible temperature change in a material upon application of an external electric field at adiabatic conditions. Materials exhibiting a large ECE over a temperature range of a few 10 K close to room temperature include the (1-x) $Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PMN-100xPT) solid solution, especially the PMN-rich compositions with a pronounced relaxor character.

The largest EC temperature changes have been obtained in thin ceramic or polymer films, exceeding for an order of magnitude the highest reported values obtained in bulk ceramics, which is also a consequence of the high breakdown strength of the former. Nevertheless, bulk ceramic cooling elements could be efficiently employed in cooling devices. By introducing multilayer cooling elements, the applied voltages could be even further reduced as compared to diced bulk ceramics.

In the contribution we discuss different effects introduced by processing and evidenced in the microstructure which are reflected in the electrocaloric response of bulk relaxor ceramics. The viability of relaxor ferroelectric ceramic materials in solid-state cooling is assessed both from the points of view of processing and application in demonstrator devices.

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Molecular design of organic ligands for functional inorganic nanoparticles dispersion in organic solvents and polymer

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Keywords: nanoparticle/polymer composite, optical behaviour, interface structure design

In our previous study, TiO_2 nanoparticles modified with a commercial phosphoric acid surfactant can be dispersed in both polar and less-polar organic solvents and polymers. However, the relationship between molecular structure and colloidal stability is not clear and the

structure is not optimized for better dispersion. In this study, we designed and synthesized a series of novel amphiphilic organic ligands with various molecular structure and used them to modify TiO_2, ZrO_2 and Ag nanoparticles. We designed the amphiphilic organic ligands with different lengths of alkyl and ethylene glycol chains and a phosphoric acid group for TiO_2 and ZrO_2, and NH_2 group for Ag. A series of the ligands were synthesized in 3 steps from commercially available alkyl bromides. The modified nanoparticles were aggregated in the aqueous solution, which were then collected by centrifugation and washed with water to remove free ligands and dried in vacuum. The resulting modified nanoparticles were then dispersed in several organic solvents to study the relationship molecular structure and colloidal stability. We discovered the optimum lengths of alkyl and ethylene glycol chains to disperse TiO_2 nanoparticles into various polar and nonpolar organic solvents using sonication. Furthermore, this optimum ligand modified TiO_2 nanoparticles were able to be uniformly dispersed into polymer.in high concentration.

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Local field engineering for tailoring electrical properties in ferroelectric-based composites

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The interfaces between regions with contrasting permittivities in composites modify the local field distribution. The effective macroscopic properties of composites are a result of this local field inhomogeneity and therefore, the properties of ferroelectric-based composites can be tailored by controlling the microstructure characteristics (local field engineering) or by adequate choice of the phase constituents and phase interconnectivity. This approach can be applied to design ferroelectric-magnetic composites with specific dielectric/ferromagnetic properties. Since the local field inhomogeneity increases when the difference in permittivities of the constituent phases is higher, porous ferroelectric structures ensuring a maximum permittivity contrast have a great potential in order to reach desired ferro/dielectric properties, although porosity is usually considered detrimental in electroceramics.

Based on this idea, 3D FEM models have been developed to compute local field distributions in realistic microstructures in order to explore the possibility to maximize their ferroelectric (switching) or non-linear dielectric responses (tunability). The role of nanostructuring and of porosity on the macroscopic properties (effective permittivity, tunability, P(E) hysteresis loops) were studied theoretically and validated for BaTiO3 nanostructured ceramics, for a few types of PZT ceramics with various porosities, including anisotropic, and for PbTiO3 films with vertical nanoporosity. As a first step, different realistic 3D microstructures were generated. Local field distributions were computed by 3D FEM calculation and used as inputs in switching (Preisach) or tunability (Johnson) models, in order to derive the ferro/dielectric and tunability responses. If properly engineered in well-controlled microstructures, porosity may be used as an elegant factor to enhance functionalities as result of the field concentration in specific regions.

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Sucking the heat out of ceramic processing

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For over 30,000 years, the general practice of sintering ceramics has involved a high temperature thermal treatment to drive the transport processes to densify the particles and minimize the surface energy of the material. Typical sintering temperatures consider 0.6 to 0.8 of the melting temperature (T_m) for many oxides; this means we sinter around 800 °C to 1200 °C for 2 to 10 hours. Here we introduce a broad body of systems that utilize a transient aqueous based liquid phase (1 to 10 wt%) that sinters under a uniaxial pressure, while being heated from room temperature to 250 °C, over a time period of 10 to 60 minutes. During this process, there are all the aspects of liquid phase sintering, namely particle rearrangement, dissolution precipitation, and grain growth. We believe transport processes are enhanced through mechanisms such as diffusiophoresis, which in turn is driven by concentration gradients. This phenomenon has very fast transport velocities, and therefore does not require high temperatures ~ 10 micrometers/sec. The driving for precipitation is also enabled by the transient evaporation of the water and a sustained supersaturation under local hydrothermal conditions. These mechanisms work together to create a pathway to sinter ceramics under extremely low temperatures and fast times; many of the systems that we will show are sintered at 120 °C, 15 minutes, under 300 MPa uniaxial pressure. We have termed this fabrication method the Cold Sintering Process (CSP). We fully realize that there are many subtle differences in the CSP of each system, but as this is the start of a new approach, we will share our qualitative understanding, as determined from microstructural observations. We have also benchmarked and compared properties where possible, and it will be seen that the properties are in comparison to conventionally processed materials; we will in particular contrast conduction and dielectric properties.

Given the massive drop in sintering temperature of the ceramic, this offers many new opportunities in material design, especially in composites. We will show three different types of polymer ceramic composites with high percentages of ceramic, 100% to 60%, with the thermoplastic polymers for dielectric applications, ionic electrolytes, and semiconducting composites. We will also show preliminary data with CSP with multilayer ceramics and printable electronics.

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Static and dynamic magnetoelectric coupling in multiferroic hexaferrites

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Keywords: magnetoelectric effect, multiferroics, hexaferrites, electromagnon

The static magnetoelectric (ME) coupling, which is responsible for the magnetic-field-induced electric polarization or the electric-field-induced magnetization, is well understood in terms of symmetry.[1,2] Several microscopic models were proposed to explain the observed ME effects.[1,2] In some hexaferrites, i.e. iron-containing oxides with hexagonal crystal structures, a ferroelectric polarization was observed due to conical spin arrangements in external magnetic field at temperatures close to the room temperature,[3] and even without external magnetic field after a proper ME poling.[4] The existence of the polarization can be explained by the inverse Dzyaloshinskii-Moriya interaction.

Multiferroics combining magnetic and electric ferroic orderings also exhibit dynamic ME effects, which are represented by electromagnons, i.e. electric-dipole active collective spin excitations. Interestingly, the oscillating electric polarization emerging via the electromagnons usually appears in the direction perpendicular to that of the static polarization. We observed such effect in the Y-type hexaferrite $BaSrCoZnFe_{11}AlO_{22}$ and in the Z-type hexaferrite $(Ba_{0.2}Sr_{0.8})_3Co_2Fe_{24}O_{41}$.[5] Although the static polarization lies in the hexagonal plane, we detected electromagnons polarized along the hexagonal axis. The electromagnons are active already in zero magnetic field and they disappear from the THz spectra at higher magnetic fields (2–4 T), due to a change of the magnetic structure. The mechanisms of the electromagnons' activation will be discussed.

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Complex thin and ultrathin films through solution synthesis

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Solution based synthesis routes using metal alkoxides and organically coordinated metal salts have been used to prepare complex oxides, nano-composites and nano-structured metals. Oxides of varying complexities including doped and non-doped Fe_2O_3, TiO_2 and ZnO, as well as spinels and perovskites have been prepared in the forms of thin- and ultra-thin films on flat and nano-structured surfaces including wires and porous nano-structures. Further, synthesis routes using organically coordinated metal salts developed to yield thin or ultra-thin films and coatings of metals and metal-in-oxide nano-composites have been developed and will be described. Synthesis of metals with crystallite sizes below 10 nm, as well as ultra-thin coatings at temperatures in the range 150–500 ^oC have been achieved. Similar salt based systems were also used for synthesis of thin- and ultra-thin metal-in-ceramic composite films with metal particle sizes down to a few nm and loadings of up to over 80%. The influence of the precursor, reaction kinetics and thermal treatment will be discussed in relation to the structures and properties obtained, as well as the possible synthesis of oxides with extended, metastable doping-levels. The syntheses and products were studied with a wide array of analytical techniques including; SEM, TEM, XRD, TGA, DSC/DTA, IR and Raman spectroscopy. Such simple low cost synthesis routes to highly complex nano-materials are required for practical application in many areas of sustainable energy conversion and storage, catalysis and magneto-electric applications.

Oral presentations

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Investigation of crystal structure and magnetic properties of Ba and Nd co-doped $BiFeO_3$ multiferroics at morphotropic phase boundaries

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To investigate the crystal structure and magnetic properties Ba and Nd co-doped $Bi_{0.8}Ba_{0.2-x}Nd_xFeO_3$ (with x = 0.5, 0.1, & 0.15) multiferroics were synthesized by solid state reaction method. The crystal structure (as evaluated by Rietveld refinement of XRD patterns through FullProf Suite) of the samples is found to exhibit mixed symmetry in all three compositions. With x = 0.05, the best fits were obtained with mixed symmetry of rhombohedral R3c (≈61%) and triclinic P1 (≈39%), while at x = 0.10 the phase fraction changes to 51% R3c and 49% P1. In the next composition with x = 0.15, the structure changes to mixed rhombohedral R3c (≈88%) and orthorhombic Pnma (≈12%). The reason of such phase transition may again be attributed to the mismatch in the ionic sizes of Ba^{2+} and Nd^{3+} in place of Bi^{3+} ion. This results in disturbance of FeO_6 octahedra and eventually in the phase transformation. Change in the magnetisation is observed with increasing Nd content. It has been well established by the previous reports that Ba doping destroys magnetisation in $BiFeO_3$ by distorting the inherent spirally modulated structure of spins which in turn locks the linear magnetisation. The doping of smaller sized Nd ion which causes the reorientation of magnetic dipoles may associate different grounds for magnetisation via the in homogeneity in Ba doped $BiFeO_3$.

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Dielectric properties and interface effects in multilayer $BaTiO_3/NiFe_2O_4$ multiferroic thin films

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Design and development of new materials have always been a base for new achievements in modern technology. Composite multiferroic materials are a unique group of materials with application in microchip components with a unique ability to exhibit more than one ferroic property, and most importantly produce interaction between two phases giving rise to magnetoelectric coupling effect. In this research dielectric behavior of multilayer thin films composed of ferroelectric $BaTiO_3$ and ferromagnetic $NiFe_2O_4$ phases, obtained by obtained by spin coating, have been analyzed at increased temperatures (30–200 °C) in frequency range from 100 Hz to 1 MHz. Characterization of different layer geometries have shown complex influence on dielectric constant and loss tangent. Values of dielectric constant on room temperature were almost constant and relatively low in whole frequency range, along with very low loss tangent. Temperature induced charge transfer gradually increased loss tangent, especially in frequency region below 10 kHz, as well as higher dielectric constant due to charge accumulation on interfaces, closely resembling Debye behaviour. The conductivity of multilayer films was limited by highly resistive titanate layers and fetire/titanate interfaces.

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Dielectric and energy storage properties of $Na(Nb_{1-x}Ta_x)O_3$ ceramics prepared by spark plasma sintering

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Keywords: $Na(Nb_{1-x}Ta_x)O_3$, spark plasma sintering, dielectric and ferroelectric properties, energy storage

$Na(Nb_{1-x}Ta_x)O_3$ (x = 0.2, 0.4, 0.6, 0.8) ceramics were prepared by spark plasma sintering (SPS). The structure and microstructure were characterized by XRD, SEM, TEM and XPS analysis. The dielectric and energy storage properties were investigated by impedance analyzer and ferroelectric analyzer. Single phase and dense $Na(Nb,Ta)O_3$ ceramics could be obtained by SPS. Reduction of Nb^{5+} was confirmed in Nb-rich compositions. The Tc temperature decreased with the increased of x. Weak double P-E loops could be observed for x = 0.4 and x = 0.6 compositions. The x = 0.8 composition demonstrated incipient ferroelectric characteristics. The temperature dependent dielectric permittivity exhibited hysteresis for x = 0.2 and x = 0.4 compositions. The dielectric loss decreased with the increase of x. The energy storage properties were improved with the increase in Ta content. Maximum energy density of ~0.90 J/cm^3 could be obtained for x = 0.6 composition with the BDS of 159 kV/cm and efficiency of 87.5%.

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Integration of screen-printed tunable BST thick films in LTCC modules for microwave applications

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Reconfigurable microwave components play an important role in modern communication systems to meet the increasing demands for functionality and flexibility of the systems. Various technologies, such as semiconductor technology, microelectromechanical systems (MEMS) or ferroelectric thin and thick films, are suitable for the realization of tunable microwave components. Ferroelectric materials are characterized by high tuning speeds, negligible power consumption and low manufacturing costs. In particular, ferroelectric thick films based on barium strontium titanate ($Ba_xSr_{1-x}TiO_3$, BST) are promising systems for use in the frequency range up to approx. 12 GHz. However, due to the high sintering temperatures above 1100 °C for pure BST thick films, the fabrication of tunable components based on silver or gold electrodes is limited to planar structures, which are applied after the sintering process.

In this presentation, it will be shown the development of BST-ZnO-B_2O_3 composite materials for reducing the sintering temperature to 850–900 °C. Furthermore, the material and component properties of these composites or rather corresponding MIM (metal-insulator-metal) varactors are presented and compared to planar-structured varactors. The LTCC integration potential of such fully screen-printed MIM varactors based on the developed low sintering BST composites are investigated by the fabrication of phase shifters embedded in LTCC modules.

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Transparent Cr:YAG ceramics: role of Cr_2O_3 and co-dopants on the reactive sintering

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Keywords: reactive sintering, transparent ceramics, Cr:YAG

Polycrystalline transparent ceramics have received considerable attention due to their applications as high-power laser gain media. Indeed, ceramics can be easily fabricated in relatively large size and/or with complex architectures.[1] In addition, these materials can incorporate high amount of luminescent dopant. The flexibility of ceramic processes allows new designs for laser amplifying media architecture to improve their thermo-optical efficiency.[2] According to this approach, the present study concerns the manufacturing of Cr^{4+}:YAG ceramic which could be used as a saturable absorber (passive Q-switch) for high peak power pulsed laser operation.

Since a Q-switch effect has been observed for a long time with a Cr^{4+}:YAG single crystal,[3] few recent works dealed with the elaboration of Cr^{4+}:YAG ceramic, which can be considered as a promising component for high peak power pulsed lasers. In YAG crystalline matrix, Cr^{4+} ions are preferentially substituted to the Al^{3+} ions and co-dopants have to be used for charge balance. Ca^{2+} and Mg^{2+} are the most common co-dopants to ensure Cr^{4+} stability within the YAG matrix.[4,5]

In this context, this study focused on the understanding of the role of Cr_2O_3 and co-dopants (CaO and MgO) during sintering. The corresponding sintering maps (densification as function of the microstructure evolution) were built as a function of the composition of YAG ceramics. Spectroscopic characterizations were also conducted to determine the respective amount of Cr^{3+} and Cr^{4+} ions in transparent material so-obtained.

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High-frequency dielectric spectra of $BaTiO_3$-$PbMg_{1/3}Nb_{2/3}O_3$ ceramics

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Keywords: dielectric spectroscopy, ferroelectric ceramics, phase transitions

Dielectric spectra of the high-density perovskite ceramic solid solutions of $(1\text{-}x)BaTiO_3$-$xPbMg_{1/3}Nb_{2/3}O_3$ (BT-*x*PMN, $x = 0.075, 0.10, 0.15$) prepared by a two-step conventional solid phase sintering process[1,2] were studied in the high-frequency, microwave and THz ranges (10^6–10^{12} Hz). Dielectric dispersion was observed at all temperatures from 100 to 450 K in the whole investigated frequency range. In contrast to relaxor ferroelectric PMN[3], the $\varepsilon'(T)$ maximum does not shift remarkably with increasing frequency up to 1 GHz. The main dispersion takes place in the 10^9–10^{12} Hz range, similar to that in the ferroelectric BT ceramics. THz spectra show presence of the relaxation (central) mode besides the soft phonon one, similar to that observed in the tetragonal BT[4] and PMN.[3,5] Dielectric spectra of BT-*x*PMN are analyzed and compared with those of BT ceramics and PMN single crystals.[3] Origin of the microwave dielectric dispersion is discussed in the framework of relaxor behavior, diffuse phase transition and concept of polar nanoregions.

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The magnetic formation in oxide semiconductors under influence of native defects and impurity atoms concentration

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Keywords: magnetotransport, oxide semcionductors

The control of native defects and impurity atoms concentration in the lattice manage the electrical, optical and magnetic properties of semiconductors use in technology. The native defects, forming the shallow energy levels that lead the physical properties, can be defined as cation or anion vacancies, anti-site located host atoms and interstitial atoms.[1–3]

The wide band gap transparent conducting oxides, such as ITO, ZnO, SnO_2, TiO_2, etc., are intensively investigated structures in technological usages. Additionally, the dependence of magnetic structure on point defects is an important focus area in especially oxide semiconductors. The magnetic semiconductors created by doping a few percent of transition metals are known as diluted magnetic semiconductors (DMSs). Doping with transition metals, in addition to defects in the lattice, is also known to be a necessary variable in oxide semiconductors in order to generate magnetization and thus polarized spins currents. Many theories on ferromagnetism defininion in oxide semiconductors are the strong exchange coupling between 2p levels of oxygen and d levels of transition metals, transitions between different valance states of transition atoms, shallow donors due to s-d interactions in n-type doping and hybridization between the impurity bands of defects and 3d bands, known as d^0 ferromagnetism.

In this study, solid state reaction technique and RF magnetron sputtering were used to synthesize oxide semiconductors ($(Zn_{1-x},Co_x)O$ and $(Zn_{1-x},Co_x)Ga_2O_4$ (x = 0.05, 0.10 and 0.20)) as powders and thin films, respectively. The characterization of the particles was also improved using X-ray photoelectron spectroscopy (XPS), RAMAN and Fourier transforms infrared (FT-IR) spectroscopy measurements. The optical analyses were done with UV-visible spectroscopy. Furthermore, the study is improved on understanding the magnetic formation depending on Co atoms in both tetrahedral and octahedral sides in ZnO and $(Zn_{1-x},Co_x)Ga_2O_4$ (x = 0.05, 0.10 and 0.20) structures. The effects of substituted Co atoms to magnetic character were analyzed using Curie-Weiss law. The magnetic change was related to the high Co amount in tetrahedral side which increasing the number of antiferromagnetic couplings.[2–4]

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Phase transitions and polar order in $BaCe_xTi_{1-x}O_3$ (x = 0.02 – 0.30) ceramics

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The incorporation of homovalent M^{4+} ions at the Ti site of $BaTiO_3$ with formation of the $BaM_xTi_{1-x}O_3$ solid solutions (M = Sn, Zr, Hf, Ce) determines interesting modifications of the phase transitions, polar order and functional properties. In particular, an evolution of the polar order from conventional ferroelectric to diffuse phase transition behavior and to relaxor state is observed with increasing x. Unlike the systems containing Sn and Zr, Ce-doped barium titanate ceramics have not been fully investigated despite the potential applications as lead-free dielectric and piezoelectric materials.

Dense (97–99% rel. density) ceramic samples with composition $BaCe_xTi_{1-x}O_3$ (x = 0.02, 0.05, 0.06, 0.10, 0.12, 0.15, 0.175, 0.20 and 0.30) were prepared by the conventional solid-state route starting from fine precursor powders and sintered at 1450–1500 °C. The average crystal structure at different temperatures in the range 100–400 K has been determined from the Rietveld refinement of high-energy X-ray diffraction data collected at ESRF. The pair distribution function analysis has been used to investigate the local structure and the level of disorder. The phase transitions and the evolution of polar order with composition have been studied using dielectric permittivity measurements at 100 Hz-1 MHz between –150 and 150 °C, variable temperature Raman spectroscopy (from –195 to 165 °C) and differential scanning calorimetry (–100–150 °C). Overall, the data provide a detailed picture of the $BaCe_xTi_{1-x}O_3$ system and a tentative composition-temperature phase diagram will be proposed. The results indicate that the three transitions (rhombohedral/orthorhombic, orthorhombic/tetragonal and tetragonal/cubic) meet at a critical point located at $x \approx 0.10$ and T = 115 °C. Relaxor behavior is observed at $x \geq 0.20$. In contrast to the homologous systems $BaSn_xTi_{1-x}O_3$ and $BaZr_xTi_{1-x}O_3$, a diffuse ferro/para transition is already observed at x = 0.05 as a consequence of the high level of lattice disorder.

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Size effects of BiT template on piezoelectric properties of textured BNKT ceramics by screen-printing method

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Keywords: $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$, $Bi_4Ti_3O_{12}$, topochemical microcrystal conversion, reactive-templated grain growth

The size effect of templates on the texturing and piezoelectric properties of textured $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ (BNKT) ceramics prepared by reactive-templated grain growth (RTGG) process using different sizes of $Bi_4Ti_3O_{12}$ (BiT) template was investigated. The BiT template was synthesized with 3 different sizes of 1.86, 4.37 and 10.31 um by molten-salt synthesis at 3 different heating conditions. BiT templates were aligned in a matrix powder by screen-printing process. Chemical reaction between the BiT template and the matrix powder during calcination produced BNKT composite consisting of aligned plate-like BNKT templates and randomly distributed BNKT matrix powders. Textured BNKT ceramics were prepared by sintering the BNKT composite at 1150 °C for 4–50 h. The piezoelectric constant of textured BNKT was dependent on the size of template due to the sintered density and grain orientation factor. The grain orientation factor was increased while the sintered density was decreased as increasing the size of BiT template. Regardless of sintering time, textured BNKT ceramics prepared by 1.86 um BiT template exhibited higher piezoelectric constant than that of non-textured BNKT ceramics. Piezoelectric constants of textured BNKT ceramics prepared by 4.37 and 10.31 um BiT templates were lower than that of non-textured BNKT ceramics when the sintering time was 4 h while they were higher than that of non-textured BNKT ceramics when the sintering time was longer than 20 h. In order to prepare textured BNKT with high piezoelectric constant by improving grain orientation factor, larger BiT templates are favourable but, in this case, advanced sintering process to get high sintered density is needed.

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Influence of yttria doped thoria microstructure on its compatibility with liquid sodium

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Keywords: ASTRID, electrochemical sensors, yttria-doped thoria, synthesis, oxides, sintering map, sodium, impedance spectroscopy

In the framework of the development of the fourth generation of nuclear reactors, a Sodium cooled Fast Reactor (SFR), named ASTRID (Advanced Sodium Fast Reactor for Industrial Demonstration) is planned to be operated in France in the 2020s.

The sodium coolant in SFR must have specified oxygen content in order to control the corrosion of the steels structures of the core (claddings…). Electrochemical sensors allow to obtain a fast and specific measure in complement to other devices (plugging indicator). The solid electrolyte has a fundamental role in the performance of the sensor. It should be compatible with sodium at high temperature (about 400 °C), mechanically resistant and a purely ionic conductor. Yttria-doped thoria (i.e. $Th_{1x}Y_xO_{2-x/2}$) is well known as a potential electrolyte material to be used in liquid sodium, provided its microstructure is controlled: low impurity content, small grain size, high density...

The preparation of several $Th_{1-x}Y_xO_{2-x/2}$ ceramics was undertaken from oxalate precursors to assess the influence of yttrium content on the material microstructure[1]. The sintering of the oxide samples, obtained after a heat treatment at 600 °C of oxalate powder was investigated to create sintering maps of $Th_{1-x}Y_xO_{2-x/2}$ by correlating the average grain size and the relative density values. Theses maps show the different behaviour of the yttrium content on the final microstructure of sintered thorium-yttrium oxides. Yttrium doping prevents the grain growth, as the lowest yttrium content samples exhibit higher grain sizes. Impedance spectroscopy measurements show that the electrical conductivity increases with the yttrium content up to 8% and then decreases for the highest doping value (22%).

In addition, the study of the compatibility of the ceramic with liquid sodium (100 hours at 500 °C) shows a good chemical and mechanical resistance whatever the yttrium content considered.

Finally, electric characterizations, provided by impedance spectroscopy, before and after the different compatibility tests revealed a significant variation of the conductivity on the grain boundaries while the conductivity response due to the grain were relatively the same.

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High transmittance infrared ray ZnS lens prepared by hot pressing using homogeneous cubic ZnS nano-powders

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Keywords: hydrothermal method, ZnS, cubic, hot pressing, IR lens

ZnS nanoparticles with various S/Zn ratios of 1.0~1.8 were synthesized using hydrothermal treatment at 220 °C for 12 h and they were sintered using hot pressing under vacuum for the application to the infrared ray lens. Crystal structure and grain morphology of ZnS nanoparticles were investigated using XRD, SEM and TEM analysis. The homogeneous cubic ZnS nanoparticles were formed in the specimens synthesized with S/Zn ratio of 1.3 under reaction temperature of 220 °C and the average size of these ZnS particles was approximately 50 nm. The optical properties of the ZnS nanoparticles with various S/Zn ratios were also measured. A photoluminescence (PL) emission peak appeared at 495 nm for the specimen with low S/Zn ratio of ≤ 1.0 due to sulfur vacancies. However, the specimens having high S/Zn ratio of ≥ 1.0 showed a PL emission peak at 520 nm due to the presence of elemental sulfur species. In this work, these ZnS nanopowders were sintered via hot pressing under vacuum at various sintering conditions and their microstructural and optical properties were investigated. Moreover, the commercial ZnS powders were also sintered using hot press under vacuum and their microstructures and optical properties were compared with those of the specimens prepared by ZnS nanopowders.

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Field-induced metastable ferroelectric phase in PLZT ceramics

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Keywords: antiferroelectricity, ferroelectricity, field-induced antiferroelectric to ferroelectric transition

The polarization–electric field *P(E)* dependence of antiferroelectric (AFE) $Pb_{0.97}La_{0.03}(Zr_{0.9}Ti_{0.1})_{0.9925}O_3$ (PLZT 3/90/10) ceramic indicates that the AFE phase can be turned into a ferroelectric (FE) one. The FE phase can be maintained at room temperature after removal of the electric field and it shows a remanent polarization P_r of 30 μC/cm^2 and a piezoelectric constant d_{33} = 100 pm/V.[1] XRD analysis on virgin and poled ceramics evident a field-induced phase transition during AFE-to-FE switching. It is of high scientific significance and potential technological impact to clarify the temperature stability of the induced FE phase. Dielectric and temperature dependent *in situ* X-ray diffraction techniques were employed to study the phase transition of virgin and poled PLZT 3/90/10 ceramic during heating from room temperature up to 300 °C. When compared with the virgin sample, in addition to the AFE-PE dielectric maximum, an anomaly was observed in the dielectric properties of poled ceramic. This anomaly is observed at much lower temperatures with respect to the Curie range. *In situ* temperature XRD data evident that the AFE phase recovered from FE phase in the same temperature range. Thus, this dielectric anomaly corresponds to the AFE-to-FE temperature induced phase transition. The temperature-induced FE-AFE transition is diffuse and it takes place in the broad temperature range of (72–124 °C). Therefore, the field-induced FE phase loses its stability and transforms back into AFE state when the temperature increases from room temperature to 124 °C.

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Effect of porosity on the dielectric, switching and DC-tunability properties of $BaTiO_3$ ceramics

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Materials with controlled porosity exhibit special properties that usually cannot be achieved by their conventional dense counterparts. Porous materials find nowadays many applications especially for environments where high temperatures, extensive wear and corrosive media are involved as well as for advanced applications as magnetoelectric, piezoelectric energy harvesting device. The advantages of using porous ceramics in these applications are usually the high melting point, tailored electronic properties and wear resistance in combination with the features gained by the replacement of solid material by voids in the component. The functional properties of the porous ceramics can be tailored for each specific application by controlling the composition, type of porosity (open or closed), pore size distributions, pore morphology and interconnectivity

Starting from this idea, our theoretical approach based on Finite Element Method (FEM) calculations[1] demonstrated that porous ferroelectrics might show promising tunability properties for applications in wireless technology. Using this approach, we proved that the case of porous ferroelectrics with closed porosity is the best solution to fulfil the tunability requirements (low losses: $\tan\delta < 3\%$, high tunability and moderate permittivity $\varepsilon < 1000$), because the tunability is very sensitive to the dielectric permittivity of constituents.[2] For this reason, the highest contrast between dielectric phase permittivity (1 for pores) and permittivity of regions (thousands in case of paraelectric/ferroelectric matrix) ensures highest local field inhomogeneity and strongly enhance the nonlinear dielectric response.

The aim of the present work was to investigate in a systematic way the role of the pores concentration and phase interconnectivity (0–3, 3–3 and 1–3) on the functional properties of $BaTiO_3$ porous ceramics. The obtained results show that by increasing porosity a systematic reduction of permittivity was obtain, while the tunability is almost constant. The results were explained using the concept of local field engineering, in order to propose new porous configurations with improved tunable properties.

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Textured PMN-PZT piezoelectric ceramics for high power applications

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Keywords: piezoceramics, texture, PMN-PZT, ultrasonic motors

High power piezoelectric materials combine “hard” and “soft” electrical characteristic for device applications such as ultrasonic motors, transformers and medical ultrasound. Therefore, piezoelectric materials with a high mechanical quality factor (Qm) is desirable to meet the high power requirement, and high piezoelectric constant and electromechanical coupling are required for improved strain performance.

In this study, combination of two approaches has been used to obtain the high power characteristics, namely; texturing to increase “soft” characteristics and Mn-doping to obtain “hard” characteristics. Textured $0.4Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.25PbZrO_3$-$0.35PbTiO_3$ (PMN-PZT) piezoceramics with properties that are comparable to single crystals in certain crystallographic directions were synthesized by Templated Grain Growth (TGG) method using $BaTiO_3$(BT) template particles.

Textured PMN-PZT ceramics with Lotgering factors of up to 0.85 and with % 1.5 mol MnO_2 doping exhibited hard and soft combinatory properties with piezoelectric coefficients of d_{33} = 600 pC/N, k_p=0.78, tanδ=0.3 %, K^T=1320 and Q_m=550. The high power performance of textured PMN-PZT was also successfully demonstrated in an ultrasonic motor with a cubic and a hexagonal stator geometry.

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Structural and electrical characterisation of composite humidity fibre sensors prepared by electrospinning

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Keywords: humidity sensing, composites, impedance spectroscopy, electrospinning, fibres

The changes observed in a ceramic metal oxide impedance sensor exposed to a certain moisture concentration, are a key role in the determination of its potential use for humidity measurements: furthermore, the sensitivity of the ceramic sensor is influenced by the microstructure, *viz.* higher surface area, and surface reactivity with the relative humidity (RH). If the sensitivity of these sensors depends on the microstructure, then their composition is a strategic tool to improve their response. The electric conduction mechanisms of the impedance humidity sensors can be either ionic, either electronic, or mixed: the mixed ones may have higher activity, and sensitivity. In a recent work by Farahani et al.[1], a survey regarding moisture sensing was presented: in addition to the electrical behaviour of several semiconducting oxides, other aspects were reported: for instance, methods for optimization of the microstructure of sensors, usage of dopants or hybrid compositions on the sensing ceramic-based materials, fabrication techniques for producing sensors, and so on. With the study of composite/doped materials, a better sensitivity of these sensors is aimed, comparing with the ones made out of a unique metal oxide, due to the modifications established by the atomic disposition of a more complex structure. In fact, the electrical response of a ceramic, is not only affected by water adsorption on the oxide surface[2], but also by factors such as stress-strain and atomic defect distribution: so in the case of dominant single covalent/ionic adsorption, if some of the positions initially occupied by atoms of one metal are now occupied by atoms of another metal, the material electrical response to humidity is altered (the electronegativity of the occupying metal atoms may be used to regulate the sensitivity). In this work, the authors report on the electrical response to moisture of sensors based on theTiO_2:WO_3 pair doped with different proportions of V_2O_5: thick films with two different number of electrospun layers and sintered at 500 ºC were prepared and characterised. The dependence of their complex impedance spectra, measured in the range 400 Hz–40 MHz, on the relative humidity (RH) is shown and discussed. Sensors structure was studied by means of several techniques (SEM, X-ray diffraction, Raman spectroscopy) and is debated: explanations for the found sensors microstructure and the observed electrical response relation, are advanced.

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Antiferromagnetic crystal size dependence in exchange-biased nanostructured ceramics

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Keywords: permanent magnets, exchange-bias, Spark Plasma Sintering, nano-structured ceramics

The present research highlights the importance of antiferromagnetic phase crystals size in establishing the exchange-bias inside nanostructured ceramics. Two different ferromagnetic (FM) – antiferromagnetic (AF) systems were studied in order to compare their microstructural and magnetic features. In both cases, Fe_3O_4 was used as FM phase, while the AF one was varied between CoO and NiO. In both systems the mass ratio of FM and AF phases is about 75% and 25% respectively. Firstly, exchange-biased FM-AF core-shell nanoparticles (NPs) were synthesized using the polyol method that is a soft chemistry route known to be efficient for seed mediated growth of nanocrystals in solutions.[1] Then, the NPs were consolidated by Spark Plasma Sintering (SPS); this technique was performed within optimized conditions, which allowed keeping nano-structuration inside the final ceramic.[2] The microstructural analysis on powders and sintered ceramics shows that the epitaxy between the FM and AF phases of core-shell NPs is kept after sintering, as well as the massive ratio composition adopted for synthesis precursors. Nevertheless, the mean crystals size obtained for NiO is considerably smaller than the CoO one also after sintering. The mean size of NiO crystals was observed by High Resolution Transmission Electron Microscopy (HR-TEM) to be smaller than 10 nm in the ceramic sample. Contrary in the case of CoO, grains of about 50 nm are observed in the ceramic. The magnetic characterisations show evidences of exchange-bias only in the Fe_3O_4-CoO system. This result is in agreement with the microstructural observations and allows concluding that Fe_3O_4-NiO system is not favourable to create a spin coupling between FM and AF phases. The small NiO domains size leads to stressed NPs surface that affect the AF spin ordering of NiO in this region and thus the magnetic interactions between adjacent phases.

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Electrocaloric stability of relaxor multilayer elements

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Keywords: electrocaloric, multilayer, relaxors, fatigue, PMN

Electrocaloric (EC) effect is an adiabatic temperature change induced in a polar material by application or removal of an external electric field.[1] Therefore it has a potential for exploitation in cooling applications, especially where small and energy efficient devices are needed. The highest temperature changes (~4 K) were measured in relaxor ferroelectric or ferroelectric bulk ceramics at very high electric field amplitudes, i.e., in the range of 150 kV/cm, quite close to the dielectric breakdown.[1] Since in an EC cooling device the electric field will be applied and removed numerous times, it is crucial to investigate the stability of EC effect during high electric field cycling. The fatigue phenomena or deterioration of material properties with electric field cycling is well-known in the field of ferroelectric actuators, but according to our knowledge the studies on the EC fatigue have not been realized yet. Moreover the fatigue investigation of the EC materials should be conducted at the conditions which are representative for a real device, e.g., such as reported by Plaznik et al.[2]

In this contribution we report on the investigation of the stability of the EC effect with electric field cycling performed on a relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$. The samples were prepared in the form of multilayer (ML) elements, in which five ceramic layers with the thickness of 32 μm are separated by platinum electrodes of about 4 μm, following the procedure described in Fulanović et al.[3] By using ML elements the thickness of individual layers was reduced in comparison to diced bulk ceramic samples, which resulted in lower applied voltages. The electric field cycling at the amplitude of 110 kV/cm was carried out with a step signal and the frequency of 2 Hz, while 5 mHz was used for control measurements.

The results are presented as the measured temperature change versus the number of electric field cycles. The initially measured EC temperature change of 1.45 K decreased only by 0.01 K after 10^6 cycles. In addition, the temperature dependant dielectric permittivity and polarization versus electric field were measured prior and after cycling, exhibiting slight changes. The microstructure of the cycled element was analysed with scanning electron microscope and no evidence of microcracking could be detected.

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Milling and quite-fast sintering as key production steps to obtain fully dense PZTN-CF particulate composites

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Keywords: multiferroic particulate composites, PbO loss, quantitative XRD

In the near future (within ten years) magnetoelectric multiferroics could be implemented into the emerging technologies such as wireless power, internet of things, machine-to-machine communication services, mesh network, etc. Remarkable efforts have been done to develop laminated bi-layer and multilayer multiferroic composites as bulk or thin films. These structures lead to remarkable magneto-electric coupling coefficients of a few Volts / cm·Oe because the ferroic layer is a “full dielectric” which can be completely poled in the conventional way. On the other hand in the particulate ceramic composites the requirement for “full dielectric” is no longer applicable, since the ferroic phases are fully separated within the composite. The strengths of particulate ceramic composites are low cost, simple production technology, higher strain mediated magneto-electric coupling (since electric order phase/magnetic phase interface density can be higher) and easy control of electrical and magnetic properties if the ferroelectric phase (generally a perovskite) and the ferromagnetic one (a ferrite with spinel structure) are mixed in a favourable proportion under the percolation threshold of the ferromagnetic phase.

A great research effort is in progress to improve the fabrication of PZT–$CoFe_2O_4$ (PZT–CF) composites in order to avoid the unwanted reactions, which occur during densification of PZT–CF materials at 1100–1200 °C, and to achieve the electric saturation during the poling. Up to date, by setting a quite-fast sintering, full densification and prevention of unwanted reactions were achieved for the PZT:CF 74:26 composites,[1] but achieving electric saturation is still a challenge. Further important results were: the understanding that the main cause of reactions is the PbO loss;[1] the proposal of an equation to calculate the PbO loss through XRD analysis, considering the amount of ZrO_2 and variation of perovskite’s tetragonality;[1] and the ability to design the ceramic process (milling of the CF powers in particularly) to control the CF grain size distribution, which can be mono- or bi-modal, and overgrowth.[1,2]

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Photoluminescence of Eu^{3+}/Eu^{2+} doped glass microspheres in the system Y_2O_3-Al_2O_3 with eutectic composition

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Keywords: aluminate glasses, YAG, Eu^{3+}/Eu^{2+} doped glass, photoluminescence, lifetime, phosphors, pc-WLED

The Eu^{3+} doped glasses in the Y_2O_3-Al_2O_3 system with eutectic composition (76.86 mol. % (60 wt. %) Al_2O_3 and 23.13 mol. % (40 wt. %) Y_2O_3, corresponding to ~50 mol. % of YAG and ~50 mol. % of Al_2O_3) were prepared by flame-spraying synthesis in the form of glass microspheres form precursor powder synthesized by sol-gel method.[1] The doping level ranges from 0.5 to 2.0 at. % of Eu^{3+}. The prepared glass microspheres were found to be almost XRD amorphous within detection limit. The DSC analysis revealed the two exothermic effects corresponding to crystallization of glasses at characteristic temperatures; peak 1: T_{x1} ~ 920 °C (onset), T_{p1} ~ 935 °C (peak), peak 2: T_{x2} ~ 990 °C and T_{p2} ~ 1000 °C, respectively. The origin of the two crystallization peaks (exothermic effect) was examined by high temperature XRD (HT XRD) that revealed the crystallization of YAG phase ($Y_3Al_5O_{12}$) up to 1200 °C. The crystallization of α-Al_2O_3 phase was observed at temperatures above 1300 °C. The both exothermic effects in DSC traces thus unusually correspond to YAG phase crystallization; the first peak mainly to nucleation and partial crystallization of YAG phase, the second peak to crystal growth of YAG phase. The polycrystalline phosphors were prepared from the glasses by controlled crystallization at selected temperatures. The photoluminescence (PL) properties (both steady-state and time-resolved PL) of glasses and polycrystalline phosphors were studied in detail. In as prepared glasses the both oxidation states of europium, Eu^{3+} and Eu^{2+}, were found to coexist in glass matrix. The emission spectra of Eu^{3+} glasses under UV excitation at 393 nm exhibit intensive red emission in the spectral range of 570–720 nm due to intra-configurational 4f-4f transitions, while Eu^{2+} containing glasses (excited at 345 nm) emit the light in broad spectral range from 400–700 nm with the emission maximum at ~520 nm. The PL properties of Eu^{3+}/Eu^{2+} glasses and corresponding polycrystalline phosphors were compared. Moreover, the temperature dependent luminescence of the prepared phosphors and the lifetime using the TCSPC technique were studied in detail. The prepared materials are potential candidates for pc-WLED applications.

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Magnetron sputtered ceramics for high temperature electrical insulation

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Keywords: magnetron sputtering, reactive sputtering, pulsed reactive sputtering, alumina, electrical insulation

Thin films of Al_2O_3 up to 2.5 μm thick were deposited onto copper substrates for high thermal stability electrical insulation, for application in aerospace and automotive industries. Inclusion of SiO_2 layers and blends have been investigated in an attempt to reduce leakage current. Isolative measures with improved thermal stability are of great interest for high temperature applications such as in motor windings. Current polymer insulation solutions can involve a number of multi layers and normally have a maximum stability of about 300 °C, with polyimide insulation being a common solution. Ceramic insulation systems are often limited by a thick coating which is normally deposited by solution based methods. These thicker coatings can suffer from mechanical problems, poorer bending radius being a concern, especially in winding applications. Thin films are of further interest within the electronics industry in respect to capacitor and multi-layered electronics.[1]

Physical vapour deposition (PVD) using reactive magnetron sputtering was used as it is highly tuneable and has the ability to deposit oxide and non-stoichiometric oxide coatings with and without additions. Here direct current (DC) and pulsed DC power (PDC) have been used to deposit Al_2O_3 films onto copper substrates in order to test mechanical and electrical properties with respect to their substrate.[2] Adhesion of DC films was improved by the incorporation of a mixed aluminium copper interlayer. Pull off adhesion tests showed good adhesion ranging from 63.0 to 76.2 MPa strength for adhesive and cohesive failures. This criterion was met for films below 2 μm thick, with thicker films failing below 25 MPa due to increased stresses incorporated into the film during the longer depositions. Dielectric breakdown properties were unaffected by the use of this interlayer. However the use of pulsed power has improved the film adhesion and electrical properties by removing damage caused by target arc events.[3] Different pulsed power delivery profiles were investigated to optimise the removal of target arcing seen in reactive DC sputtering and prevented deposition of elemental aluminium as observed in DC films; while maintaining practical deposition rates. Pulsing parameters including duty cycle and frequency and substrate bias were explored further to maximise dielectric and adhesive strength and increase film density.

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New ZnO-based glass ceramic sensor for H_2 and NO_2 detection

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The demand for rugged and reliable chemical sensors able to operate in harsh industrial environments, as well as for public health and security is still high. These sensors have to cover a wide range of industries such as metallurgy, glass, ceramic, paper, automotive, aerospace and energy.[1] Yet, despite the high request, major advances in these sensors in terms of simple structure, lower cost, better selectivity, durability and reliability are always needed. Thus, in this research, ZnO crystals were grown from a glassy matrix having the composition $58ZnO:4WO_3:4Bi_2O_3:33.3B_2O_3$ by melt quenching technique. The powder was characterized by laser granulometry, thermal analysis and Field Emission-Electron Scanning Microscopy. XRD pattern evidenced the presence of two different crystalline phases: ZnO (JCPDS card no°1389-0511) and Bi_2WO_6 (JCPDS card no°1373-2020). ZnO was the main crystalline phase, whereas Bi_2WO_6 appeared as the secondary crystalline phase. A gas sensor was then fabricated using a ZnO sol–gel phase as a permanent binder of the glass-ceramic to a commercial alumina substrate with interdigitated platinum electrodes. The gas sensing properties of this material were investigated at different operating temperatures with respect to water vapor, NH_3, H_2 and NO_2. The sensor response depends on the operating temperature and on the concentration of the target gas. The highest response to NO_2 was observed at an operating temperature of 150 ºC. However, a certain interference with water vapor was evidenced at this temperature, even if the higher the working temperature (250 °C in our case), the lower the influence of water vapor is.

Though the response of our sensor in the sub-ppm NO_2 concentration range was not explored, the observed results are comparable with recent data from the literature.[2–4]

Glass ceramic materials are thus promising in sensors application not only as humidity sensors but also for detecting other gases.

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Structural, optical, and optoelectronics properties of Cr incorporated WSe_2 layered compounds

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Keywords: transition-metal dichalcogenides, 2D material, optical property, structural property, crystal growth

We have grown chromium-incorporated $W_{1-x}Cr_xSe_2$ single crystals with different Cr compositions of x = 0, 0.01, 0.05, 0.1, and 0.2 using chemical vapor transport (CVT) method with iodine as the transport agent. X-ray diffraction (XRD), Raman measurement, X-ray photoemission spectroscopy (XPS) are implemented to characterize structural phase and composition of the $W_{1-x}Cr_xSe_2$ ($0 \leq x \leq 0.2$) series crystals. Thermoreflectance (TR) measurement investigates band-edge excitonic and interband transitions. The XRD results show that lattice constants of the $W_{1-x}Cr_xSe_2$ ($0 \leq x \leq 0.2$) series crystals decreased with the Cr content was increased in the layer compounds. For the higher Cr composition of x = 0.1 and 0.2 crystals, some additional XRD peaks corresponding to the Cr-Se system (other than WSe_2) are detected. The Cr $2p_{1/2}$ and $2p_{3/2}$ electron peaks in the XPS spectra also reveal that Cr^{3+} and Cr^{6+} features can be detected in the $W_{1-x}Cr_xSe_2$ series. Raman spectroscopy shows that the general E^1_{2g} and A_{1g} related vibration modes shift to lower wavenumber with respect to the increase of the Cr content in the $W_{1-x}Cr_xSe_2$ ($0 \leq x \leq 0.2$) series. For the higher Cr of x = 0.1 and x = 0.2 samples, two extra peaks related to the chromium dopant effect are also detected. The XRD and Raman results show that the lower Cr content crystals (i.e. $W_{0.99}Cr_{0.01}Se_2$ and $W_{0.95}Cr_{0.05}Se_2$) are maybe similar to that of WSe_2, while the higher Cr compositions of x = 0.1 and x = 0.2 may coexist with major WSe_2 and a little Cr-Se phase. The A and B excitons of the Cr doped WSe_2 demonstrate an energy blue shift behavior with respect to the increase of the Cr content in the crystals detected by TR. The band gap enlargement can also be verified

by surface Schottky diodes of undoped WSe_2 and $W_{0.8}Cr_{0.2}Se_2$ using Cu as the Schottky contact. The forward cut-in voltage of the $W_{0.8}Cr_{0.2}Se_2$ surface Schottky diode is increased with respect to that of the undoped sample. Meanwhile the reversed breakdown characteristic has also been improved in the Cr-incorporated WSe_2 surface Schottky diode.

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Modification of a-site stoichiometry in $Na_yBi_xTiO_3$-$BaTiO_3$ (NBT-BT)-based capacitor materials

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Keywords: NBT-based, non-stoichiometry, impedance spectroscopy, capacitor

High-temperature capacitor materials are required to enable reliable electrical circuits in engineering applications with elevated operation temperature. The demand for capacitor materials which can handle temperatures higher than 200 °C, with only a small deviation of the key properties of a capacitor, has increased significantly in the last years.[1] In future, electronic components shall be placed close to areas with elevated temperatures for economic reasons.[1] Therefore, it is of major importance to identify promising candidates for capacitors with advanced temperature stable properties such as capacitance, permittivity, loss factor, energy density and volumetric efficiency.[2] One of the most promising materials are the Na_x-Bi_xTiO_3 (NBT)-based materials. These show a broad permittivity plateau and good electrical properties at elevated temperatures.[1,3] However, to further decrease the dielectric loss of the samples mobile ionic defects need to be reduced.[4]

In this work the impact of A-site non-stoichiometry on the loss will be evaluated. Three high-temperature dielectric compositions, $0.82(0.94Na_xBi_xTiO_3\text{-}0.06BaTiO_3)\text{-}0.18(K_{0.5}Na_{0.5}NbO_3)$ (NBT-BT-KNN), $0.85(0.94\ Na_xBi_xTiO_3\text{-}0.06BaTiO_3)\text{-}0.15(CaZrO_3)$ (NBT-BT-15CZ) and $0.80(0.94\ Na_xBi_xTiO_3\text{-}0.06BaTiO_3)\text{-}0.20(CaZrO_3)$ (NBT-BT-20CZ) with $x = 0.49$, 0.5 and 0.51 are synthesized with the solid state synthesis route to investigate their potential as high-temperature capacitor materials. With the help of the Impedance Spectroscopy (IS), Permittivity measurements und E-P-Curves, the characteristic electrical properties of a capacitor material are determined. Additionally, X-ray diffraction (XRD), Secondary Electron Microscopy (SEM) are used to evaluate the influence of the Bi-non-stoichiometry on the microstructure.

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Investigation of silicon content and distribution in YAG ceramics during the production process

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Keywords: transparent ceramics, YAG, silicon, sintering aid, SiO_2, LIBS

Silica is typically used as a sintering aid in the production of transparent YAG ($Y_3Al_5O_{12}$) ceramics, allowing for the achievement of nearly pore-free microstructures and the lowering of sintering temperatures. However, it was also found to introduce undesired color centers in the sintered material[1] as well as segregate at grain boundaries leading to the formation of amorphous or crystalline secondary phases (Y_2SiO_5),[2] which decrease the optical properties and compromise the use of the material as a laser medium. Thus, while the addition of silicon (in the form of SiO_2 or as tetraethyl orthosilicate, TEOS) is often required, it is desirable to obtain materials with low Si content and homogeneous distribution. This work studies the amount of Si and its distribution in YAG and Yb:YAG ceramic materials produced by reaction sintering of a mixture of oxide powders throughout the whole preparation process. Monitoring the Si content step by step provides important information about the reproducibility and consistency of the fabrication process, crucial for any further optimization. We have shown that Laser-Induced Breakdown Spectroscopy (LIBS) allows sensitive and accurate quantification of silicon in ceramics down to 60 ppm and our experimental LIBS setup was used to analyze the evolution of the silicon content in samples at various steps of the fabrication process.[3] The distribution of Si in sintered ceramics was studied with High Resolution TEM to detect any possible nano-precipitates, and EDX nano-probe chemical analysis to check for segregation at grain boundaries and evaluate Si concentration within the YAG grains. The amount of Si present in the sintered materials has been found to be as low as 30% of that introduced into the initial mixture.

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Hexagonal tungsten trioxide produced by novel solution combustion method

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Keywords: solution combustion synthesis, tungsten trioxide, fuel and oxidizer ratio

Solution Combustion Synthesis (SCS) is a novel method to produce powders having high surface area and high purity within a short period of time. This uniqueness of the process depends on three features. First, because of liquid reaction medium, reactants can be mixed at molecular scale homogenously. Second, high reaction temperature allows to produce high crystallinity and high purity products. Third, short process time and huge amount of gasses released during reaction allows us to produce nano scale products with high surface area. This method is based on self-propagating reaction after an ignition temperature is reached between oxidative precursor (metal nitrates) and fuels (urea, glycine, oxalic acid, etc.). There is a critical ratio between fuel and oxidizer to control combustion efficiency and powder properties. Once that ratio is equal to 1, it means that reaction is occurring at highest efficiency.[1]

Tungsten trioxide is an attractive material because of its wide range of applications. Due to its high coloration efficiency and high cyclic stability, it is a good candidate for thermochromic applications such as smart windows, antiglare mirrors, high contrast displays, and active camouflage. In these applications, WO_3 is generally preferred to be amorphous because of higher electrochromic performance than crystalline phase. However, amorphous phase is not robust as crystalline phase, and causing to some problems in application. Nano structure can resolve this problem by increasing the effective surface area.[2,3]

In this study, is aimed to develop a nano scale hexagonal WO_3 having the same electrochromic efficiency as in amorphous state by using unique capability of SCS at producing nano sized powders. In that perspective, effect of SCS parameters such as fuel type, fuel oxidizer ratio, homogenization on final product were studied. XRD, SEM, and BET analysis were conducted to determine powder properties.

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The effect of vibratory milling on the electrical properties of zinc oxide varistors

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Keywords: ZnO varistors, vibratory milling, powder characteristics, zirconium concentration, electrical properties

Zinc oxide varistors are surge protection devices which are typically made from zinc oxide as the main constituent and smaller concentrations of bismuth, antimony, manganese, cobalt, tin and nickel oxides. These smaller concentrations are collectively termed as multi-elemental metal oxide additives (MMOA)[1]. Their quantity in total is 4 mol. %. The electrical properties are highly sensitive to the composition, phase, purity, size, morphology and fabrication processes of all of the metal oxides present from the starting powder stage to the final surge device. In this paper the authors describe and discuss the effect of multi-elemental oxide additives, having been milled for different durations using a vibratory mill with cylindrical zirconia media, on the electrical properties. The electrical properties include each aspect of the I-V curve and the energy absorption capability. A commercial ZnO varistor formulation was used and the final sintered varistor devices formed were similar in size to commercial high voltage devices. A strong relationship between the milling duration of the multi-elemental oxide additives and most of the electrical properties are observed.

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Quality factor control of $MgTiO_3$-based ceramics by cation substitution

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Keywords: magnesium titanate, microwave dielectric properties, ilmenite structure, octahedral distortion

Microwave dielectric materials with high quality factor, required for rapid signal propagation and prominent frequency selectivity at microwave and/or millimetre-wave frequencies, are in great demand for 5G wireless communication systems, such as global communication satellites, mobile communications, and radar detectors. $MgTiO_3$-based ceramics, as high quality factor dielectrics, have been widely investigated recently regarding the further improvement of quality factor by the substitution of divalent and/or tetravalent cations for Mg^{2+} and/or Ti^{4+} of $MgTiO_3$. Most of these studies discussed for the relationships between the dielectric properties of $MgTiO_3$-based ceramics and extrinsic factors, such as a secondary phase, density, and microstructure. However, fundamental studies should be carried out to understand the dependence of the microwave dielectric properties on the structural characteristics, which enables control and improvements in the microwave dielectric properties of $MgTiO_3$-based ceramics. $MgTiO_3$-based ceramics with ilmenite structure are composed of two types of octahedra: divalent-cation octahedra (MgO_6) and tetravalent-cation octahedra (TiO_6). The two types of octahedra share edges along the a-axis and faces along the c-axis. The bond lengths between the cation and oxygen ions in oxygen octahedra are affected by the ionic characteristics of the central ion. Therefore, the substitution of other cations at Mg or Ti sites may change the bond length and bond strength, which affects the dielectric properties of $MgTiO_3$-based ceramics as well as the characteristics of the ilmenite crystal structure. By changing the type of divalent and/or tetravalent cation, the characteristics of the bond between the cations and oxygen ions in oxygen octahedra can be modifies to affect the dielectric properties of $MgTiO_3$-based ceramics. Typically, three types of cation substitutions will be discussed; single ion substitution for Mg- and/or Ti-site, aliovalent cations substitution for Ti-site, and nonstoichiometric substitution for Ti-site, based on the relationships between the structural characteristics and microwave dielectric properties of $MgTiO_3$-based ceramics.

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Fabrication of transparent $MgAl_2O_4$ spinel via spray freeze drying of microfluidized slurry

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Keywords: transparent, $MgAl_2O_4$, spray freeze drying, freeze granulation, microfluidization

Spherical granules were prepared from a monodispersed slurry by combining the microfluidization method[1] and the spray freeze drying (SFD) process[2,3]. Starting with those prepared granules, transparent $MgAl_2O_4$ ceramics were fabricated through the pressureless sintering and following hot-isostatic-pressing. As a result of comparison with a poly-dispersed slurry by ball-milling method, it was successful to have a mono-dispersed state by microfluidization method, and 80% of visible in-line transmittance was obtained at 600 nm wavelength from a process starting with the monodispersed slurry of low solid content. The microstructure analysis of the green bodies, pre-sintered bodies and hot-isostatic bodies of $MgAl_2O_4$ ceramics, revealed that the slurry dispersion process should be controlled to a high level in order to suppress scattering sources such as pores and microcracks affecting the in-line transmittance of visible light.

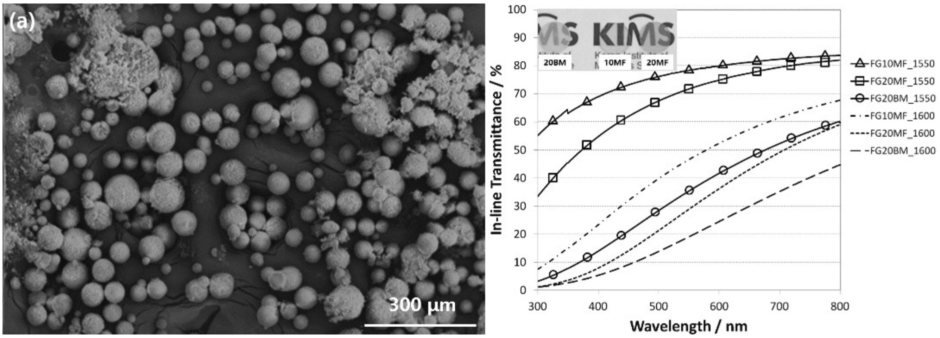

Fig. 1. (a) Spherical granules from SFD process **(b)** In-line transmittance of specimens

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Glass/Al_2O_3/GO,CNT composite with high bending strength and thermal conductivity for package of super capacitor

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Keywords: LTCC, glass/Al_2O_3 ceramic, bending strength, thermal conductivity

A new LTCC ceramics consisting of CaO-B_2O_3-SiO_2 (CBS glass)/Al_2O_3/GO,CNT are introduced in this paper. Glass/Al_2O_3/GO,CNT composites were fabricated and their sintering mechanism, mechanical and thermal properties were investigated. The composite containing CBS, 40wt% Al_2O_3 and 1wt% $GO_{0.25}CNT_{0.75}$, which was sintered at 900 °C for 1 h and subsequently annealed at 850 °C for 1 h, showed a high relative density of 92.5% of the theoretical density. Moreover, it also showed a high bending strength and good thermal conductivity of 420 MPa and 5.51 W/mk, respectively. Microstructure characterization and ceramic-metal additive model analysis indicate that the increased thermal conductivity of this composites was due to the formation of thermal connecting link networks in the composite by CNT. These results showed that the CBS glass/Al_2O_3/GO,CNT composite can be used for the package of super capacitors. In this work, the detailed investigation on variation of microstructure with respect to sintering conditions was studied. Moreover, the relation between microstructure and mechanical and thermal properties of the specimens were also discussed in this work.

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New lead-free perovskite compounds with $(A_{1/2}Bi_{1/2})(Mg_{1/3}Nb_{2/3})O_3$ formula (A = Na,K)

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Keywords: lead-free materials, perovskite, electrical properties

Nowadays, $PbZr_{(1-x)}Ti_xO_3$ (PZT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ – $PbTiO_3$ (PMN – PT) compounds are the most common piezoelectric ceramics owing to their high electromechanical performance and low cost. However, because of the restrictions on the use of hazardous substances, such as lead, the PZT and PMN materials must be substituted by lead-free compounds. These new materials are thus highly investigated for their piezoelectric properties. Actually, the most promising compounds are (i) alkaline-niobates, such as $(Na,K)NbO_3$, (ii) alkaline and bismuth titanates, such as $(Na, K)_{1/2}Bi_{1/2}TiO_3$ (NBT and KBT), and (iii) solid solutions based on these compounds such as $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$.

The present work is devoted to the search of new lead-free materials based on NBT and KBT, initially reported by Smolenskii et al. in 1961. Indeed, these two compounds demonstrate the possibility to replace the lead cations in A-site of perovskite compound $PbTiO_3$ by the alkali/bismuth pseudo-ion (Na^+/Bi^{3+}) or (K^+/Bi^{3+}). If this substitution has been successfully tested for NBT and KBT titanates, this is not the case for other perovskites compounds containing lead in A-site of the perovskite lattice. For example, only one article reports briefly this possibility in PMN. However, there is no more information about the structure of the compounds or its properties, except that the synthesis induces a large number of secondary phases.

Thus, the two compositions $(Na_{1/2}Bi_{1/2})(Mg1_{/3}Nb_{2/3})O_3$ (NBMN) and $(K_{1/2}Bi_{1/2})(Mg1_{/3}Nb_{2/3})O_3$ (KBMN) have been synthesized by solid-state reaction, with a two steps B-site precursor route, similar to the one used for PMN. In both case, the XRD patterns evidence for the formation of a perovskite compound, though it is not a pure phase. Indeed, secondary phases remained in each composition. But using a systematic study of the synthesis conditions, we managed to have less than 5% of impurity at the end of the thermal cycles.

These two compounds have been studied by XRD and Neutron Diffraction, in order to identify their crystalline structure and the nature of the secondary phases formed during synthesis. The dielectric and ferroelectric / piezoelectric properties of these compounds are presently under investigation, in order to determine if they could be candidates to the replacement of the PZT and PMN compounds.

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Luminescent properties of lanthanide oxide and fluoride doped ternary silicon nitride-based phosphors

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Keywords: luminescence, ternary nitrides, lanthanide

Lanthanide (Ln) doped $LaSi_3N_5$ based phosphors were prepared experimentally and their electronic structure and band gaps were calculated using the screened Coulomb hybrid HSE06 functional. The synthesized $LaSi_3N_5$:Ce phosphor emits violet-blue light, $LaSi_3N_5$:Eu – green-yellow and $LaSi_3N_5$:Sm red light. There were a differences in the shape of emission bands depending on the type of lanthanide dopant, i.e. oxide or fluoride.

The calculations showed that with increasing atomic number the band gap of Ln^{3+}-doped $LaSi_3N_5$ smoothly decreases from 4.6 eV (Ce) to 0.5 eV (Eu). The band gap of Ln^{2+}-doped $LaSi_3N_5$ increases from 0.80 eV (Ce, Pr) to 0.95 eV (Nd, Pm), 1.43 eV (Sm), and to 3.28 eV (Eu). There was a reasonable agreement between the calculated band gaps and those data published in the literature or measured on our samples using diffuse reflectance spectroscopy.

The lanthanides were added experimentally in a form of fluorides (LnF_3) and oxides (Ln_2O_3). In the case of oxides also the influence of N/O substitution on the band gap of $LaSi_3N_5$ was calculated. The results showed that with increasing oxygen content in the cell of $LaSi_3N_5$ the band gaps decreased by 0.2–0.6 eV. Some of the lanthanides were added to $LaSi_3N_5$ also in the form of fluorides and their photoluminescent properties were compared with Ln_2O_3-doped phosphors.

The energy level locations were constructed from the ab initio calculated electronic structures and compared with the empirical energy level diagram. There is a good agreement between calculated and experimental data and the method can be used for the design of phosphors.

Similar to $LaSi_3N_5$, also LnF_3 and Ln_2O_3 doped $MgSiN_2$-based phosphors have been prepared and their photoluminescent properties were characterized.

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Electrical properties of barium titanate ceramics doped with 2.1% La and 1.0% Mn as a function of temperature and oxygen partial pressure

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Keywords: donor-doped barium titanate, impedance spectroscopy, DSC measurements, defect chemistry

Donor doped $BaTiO_3$ represents an important model system for interfacially controlled electroceramics.[1] It is the aim of this contribution to present the characterization of the electrical properties of n-type barium titanate as a function of temperature and oxygen partial pressure. The experimental results are interpreted in terms of a proper defect chemical model. Barium titanate ceramics doped with 2.1% La and 1.0% Mn have been prepared by means of the Pechini process. Disk-shaped samples with the nominal compositions $Ba_{0.979}La_{0.021}Ti_{0.99}Mn_{0.01}O_{3-}\delta$ and $Ba_{0.979}La_{0.021}Ti_{1.01}Mn_{0.01}O_{3-}$ have been obtained by isostatic pressing and sintering in air at 1350 °C. The relative densities are around 90–94% and the mean grain size is in the range from 0.75 to 1.3 µm. The electrical properties have been measured in air by employing impedance spectroscopy in the temperature range from 35 to 900 °C. Moreover, the oxygen partial pressure has been varied between 1 and 10^{-20} bar at 900 °C by appropriate gas mixtures of pure O_2, Ar, 1%-O_2/Ar, and 1%-H_2/Ar. The temperature dependence of the dielectric constant reveals a Curie-temperature for the ferroelectric - paraelectric phase transition of 70–72°C which is in close agreement with DSC measurements where a peak of the heat capacity has been found around 75 °C. In contrast to PTC resistors, the samples of the present study, containing a fairly high amount of dopants, are insulating at room temperature most probably because of ionic compensation by cation vacancies. The variation of the electronic conductivity of bulk regions with temperature shows an almost perfect Arrhenius-type behaviour with activation energies around 1.3–1.4 eV which can be interpreted in terms of trapping equilibria of electronic charge carriers by the mixed-valent (redox-active) acceptor co-dopant (Mn). The oxygen partial pressure dependence of the electronic conductivity under reducing conditions follows the well-known power law $\sigma \propto p(O_2)^{1/6}$ owing to the formation of oxygen vacancies which are compensated by electrons. In the oxygen partial pressure region above 10^{-5} bar (oxidizing conditions) the bulk conductivity is almost independent of $p(O_2)$, indicating the predominant ionic compensation of the dopants by cation vacancies which are frozen-in at 900 °C due to very low cation diffusivities in the perovskite lattice at this temperature.[2]

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The formation and high EM wave absorption properties of doped barrium ferrite over millimeter frequency range

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Keywords: barium ferrite, Nb doped, absorber, high EM absorption properties

Nowadays, absorbing materials are important in one hand to attenuate electromagnetic pollution arising from explosive development of information technology, and on the other hand to defend against radar detection in use for the stealth. Recently, the barium hexaferrite $BaFe_{12}O_{19}$, a kind of versatile material, has been widely used as permanent magnet and high-density recording media due to its large saturation magnetization, high coercive force and corrosion resistivity. Herein, we investigate the ferrite as high quality EM absorption material in this work, in which the Nb^{5+}-doped barium ferrites of $BaFe_{12-x}Nb_xO_{19}$ is prepared by sol-gel method. The perfect phase of $BaFe_{12-x}Nb_xO_{19}$ with x = 0~0.6 can be obtained as they are prepared at 1100 °C~1300 °C for sintering time of 0~3 h. The plate-like grains form typically in the ferrite with increasing Nb^{5+} from x = 0 at 1300 °C to x = 0.6 at 1100 °C, respectively. Controlled by decreasing barrier of jumping atoms from one grain to the other, the large grain size of the crystalline phase, reaching 4~6 µm, is obtained in the ferrite with doping Nb^{5+} of x = 0.6 at 1300 °C for 3 h. The ε' and ε'' of the ferrite are relatively high to be ~7.9 and ~0.95 respectively at microwave frequency, being about 2 and >10 times higher than the ferrite without doping of Nb5+ ion. Controlled by intrinsic natural resonance of Fe^{3+} ions and other associated Fe^{2+} and O^- ions formed simultaneously, the multi resonant peaks at different frequencies are formed in μ' and μ'' of the ferrite with doping of Nb^{5+} ions. It will be modified from the range at high frequency of >40+ GHz to low frequency range of 26~37 GHz based on the decrease in Ha with substituting for Fe^{3+} ions by non-magnetic Nb^{5+} from x = 0 to x = 0.6. With respect to the modification of the multi natural resonance peaks, the related multi reflection loss peaks appear at frequency range around millimetre wave of ~35 GHz in the ferrite with x = 0.6 sintered at 1300 °C for 3 h, with which the broad bandwidth of the wave absorption of >12 GHz from 28 to 40+ GHz is obtained. Meanwhile, the small RL_{min} of <-40 dB is revealed with only thin d_m of ~0.76 mm being requested in this case due to the high ε_r which is much closer to the μ_r. It is obviously the excellent absorbing material at millimetre wave absorption.

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Broadband spectral upconversion in $CaTiO_3$: Ni^{2+},Er^{3+} for solar energy harvesting

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Keywords: broadband-sensitive upconverter, Ni^{2+} sensitizers, solar cell, energy

Solar energy harvesting is one of the most important and utmost research directions for the sustainable society. Upconversion (UC) materials, that utilize two or more low energy photons to emit a high energy photon, can be applied to improve the conversion efficiency of present solar cells. There are some reports to utilize Er^{3+}-doped upconverters for solar energy harvesting but marginal improvement has been realized due to the narrow absorption band at 1450–1600 nm.[1]

Recently, we have reported broadband-sensitive UC in Er^{3+}, Ni^{2+} codoped $CaZrO_3$[2] and $La(Ga,Sc)O_3$[3] and demonstrated spectral conversion of 1100–1600 nm photons to 980 nm. Ni^{2+} ions located at the centers of octahedrons absorb 1100–1450 nm photons and transfer the energies to the Er^{3+} ions. Thus, 1100–1450 nm photons are also upconverted to 980 nm, in addition to 1450–1630 nm photons that are directly absorbed by the Er^{3+} ions, as shown by the excitation spectrum in Fig. 1. However, those upconverters suffer from low UC efficiency. Here, we report remarkable improvement of the UC efficiency in the newly developed $CaTiO_3$:Er^{3+},Ni^{2+} broadband-sensitive upconverter. Effect of Ca/Ti composition played a vital role to improve the UC emission due to more efficient Ni^{2+} sensitization and improved UC of Er^{3+} itself.

The newly developed broadband-sensitive upconverter can be applied to boost the output power of solar-pumped lasers. A 980 nm laser emission can be achieved using Er^{3+}-doped upconverters for the laser media, where photons with wavelengths longer than 980 nm would also contribute to laser emission. When these are coupled with crystalline silicon solar cells (current density ~40 mA/cm^2), 7.8 mA/cm^2 gain can be achieved that accounts ~4.8% efficiency improvement (absolute), supposing perfect UC.

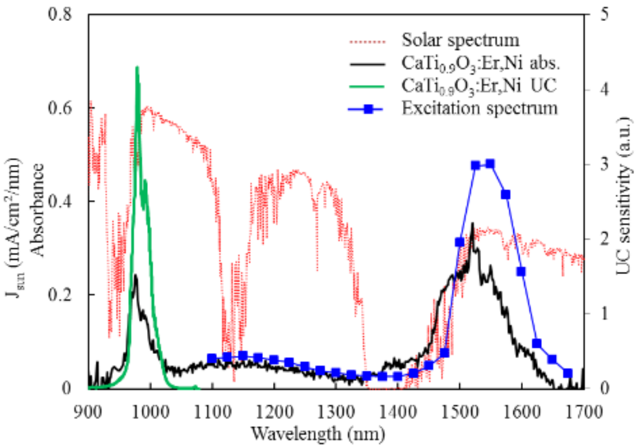

Fig. 1. (a) Broadband-sensitivity of the $CaTiO_3$:Er,Ni upconverter along with Ni^{2+} and Er^{3+} absorption bands, and solar spectrum

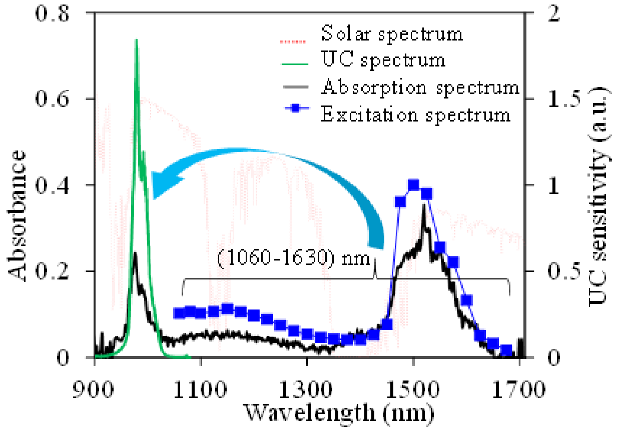

Fig. 1. (b) Broadband-sensitivity of the $CaTiO_3$:Er^{3+},Ni^{2+} upconverter compared with AM1.5 solar spectrum

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Synthesis and properties of lead-free BNBT-based PTCR thermistor ceramics

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Keywords: PTCR thermistors, perovskites, semiconducting oxides

PTCR (Positive Temperature Coefficient of Resistivity) ceramics show an anomalous increase of their electrical resistance near the Curie temperature (Tc). These components are typically used as over-current protection and as self-regulating heaters. Lead-substituted barium titanate (BT) materials are typically used for heater applications. (1–x) (Bi1/2Na1/2) TiO3 – (x)BaTiO3 (BNBT) perovskites were reported as alternative lead-free PTCR material. We report on investigations of the PTCR behavior of several compositions of the BNBT solid solution. Starting from BT, T_c is increased upon BNT addition. Since BNBT ceramics are insulators, semiconducting behavior is achieved through n-type donor doping. Sintering in reducing atmosphere followed by a re-oxidation in air was investigated as alternative route. Unfortunately, both methods result in limited PTCR performance. Recently, CaO-substituted BNBT ceramics were proposed as alternative lead-free BNBT PTCR thermistor compositions.[1] We will present the results of CaO-substituted BNBT perovskites and will discuss correlations between composition, microstructure and PTCR properties. Addition of CaO significantly lowers the sintering temperature and allows sintering at 1235 °C. 0.05% SiO_2 effect the sintering behavior and increases the resistivity jump while keeping a low room-temperature resistivity. 0.02% SiO_2 addition increases the room temperature resistivity significantly.[2] Even larger amounts of SiO_2 precipitate as second phase. Acceptor dopants Mn or Fe are used to optimize the PTCR behavior. These dopants induce a sharper rise of resistivity at the Curie temperature. We will discuss the synthesis, microstructure formation and effect of dopants on the performance of CaO-substituted BNBT ceramics as PTC thermistors.

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Electrocaloric effects and temperature distribution analysis of $BaTiO_3$-based ceramics and multi-layer capacitor

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Keywords: electrocaloric effects, $BaTiO_3$, lead-free, multi-layer capacitor

The electrocaloric effect (ECE) is a phenomenon in which a material shows a reversible temperature change under an applied electric field. There has been some problem in the conventional refrigerator. Since the conventional refrigerator operates by using a compressor, vibration generation is inevitable. The other disadvantage includes the difficulty in downscaling. From the viewpoint of the refrigerator innovation, new refrigerators based on the new mechanism are expected. ECE is considered to be one of the new cooling mechanisms. By using ECE, the application to compact a high energy-effective, inexpensive, and safe refrigerator would be considered. In order to create ECE cooling devices, materials with large ECEs are required. For direct measurement of the ΔT, there are some difficulties. Most probably due to these difficulties, the reports on the direct measurement of ΔT are limited thus far.

In this study, the electrocaloric temperature change, ΔT, due to applied ΔE, of the $BaTiO_3$-based ceramics is estimated and directly measured. Temperature-electric field (T-E) loops of the $Ba(Zr,Ti)O_3$ and $(Ba,Sr) Ti)O_3$ ceramics and $BaTiO_3$-based multi-layer capacitor are measured. ΔT of 0.7K are observed in the $BaTiO_3$-based multi-layer capacitor at room temperature. The comparison with the estimations from indirect approach based on Maxwell's equation will be discussed. And temperature distribution analysis of the $BaTiO_3$-based multilayer capacitor will be discussed for the realization of the cooling devices.

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Effect of electrode configuration on dielectric strength testing

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Keywords: ceramic substrates, dielectric strength, thick-film hybrid technology, ASTM D149

Dielectric strength is a critical property for materials used as electrical insulators. The measurement of dielectric strength is well established and straightforward, but the values determined in a measurement are strongly dependent on the measurement setup and the specimen characteristics. For example, the size of the electrodes has a significant influence on the results. ASTM D149 covers a range of electrode sizes and does not unambiguously prescribe the quality of the electrodes. Thus, different test setups and procedures are used in the field. Consequently, a comparison of dielectric strength values of different origins, for example material supplier and customer, is often not meaningful.

To quantify the influence of the test procedure on the dielectric strength values, a batch of industrial thick-film substrates has been tested with different electrode configurations under AC conditions. Opposing cylinders with diameters of 6.4 mm and 25 mm, and a thick-film metallization with a diameter of 25 mm were used in the study. At least 20 specimens were tested with each type of electrodes. The results range from 21.7 ± 0.7 kV/mm measured with printed electrodes to 26.7 ± 1.2 kV/mm measured with reused 6.4 mm cylinders. This means a difference of 23%. Measurements performed with 6.4 mm cylinder electrodes produce significantly lower values (ANOVA, $\alpha = 0.01$) if a new set of electrodes is used for each measurement instead of reusing the same pair of electrodes for the entire batch. The dielectric strength measured with new 25 mm cylinders is 11.2% lower than the values determined with new 6.4 mm cylinders. No significant difference (ANOVA, $\alpha = 0.01$) was found for measurements with printed electrodes and opposing 25 mm cylinders. Weibull evaluation of the data showed that all tested electrode configurations result in a similar reliability of the specimen (Weibull modulus) but in a significantly different characteristic dielectric strength (scale factor, Bonferroni, $\alpha = 0.05$).

This study emphasizes the importance of a thorough and comprehensive documentation and communication of the test procedure for dielectric strength measurements. It further helps to evaluate the significance of differences in dielectric strength data provided by different sources.

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High permittivity BaT iO_3 ceramics prepared by SPS

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Keywords: $BaTiO_3$, SPS, permittivity

Barium titanate ($BaTiO_3$) is a perovskite structure material widely used for numerous electroceramic applications. Its high relative permittivity makes it very common in electronic components such as multilayer capacitors (MLCs), PTC thermistors, piezoelectric transducers and a variety of electro-optic devices. Nevertheless, its applications as MLCs are reduced due to its relative low Curie temperature (130 °C) and piezoelectric properties lower than those of $Pb(Zr,Ti)O_3$. However it remains attractive for environmental reasons and the progressive replacement of lead-based components.[1]

$BaTiO_3$ ceramics with relative densities above 95% and different grain sizes have been prepared by Spark Plasma Sintering (SPS). This technique combines uniaxial pressure with Joule heating and allows achieving fully dense ceramics at comparatively lower temperatures and within several minutes.[2] We have evaluated the sintering behaviour of a commercial $BaTiO_3$ powder and looked into how the microstructure and the density affect its electrical permittivity. Some of the samples showed colossal permittivity up to 10^5 and we have tried to explain the factors that induce this phenomenon.

This research reports some clues about the differences observed on the as-sintered samples and after air-annealing and it also performs a comparison between the samples obtained by conventional sintering in air and by SPS.

Acknowledgment

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Flexible micro supercapacitor based on laser scribed graphene (LSG)

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Keywords: graphene oxide, laser scribed graphene (LSG), scanning electron microscope (SEM), cyclic voltammetry (CV), galvanostatic charge/discharge (CC)

In the present work, graphene powder has been synthesized by laser scribing method. The resulted flexible light-scribed graphene is very appropriate to be utilized as micro-supercapacitors. Graphene conducts electricity and heat better than anything else and has combination of unique optical and mechanical properties. Electrons have nobilities in graphene over a hundred times those in silicon.

In the present work we used a standard optical LightScribe DVD drive to directly do the laser reduction of graphene oxide (GO) films to graphene. GO was prepared by the modified Hummers' method as reported elsewhere. Briefly, 2 g graphite powders was added to a mixture of 1 g $NaNO_3$ and 46 ml H_2SO_4 and the mixture was cooled to 10 °C using an ice bath. In the next step, 6 g $KMnO_4$ was gradually added to the solution and the reaction temperature was maintained below 20 °C. The mixture was then stirred at 35 °C for 2 h. The resulting solution was diluted by adding 92 ml of deionized water until a dark brown suspension was obtained. Then, the solution was treated by adding 340 ml H_2O_2 solution. Finally, a uniform suspension of GO nanosheets was obtained by adding water to the resulting precipitate and 12 h of sonicating. The resulting suspensions were uniformly drop casted on a LightScribe DVD disk and then dried under the air at an ambient temperature. The GO coated DVD disk was placed in a LightScribe DVD drive with a wavelength of 780 nm.

Raman result confirm that the laser irradiation properly reduce GO to graphene sheets. The structure of graphene arrays were studied by SEM images the results indicated that the laser based reduction was a useful method to production graphene layers. The CV curves of pristine rGO at various scan rates showed that the ultimate product has the power of storing energy in a supercapacitor level. Finally, the long-term charge-discharge stability of the LSG has been plotted which indicates that specific capacitance has decreased very slightly from its primary capacitance of ~ 10 F cm-3 and its cyclic stability is favorable over 1000 cycles.

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Chemothermal pulverization of perovskite-type titanates

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Keywords: thermal treatment, nano-powder, titanate, pulverization

Recently, the authors have found that grain size of some titanate powders, e.g., BaTiO3, can be reduced by thermal treatment in reactive atmosphere. Indeed, perovskite-type titanates, including SrTiO3 bulk single crystals and dense BaTiO3 ceramic, were pulverized into nano-sized powder by heating in gas stream containing air and ammonia (NH3) at high temperature.[1] In general, heating powder at high temperature results in grain growth of ceramic powders and sintering of the powders. However, our observation have indicated that bulk single crystals can be transformed into nano-sized powder by thermal treatment in air/NH_3 mixture gas. We regard the observed phenomena as Chemo-Thermal-Pulverization (CTP). In our previous report,[1] some requirements to induce CTP phenomena were determined but the mechanism behind this CTP process could not be clarified. As perovskite-type titanates are absolutely important materials in the field of electroceramics, it is very important to develop technologies relating to production of dielectric and conductive ceramics made from perovskite-type titanates.

In this paper will focus on further detail of CTP process in order to reveal mechanism behind the observed CTP phenomena. We have performed experimental studies to obtain optimized CTP process conditions to achieve efficient production of nano-sized fine $BaTiO_3$ powder from coarse $BaTiO_3$ grains. In addition, detailed characterization, including high resolution transmission electron microscope observation, for the powder obtained by CTP process was performed in order to reveal the mechanism of CTP process. As a result, we have obtained the optimized CTP process condition for $BaTiO_3$ powder and observed very characteristic grain structure of the powder obtained by CTP process.

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New dielectric material for co-sintering with LTCC microwave garnet

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Keywords: ferrite, garnet, ferrimagnetism, circulators

Ferrite circulators and isolators, which are non-reciprocal microwaves components, are essential in electronic modules for scanning antennas. The central part of these devices is the low dielectric and magnetic losses ferrite[1], which gives the non-reciprocal properties of the circulator. Due to complex mechanical assembling of the different materials (ferrite, dielectric and copper), the adaptation of these materials to a common LTCC[2] (Low Temperature Co-fired Ceramics) process could be valuable: the circulators would be produced with an additive multilayer process. In our previous work, we showed that cationic substitutions (bismuth, copper and vanadium) enable a dramatic decrease of the sintering temperature of garnets, from about 1450 °C down to less than 900 °C, allowing co-sintering with gold or silver for example.

First we tried to associate this new ferrite to a low sintering dielectric but we observed that for some configurations, the co-sintering was problematic. It was essential to find a dielectric material perfectly compatible with our garnet.

An idea was to find a garnet from the same family with dielectric properties.

Thanks to different cationic substitutions[3], we have modified the properties of the microwave garnet. The use of aluminium in iron crystallographic site leads to an important decrease of the saturation magnetization. Combined to gadolinium substitutions for yttrium, we obtained a material with no magnetic losses, low dielectric losses and a really low saturation magnetization (from 180 mT to about 0). When we add vanadium substitution, this material reaches mechanical properties (shrinkage and coefficient of thermal expansion) close to the properties of the central garnet allowing acceptable co-sintering.

Results of physical analyses will be exposed, such as thermomechanical analyses, coefficient of thermal expansion … Magnetic and dielectric properties will be discussed (permittivity, saturation magnetization, dielectric and magnetic losses). The compatibility between our two low temperature materials will be described, combined with the use of gold and silver.

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Electrical properties of ZnO varistors – inhomogeneities and anisotropic effects on the macroscopic and microscopic scale

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Keywords: varistor, asymmetric Double Schottky Barrier, piezotronic effect

Varistors are electroceramic components based on polycrystalline ZnO. They have a highly nonlinear current-voltage relationship and are used for overvoltage protection of electric and electronic systems. At small voltages varistors exhibit a high resistance which decreases dramatically if a certain threshold voltage is exceeded. This effect originates from so called Double Schottky Barriers (DSBs) at the grain boundaries. These electrostatic barriers are the origin of the high resistance at small voltages. Above the threshold voltage they break down in a self-enhanced process, leading to a nonlinear increase of conductivity.

On the microscopic scale, a varistor can be represented by a 3-dimensional network of highly nonlinear resistors. Due to the nonlinearity, energy dissipation cannot occur homogeneously throughout the whole material. This phenomenon will be demonstrated by means of thermal microscopy. Experiments showed that current merely flows in narrow pathways through the material.[1] In low-voltage varistors (with only 1–2 grain boundaries in series), the current flow can even be localized at one single grain boundary. Moreover, thermographic studies revealed the occurrence of different current paths depending on the direction of the applied electric field. This finding is the direct evidence of direction-dependent electrical properties of single grain boundaries. Micro-4-point measurements not only confirmed the anisotropic electrical behavior of single grain boundaries, but also exposed variations of the breakdown voltage and the nonlinearity coefficients. These findings can be explained by a natural piezotronic modification of DSBs. Due to the piezoelectricity of ZnO, mechanical stresses lead to the generation of polarization charges, which modify the band structure at the grain boundary and consequently the electrical characteristics (i.e., piezotronic effect). Trough micro compressive tests, it was found that the piezotronic effect can not only lead to an increase and decrease of DSBs, but also to an asymmetric potential offset. Since ZnO grains contain residual stresses, it is assumed that DSBs are inherently modified by the piezotronic effect, depending on grain orientation.[2] It is concluded that there exists a broad distribution of barrier properties in varistors, leading to the formation of preferential current paths through the material. Possible approaches for the homogenization of the electrical properties of ZnO varistors on the microscopic and macroscopic scale will be given.

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Thermal coarsening of metal-on-oxide nanowire thin films

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Keywords: titanate nanowires, surface area, sintering, thin films, grain boundaries

From painting, biocompatible coatings to solar cells, titanium dioxide (TiO_2) has a very wide range of applications and is one of the most studied oxide material in the last 30 years.[1,2,3] In most of these applications, titanium dioxide is used in the form of nanoparticles as a starting material. Much has learned on the coarsening behaviour of nano TiO_2, mainly because of recent studies almost exclusively addressed to the coarsening of these, nearly spherical, isotropic nanoparticles. Indeed, the degree of the particle anisotropy might induce a strong shape-dependent variation in properties of matter, which raises the question how the coarsening of anisotropic particles proceeds at various interfaces.

In this study coarsening behavior of 2D thin films of titanate nanowires coated with few nanometer thick noble metal (Ag, Pt, Rh, Pd, Au) thin film were studied by using various techniques: atomic force microscope (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and resistivity measurements. The aim of this study was to shed light on the temperature dependent structural and geometrical evolution of ceramic/noble metal interfaces down to the single particle, the individual titanate nanowire and precious metal nanoparticle level. Thin films of titanate nanowires were prepared by wet-chemical method. From room temperature up to 900 °C, different surface diffusion regimes were identified which correspond to the different titanate phases, from titanate $H_2Ti_3O_7$ to anatase and to rutile phase. Understanding the sintering behavior of 1D oxide nanowires and metal nanoparticles will open up new routes to design efficient heterogeneous catalyst and photocatalyst systems.

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Experimental and theoretical study of Yb:CAF$_2$ transparent ceramics thermal properties

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Keywords: transparent ceramic, optical material, thermal conductivity, phonons scattering, fluoride compounds

Since the first YAG transparent ceramic for laser applications was reported in 1995[1] which demonstrated the advantages of ceramics with respect to single crystals, rare earth-doped polycrystalline ceramics as solid-state laser host material have been widely used and studied. In the past few years, our team has been focusing on a promising new class of transparent ceramics for near-IR solid-state lasers, Yb:CaF$_2$. We recently developed a new fabrication process for such ceramics[2] leading to better optical properties[3].

However, despite their very good thermo-mechanical properties, transparent ceramics often demonstrate a lower thermal conductivity than single crystals due to their granular structure. This parameter is critical for laser material because of the heat that is generated during laser emission.

We thus report here measurements of the thermal conductivity of Yb:CaF$_2$ transparent ceramics obtained with the new fabrication process. Samples with different doping levels were studied in a temperature range from 15K to 310K. Comparisons were made with single crystals thermal conductivity. The results for doped ceramics are very similar to those obtained for Yb:CaF$_2$ single crystals with the same doping levels, which demonstrates an important improvement of the thermal properties over the previous fabrication process. However, results obtained for non-doped ceramic and single crystals differ for the maximum conductivity due to the presence of grain boundaries inside the ceramic.

Theoretical calculations were also conducted using Callaway's model[4] and demonstrated a very good agreement with experimental results. The fitting parameters found tend to indicate that the introduction of a doping element in the lattice has more impact on thermal conductivity than the presence of grain boundaries in the material.

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Surface modification of staring powder for multifunctional transparent titanate ceramics

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Keywords: powder, $SrTiO_3$, density, liquid phase sintering

Since multifunctional transparent titanate ceramics were reported, these materials have become the potential materials for the electro-optical devices. So far, the applications are limited because the fabrication of transparent titanates involve the expensive sintering techniques (e.g. hot iso-pressure sintering, vacuum sintering, and spark plasma sintering). Initially, this study synthesized the surface modified $SrTiO_3$ staring powders using spray dry. Then, the dense $SrTiO_3$ specimens were obtained using pressureless sintering. The experimental results showed that the modified $SrTiO_3$ powders exhibit a thin Ti-rich amorphous layer to increase grain boundary mobility via liquid phase sintering for dense $SrTiO_3$. Finally, the corresponding mechanisms were discussed.

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Synthesis and study of multiferroic – powders with structure 'core-shell' as a fillers for composite materials for electronics and photonics

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New composite powders, which have magnetic properties with the structure of the 'core-shell', have been prepared. They are particles of barium titanate with a 'skin- layer' on their surface. The 'skin-layer' is formed during treatment of a commercial powder $BaTiO_3$ by tetraethoxisilane-derived sols containing compounds of cobalt and iron. As a result, according to SEM, XRD and X-ray spectral analysis, the silica 'skin-layer' containing uniformly distributed there nanoparticles of cobalt spinel ferrite ($CoFe_2O_4$) is formed on the surface of the powder. The specific surface of $BaTiO_3$ powder with a 'skin-layer', measured by the method of low-temperature adsorption of nitrogen, was increases in ~17 times. This phenomenon can be bound up with the formation on the powder surface of a more or less uniform layer, which changed the surface topography. To confirm this hypothesis, X-ray spectral mapping of barium titanate particles with a 'skin-layer' was carried out. It was shown that Si, Co and Fe are uniformly distributed over the surface of the $BaTiO_3$ particles. On the basis of the zeta potential measurements the following assumption is made: the formation of 'skin-layer' takes place through the mechanism of electrostatic interactions of oppositely charged the powder particles and the sol particles ($\zeta_{BaTiO3} = -0{,}41$, and $\zeta_{sol} = +2.57$ at pH ~2).

Using the method of small-angle scattering of polarized neutrons it was found that the powder with the structure of the 'core ($BaTiO_3$)-shell ($CoFe_2O_4$)' is characterized by nuclear-magnetic interference neutron scattering, the intensity of which is described satisfactorily by the quad Lorenz. Thus, we can conclude that the barium titanate powder acquires magnetic properties by modification of its surface using 'skin-layer', that contains the ferromagnetic nanoparticles $CoFe_2O_4$ with a characteristic size ~13 nm, structured by type of short-range order with the distance between their centers of $\xi \approx 150$ nm. The larger particles $CoFe_2O_4$ ~20–50 were observed using SEM. The magnetization curves for obtained materials were studied. The synthesized powders, so called multiferroics, were used as functional fillers for dielectric composites (polymer/filler) based on cyanoethyl ether of polyvinyl alcohol (CEEPVA).

It was found that the films based on the organic-inorganic composites (CEEPVA/$BaTiO_3$–$CoFe_2O_4$) were formed under the influence of the external magnetic field. The frequency dependence of the dielectric permittivity, conductivity and dielectric loss of these composites were studied. It was found the composites (CEEPVA/$BaTiO_3$–$CoFe_2O_4$) based powders with 'skin-layer', especially, which were dried under the influence of a magnetic field, have higher permittivity ε as compared to a reference sample (CEEPVA/$BaTiO_3$) on the basis of the initial powder.[1] Thus, the dielectric loss tangent increases slightly. The synthesized composites can find various useful applications including embedded capacitors and other electronics devices, as well as sensors, electromagnetic radiation shields, etc.

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A 3-D phase diagram of lead-free $z(Ba_{1-x}Ca_x)TiO_3$-$(1-z)Ba(Zr_yTi_{1-y})O_3$ piezoceramics system determined by Raman spectroscopy

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Keywords: lead-free piezoceramics, phase transitions, Raman spectroscopy

Piezoelectric ceramics have been widely used in sensors, actuators and ultrasonic transducers due to their ability to achieve efficient conversion between electric and mechanical vibrations. There is an urgent desire to move to lead-free materials achieving comparable piezoelectric performance to lead-based materials. The most promising alternative is the pseudobinary system $zBa_{0.70}Ca_{0.30}TiO_3$-$(1-z)BaZr_{0.20}Ti_{0.80}O_3$ (BCZT) due to the presence of a morphotropic phase boundary (MPB) in the phase diagram, and reports of large piezoelectric coefficients comparable to lead-based systems[1].

However, with the development of the structural study in this lead-free system, there was a debate on the crystal structure of the MPB region: (1) MPB was a single phase boundary separating the rhombohedral and tetragonal phases[1]; (2) the MPB region was actually with orthorhombic (*Amm2*) symmetry, bridging the polymorphic phase transitions between the rhombohedral and tetragonal phases[2].

In this study, the Raman spectroscopy measurements of end member systems (i.e. $Ba_{1-x}Ca_xTiO_3$ and $BaZr_yTi_{1-y}O_3$, abbreviated as BCTO and BZTO) were initially investigated to observe the dependence of the structural phase transition behaviour on the substitution of Ca on the Ba-site or Zr on the Ti-site in the parent $BaTiO_3$ phase. The successful determination of phase transitions by Raman spectroscopy in these end member systems inspired the further investigation of structural phase transitions in the more complicated BCZT system to clarify the crystal structure of the MPB region.

BCTO ($x = 0$–0.30), BZTO ($y = 0$–0.30) and BCZT ($z = 0$–1) samples were made by solid state methods, where BCTO ($x= 0$–0.15) samples were ceramic powders. The amount of Ca substitution in BCTO (x value), Zr substitution in BZTO (y value) and $Ba_{0.70}Ca_{0.30}TiO_3$ content in BCZT (z value) were determined by XRD. In all three systems, the accurate determination of phase transition points through the rhombohedral, orthorhombic, tetragonal and cubic phases were achieved by Raman spectroscopy measurement. The construction of a 3-D phase diagram of the lead-free $z(Ba_{1-x}Ca_x)TiO_3$-$(1-z)Ba(Zr_yTi_{1-y})O_3$ piezoceramic system ($x = 0$–0.30, $y = 0$–0.20, $z = 0$–1) was therefore established.

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Preparation and characterization of Cerium-doped $BaTiO_3$ nanotubes structures

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Keywords: barium titanate, sol-gel, nanotubes

In the last years, one-dimensional structures such as nanotubes, nanowires and nanorods of ferroelectric complex oxides have attracted great interest, due to their potential applications in miniaturized devices including various types of memory, capacitors and nanoelectromechanical systems (NEMS).[1–4]

In the present study, we describe the preparation by the sol-gel method of Ce-doped $BaTiO_3$ tubes with the nominal formula $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ and their microstructure and piezoelectric properties. Porous polycarbonate membranes with channels diameter of 100 nm and 200 nm, respectively, were used as templates.

The uncalcined nanotubes obtained by using as template a polymeric membrane with channels diameter of 200 nm show an average outer diameter and wall thickness of 190 nm and 12 nm, respectively.

Crystalline Ce-doped $BaTiO_3$ tubes obtained after thermal treatment in air, at 700 °C/ 1 hour, exhibit uniform morphology. $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ tubes with diameter of 140–180 nm show larger grains (average grain size of 30 nm) larger crystallites (10–15 nm) and higher porosity.

PFM investigations indicated ferroelectric and piezoelectric characteristics for all the $Ba_{0.95}Ce_{0.05}Ti_{0.9875}O_3$ tubes prepared in this study.

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Defect chemistry and conductivity mechanisms in B-site acceptor doped and A-site non-stoichiometric $Na_{0.5}Bi_{0.5}TiO_3$

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Keywords: impedance spectroscopy, ionic conductivity, NBT

As reported by Ming Li et al., the A-site non-stoichiometry as well as the B-site acceptor doping of $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) has a dramatic influence on the oxygen vacancy concentration and ionic conductivity.[1,2] Mg acceptor doped NBT, for instance, shows extremely high ionic conductivity comparable with conventionally used solid ion conductor materials. Related to the experience with other lead based or lead free ferroelectric ceramics, this behavior was a rather unexpected result. The origin and defect chemical reason for these results are part of important ongoing research approaches. In this work, we will discuss the formation and effect of oxygen vacancies in A-site non stoichiometric B-site doped $Na_{0.5}Bi_{0.5}TiO_3$. With the help of temperature and DC-voltage dependent impedance spectroscopy (IS) the defect chemistry and the charge carrier migration process was investigated. Furthermore, phase and charge carrier dependent simulations are included according to get a deeper understanding of the origin for this unexpected conductivity behavior. From these results we are able to propose how the investigated changes to NBT may affect other NBT related materials.

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Structure and magnetoelectric properties of $0.5BiFeO_3 – 0.5Pb(Fe_{0.5}Nb_{0.5})O_3$ solid solution

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Keywords: multiferroics, crystal structure, hyperfine interactions, ab initio calculations

Materials that exhibit magnetic and electric ordering in the same phase are named magnetoelectrics. They are part of a larger group of multiferroics which posses at least two ferroic-orderings in the same phase. The most widely studied and used magnetoelectric oxides are ABO_3 perovskites which have the prototypical cubic structure. This structure is characterized by a large A cation at the corners of the cubic unit cell and small B cation which is placed in the middle of the cell in the centre of oxygen anion octahedra.

Bismuth ferrite $BiFeO_3$ (BFO) is one of the most important multiferroic perovskite oxides. It is ferroelectric with Curie temperature $T_C = 1100$ K and antiferromagnetic with Neel temperature $T_N = 643$ K.

Lead iron niobate $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) is another type of magnetoelectric material where ferroelectric active Nb^{5+} are partially substituted by magnetic Fe^{3+} of a different valence state. PFN exhibits a broad ferroelectric transition around 370–380 K and two diffuse magnetic transitions at 150 K and around 10 K.

Magnetoelectric 0.5BFO-0.5PFN solid solution adopt at room temperature rhombohedrally distorted perovskite-like crystal structure (R3c space group). In which Fe^{3+}/Nb^{5+} cations are distributed randomly in the B sublattice. It was shown that increasing the number of Fe-O-Nb linkages lead to reduction of iron magnetic moment. According to theoretical calculations the solid solution has an insulating properties with energy band gap about 1.6 eV.[1]

Magnetoelectric properties of the above solid solution were characterized using Mössbauer spectroscopy, differential thermal analysis, impedance spectroscopy, magnetization and magnetoelectric effect measurements. According to the obtained results the material is antiferromagnetic with Neel temperature 460 K and ferroelectric with Curie temperature 630 K. Magnetic hysteresis loop is not fully saturated up to 56 kOe and is characterized by small coercivity 1.5 kOe and saturation remanence 11 emu/mol.

The obtained experimental results will be compared and discussed with electronic band structure calculations.

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Local distortion determination of the (1-x)($K_{0.5}Na_{0.5}$)NbO_3-x($Ba_{0.8}Sr_{0.2}$) TiO_3 system and their influence on the electrical properties

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Keywords: KNN-BST, X-ray absorption spectroscopy, local structure distortion, conductivity, permittivity

The composition of (1-x)($K_{0.5}Na_{0.5}$)NbO_3-x($Ba_{0.8}Sr_{0.2}$)TiO_3 and termed as (1-x)KNN-xBST for x = 0, 0.1 and x = 0.2 were successfully synthesised using a combination of solid-state reaction and co-precipitation oxalate methods. Structure and local distortion determination were carried out using X-Ray diffraction (XRD), and X-ray absorption spectroscopy (XAS) *Ti* K-edge data. The XRD was utilised to investigate the phase present in the sample and crystal structure determination through Rietveld refinements, while local distortion due to the defects were studied by XANES and EXAFS at the *Ti* K-edge. XRD analysis at room temperature concluded that both KNN-BST samples behave tetragonal structure compared to orthorhombic for KNN, while EXAFS analysis using Artemis software revealed the oxygen octahedral distortion and distance of Ti_{Nb}' to its surroundings of A site ions (K, Na. $Ba_{K\bullet}$, $Sr_{Na\bullet}$) and B site ions (Nb_{5+}). Electrical characterisations of dielectric properties and conductivity were investigated to elucidate the changes in local distortion. Conductivity measurements at various temperatures showed an alteration of curves slope from positive at low temperature region become negative at high temperature. The temperature inflection of $\ln \sigma$ vs $1/T$ curves, was shift to higher temperature for doped samples, T ≈ 150 ºC for KNN and T ≈ 225 ºC for KNN-BST. The characterisation of dielectric properties exhibited a broader peaks which is a typical relaxor characteristic and was thought to be related to the distortion of oxygen octahedral arrangement surrounding the B sites in the ABO_3 structure.

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Overcoming barriers of lead-free piezoceramics – spray-pyrolysis as a preferred synthesis route

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Today, more than 98% of the world market for piezoceramic materials consists of lead-containing materials (PZT). Even though RoHS and REACH regulations are pushing towards a replacement of PZT, the absence of a reliable supply of lead-free materials is an impeding factor during the transition phase. The state-of-the art process used to produce PZT materials, solid-state synthesis, is not suitable for lead-free piezoceramics, mainly due to evaporation of volatile species and poor sinterability of the powders. Therefore, substantial effort is needed to develop and modify production and processing technologies to qualify lead-free piezoceramic materials and prove their performance and durability on a component level.

Spray pyrolysis is a scalable synthesis route with the capability to produce lead-free piezoceramic materials in excellent quality and in industrial amounts, thereby, overcoming a crucial barrier on the way to the large-scale commercialization of lead-free piezoceramics. The process spray pyrolysis yields homogeneous materials, stoichiometric control and submicron particles with excellent sinterability. Recent results from the production and subsequent characterization of lead-free piezoceramic powders will be presented.

Despite the properties and quality offered, component production protocols developed for solid-state powders cannot be directly applied to spray pyrolysed materials. Additionally, lead-free materials offer additional advantages such as the possibility to replace expensive noble-metal electrodes with low-cost nickel. CerPoTech and partners are developing components using spray-pyrolysis powders and employ industrial standard testing methods to verify the performance and consistency of the materials and components. An outlook on the demonstration of the components and the way to develop competitive products will be given.

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Fabrication of translucent and fluorescent Eu doped CASN bulk ceramics using a spark plasma sintering technique

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Keywords: $CaAlSiN_3$, spark plasma sintering, phosphor

Commercial white LEDs consist of excitation light source and SiAlON phosphor powders dispersed in a resin. For high power application, the resin is not desired because of the low thermal durability. In order to actualize the high power LEDs without a resin, transparent and fluorescent α- and β-SiAlON bulk ceramics were developed in our previous work. Although they show the good fluorescence from blue to yellow, red colour has not been achieved, yet. As a red phosphor, $CaAlSiN_3:Eu^{2+}$ has a high quantum efficiency due to 5d-4f transition even at high temperatures. In this work, the transparent and fluorescent $CaAlSiN_3:Eu^{2+}$ ceramics was fabricated by applying a spark plasma sintering. As raw powders, Si_3N_4 (SN-E10, Ube Industries Co., Ltd., Japan), AlN (H-grade, Tokuyama Co., Ltd., Japan), Ca_3N_2 (Sigma-Aldrich Co., USA) and Eu_2O_3 (Shin-Etsu Chemical Co., Ltd., Japan) were used. These powders were mixed in toluene in N_2 gas by ball-milling with SiAlON balls (φ5 mm). The mixed powder was separated from toluene by centrifugalizing at 1000 rpm for 1 min and then dried in N_2 gas for 3 hours. The dried powder was milled by Al_2O_3 mortar and it was set into a carbon die (φ25 mm). Spark plasma sintering was carried out at the temperature from 1650 to 1750 °C for 10 min in N_2 gas. The relative density was measured by Archimedes method. As a result, the relative densities of $CaAlSiN_3:Eu^{2+}$ ceramics after spark plasma sintering were over 99%. They have good translucency and red-color fluorescence excited by blue-LED of 450nm. All specimens showed broad spectrum pattern due to 5d-4f transition. The emission peak was shifted to longer wavelength depending on the concentration of added Eu_2O_3. It can be considered that the peak shift resulted from an expansion of crystal lattice of $CaAlSiN_3$ by the substitutional solid solution of Eu^{2+}.

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Nanosized titania particles for application in photocatalysis

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In this work we present simple synthetic route with low energy requirements, designed to produce high surface area titania (TiO_2) photocatalyst. Method involves usage of titanium(IV)-isopropoxide and chitosan, a polysaccharide rarely utilized in ceramics-related research. Thorough characterization of the obtained powders was conducted using several instrumental techniques (FE-SEM, XRD, BET and UV-VIS-NIR spectroscopy) which revealed the presence of sub-10 nm particles, and confirmed pure or predominant presence of anatase crystallographic phase, higher surface area than in commercial referent samples, and slightly enhanced absorption in the visible portion of the spectrum. The photocatalytic degradation of textile azo dyes under UV-enriched light source was investigated (230 mW cm^{-2}, 20 °C), showing very high adsorption capability of the powders, and superior photocatalytic behaviour compared to referent samples.

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Giant dielectric permittivity and high tunability in Y-doped $SrTiO_3$ ceramics tailored by sintering atmosphere

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Keywords: electroceramics, donor doping, polar clusters, Maxwell-Wagner interfacial polarization

Development of giant-permittivity and high-tunability dielectric materials has attracted great interest because of growing demand for smaller and faster energy-storage and electronic devices. Materials such as $CaCu_3Ti_4O_{12}$, displaying the giant dielectric permittivity due to extrinsic Maxwell-Wagner interfacial polarization effect, have previously been reported.[1] Ferroelectric materials possessing intrinsic ionic polarization due to a phase transition to the polar state have also been indicated to possess a high tunability of the dielectric permittivity by dc electric field.[2] Here, a class of the giant-permittivity materials based on $SrTiO_3$ ceramics doped with up to 1% of yttrium and their processing concept, which yields the dielectric permittivity up to ~209 000 at 10 kHz for nitrogen sintering atmosphere, and the relative tunability up to ~74% under 20 kV cm^{-1} for oxygen sintering atmosphere, is reported. The high tunability is proved to be due to polar clusters created at low temperatures by off-central Y^{3+} ions on Sr^{2+} sites.[3] The giant permittivity is explained by a coupling of the polar clusters relaxation mode with the donor substitution induced electrons at low temperatures[4] and by the Maxwell-Wagner relaxation around room temperature. Besides the fundamental understanding, this discovery opens a new development window for high-frequency and low-temperature electronic and energy-storage applications.

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Ionic conductor device for selective detection of hydrocarbons on diesel exhaust gases

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Keywords: ethylene, sensor, ionic conductor, automotive

In the recent past years the detection of hydrocarbons in exhaust gas of diesel cars has increasingly gained in importance due to air quality regulations. As hydrocarbons and other pollutants are related to health issue problems in humans,[1] both American and European legislators are reducing the emissions of these pollutants allowed.[2–4] Nowadays there are restrictions because of the impossibility to detect HCs at lower concentrations. As a health issue, more restrictive legislations will be legislated if sensors able to detect HCs at these lower concentrations are provided.

Thus, in this work an ionic conductor device is made to detect selectively ethylene. 8YSZ is pressed in order to obtain a disk, which is used as electrolyte as well as support. As working electrode $FeCr_2O_4$ is employed because of its catalytic activity toward ethylene. Platinum is usually employed as reference electrode, but in this work we used a cheaper material with ionic conductivity: LSM/8YSZ. This allows fulfilling two desired aims: the improvement of the catalytic activity toward oxygen and reduce the cost. In addition, a functionalization of the surface is performed on the WE to increase the catalytic activity toward ethylene and reduce the cross sensitivity to CO. Thus, a selective device to C_2H_4 is obtained.

Materials are obtained by sol-gel Pechini method and screen-printed onto electrolyte support. A gold coating is made to ensure contact. Here is studied sensor response to C_2H_4 and CO concentration. Voltage generated is recorded by KEITHLEY 2601 and 3706-NFP.

The structural, textural and morphological features of the resultant powders were investigated by X-ray diffraction (XRD), while devices structural characterization is performed by scanning electron microscopy (SEM).

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Internal field in asymmetric P–E curves of $BaTiO_3$:Co piezo ceramics by defect dipoles orientation

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Keywords: piezoelectric, ceramic, lead-free, doping, functional properties, charge compensation, hysteresis loop

Barium titanate ceramic (BT) was one of the first materials used in the fabrication of piezoelectric devices. However, BT was quickly supplanted by lead zirconate titanate ceramics (PZT) which exhibit both lower sintering temperatures (1200 °C rather than 1350 °C) and higher piezoelectric properties.The need for lead-free piezoceramics renewed the interest in developing $BaTiO_3$ ceramics. BT ceramics doped with Ca^{2+}, $Co^{2+/3+}$ and Nb^{5+} were synthesized using a conventional ceramic process. The addition of Li_2O as a sintering aid resulted in very dense ceramics sintered at around 800 to 1100 °C. The substitution of Ti^{4+} by $Co^{2+/3+}$ in the perovskite structure, increased the piezoelectric performance (d_{33} = 210pC/N and k_p = 38%). The co-substitution with the pentavalent ion Nb^{5+} leads to a d_{33} of 250pC/N and k_p = 42%. The same performance was measured for BT:Ca,Co ceramics.

The use of $Co^{2+/3+}$acceptor doped BT ceramics leads to a significant increase in performance and hard piezoelectric feature (Q_m~1000). Indeed, if BT ceramics present a regular P–E curve, $Co^{2+/3+}$doped ceramic exhibits double-loop and asymmetric P–E curves in non-poled and poled states, respectively (Fig. 1). This behavior is attributed to the creation of electric dipoles between the acceptor dopants and the oxygen vacancies by charge compensation during substitution of Ti^{4+} by Co^{3+}. Acceptor doped BT ceramics exhibit a defect chemistry dominated by oxygen vacancies and ionized acceptors rather than electronic carriers. The concentration of charged ionic point defects is orders of magnitude larger than the concentration of electrons and holes at RT due to high concentration of the oxygen vacancies fixed at high temperature. The defect dipoles in the material induce an internal field[1] which can be observed through the acquisition of the asymmetric ferroelectric hysteresis loop (Fig. 1b). This internal field which is tied to the concentration of defect dipoles is observed during the insertion of $Li^+/Co^{2+/3+}$. The decrease of the internal field by donor co doping (Nb^{5+}) or oxygen annealing could be consistent with the decrease in concentration of defect dipoles. The trade-off between internal field and acceptor/donor concentration and the stability of the material under electric stress will be presented.

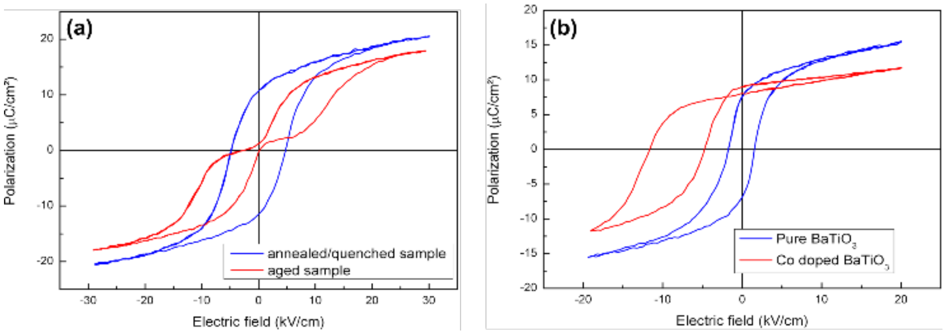

Fig. 1. Hysteresis curves of BaTi1-xCoxO3-2x/3, y Li2O ceramics; (a) non-poled samples, (b) poled samples

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Tailoring strains and physical properties of epitaxial thin films on vicinal substrates

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It is well known that controllable interfacial strain can manipulate the physical properties of epitaxial thin films. Besides using normal lattice mismatch, by using a proper design of vicinal single-crystal substrate, the interface strain in epitaxial thin films can be well controlled via a surface-step-terrace matching growth mode. Here, we demonstrate that $LaAlO_3$ (LAO) substrates with various miscut angles and miscut orietations were used to tune the dielectric properties of epitaxial $CaCu_3Ti_4O_{12}$ (CCTO) and $Ba(Sr,Ti)O_3$ thin films. A model of coexistent compressive and tensile strain domains is proposed to understand the stress relaxation mechanism. The results may help open a new avenue to manipulate the strain and physical properties of epitaxial thin films, which is critical for the design and integration of advanced heterostructures for high performance device applications.

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TeO_2/SnO_2 hybrid nanowire structures for enhanced room-temperature gas sensing

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Keywords: gas sensor, tellurium oxide, tin oxide, nanowires

We have synthesized two highly sensitive, room-temperature operating TeO_2/SnO_2 gas sensors with hierarchical nanowire structures. One is a *brush-like* nanostructure by a two-step thermal vapour-transport route, and the other one is a TeO_2/SnO_2 *bead-like* nanostructure by annealing of the former one. The TeO_2/SnO_2 nanostructures exhibit a much enhanced room-temperature gas-sensing response than the pristine TeO_2 nanowires in a sequence that the TeO_2/SnO_2 bead-like structure > the brush-like structure > the pristine TeO_2 nanowires. The response of the TeO_2/SnO_2 bead-like structure is in a range of 10 to 20 against NO_2 gas of ppm levels (3–100 ppm) at room temperature. This compares favourably to the response smaller than 2 for the pristine TeO_2 nanowires. Interestingly, the TeO_2/SnO_2 bead-like structure exhibits a typical n-type gas-sensing behaviour, in contrast to the p-type behaviour from the brush-like and the pristine TeO_2 structures. Possible hybrid growth and sensing mechanisms are discussed. The nanohybrid structure has also been extended to other oxide combinations for enhanced sensing response and gas selectivity.

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Vanadium oxide production by solution combustion synthesis

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Keywords: solution combustion synthesis, vanadium oxide, optical properties, electrochemical properties

Self-propagating high temperature synthesis called as a combustion synthesis is used for the production of advanced materials, which consist of ceramic, intermetallic compound, composite and functional materials close to the powder or final product. Solution combustion synthesis is an easy, simple and rapid method that allows the production of many nanodimensional materials. This method involves the self-propagating reaction of homogeneous

solutions which has different oxidative precursors (metal nitrates) and fuels (urea, glycine, hydrazide, etc.).[1,2]

Vanadium is a metal that can take more than one valence and thus can form different oxide compounds. These oxides have different properties due to their different compositions. For example, VO_2 and $H_2VO_3O_8$ are used as an optical, electrical, electrochemical, thermochromic and thermal switch material. VO_2 has also different polymorphic forms which can reveal stable and metastable phases. For instance, VO_2, which is a monoclinic metastable phase, is used as a cathode material especially in lithium ion batteries. Thin films of vanadium oxide (V_2O_5) is used as electrochromic and thermochromic devices, uncooled bolometric detectors, laser protection, solar cell windows, high-capacity lithium battery electrodes, electrical and optical switching devices, light modulators.[3,4]

In this study, vanadium oxide nanoparticles were synthesised by solution combustion method. Oxalic acid dihydrazide (ODH) ($C_2H_6N_4O_2$), citric acid ($C_6H_8O_7.H_2O$) and mix fuel were used as a fuel material during solution combustion synthesis (SCS), while ammonium meta-vanadate (NH_4VO_3) was used as an oxidant. The structure, morphology and chemical composition of the samples were characterized by using XRD and SEM & EDS methods. Surface area of synthesised particles were determined by BET analysis.

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Poster presentations

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Strontium oxynitride phosphor doped with Eu^{2+} ions: phase purity/optical properties relationship

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Keywords: oxonitridosilicate, flux, phosphor, photoluminescence characterization, solid state synthesis, gas pressure synthesis

Eu^{2+}-doped $SrSi_2O_2N_2$ was prepared via a gas pressure method or a solid state reaction method with various amount of Na_2CO_3 fluxing agent. The phase composition of obtained materials was studied using X-ray diffraction. The local environment of the activator ions in the structure was examined using X-ray absorption near-edge spectroscopy (XANES). The photoluminescent properties were investigated by emission, excitation and quantum efficiency measurements. Decay times and thermal stability of the powders were determined as well.

Obtained results show that nitrogen and CO partial pressure during the process of synthesis influence the phosphor crystallization. It has been found that usage of Na_2CO_3 flux improves crystallization of the desired phase, enhancement of optical properties was also visible. An optimum concentration of the flux was 5 wt% since exceeding this value resulted in formation of an excessive amount of glassy phase, as well as some evidence of the secondary phase formation.

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Grain growth behaviors and piezoelectric properties of alkali ions excess NKLNT ceramics

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Keywords: piezoelectric, microstructure, NKLNT

Lead oxide-based ferroelectrics are the most widely used materials for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties. Considering lead toxicity, there is great interest in developing lead-free piezoelectric materials, which are bio-

compatible and environmentally friendlier. Recently (Na,K)NbO_3 based ceramics have been given attention in view of their ultrasonic application and also as promising candidates for piezoelectric lead-free system. However, it is difficult to sinter the ceramics via conventional sintering process. In this study, it was investigated that the effect of additions with A-site ions in perovskite structure on electromechanical properties and grain growth behaviors in $(Na_{0.475}K_{0.475}Li_{0.05})$ $(Nb_{0.95}Ta_{0.05})O_3$ (NKLNT) ceramics. Sintering temperature was lowered by adding A-site ions and abnormal grain growth in NKLNT ceramics was observed with varying additions. These microstructural changes show the typical grain growth behavior due to the change in critical driving force for rapid grain growth in structure of the faceted interfaces or boundaries. The grain growth behavior can be explained in terms of interface reaction-controlled nucleation and growth. The piezoelectric properties of NKLNT ceramics were investigated as a function of concentration of additions. The electromechanical coupling factor and piezoelectric constant were improved in the samples with A-site ions excess NKLNT. These results show that the electromechanical properties of NKLNT ceramics can be improved by controlling the microstructures.

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Perovskite phase formation, microstructure and dielectric properties of $BaTiO_3$-based ceramic nanocomposites

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Keywords: nanocomposites, barium titanate, gold nanoparticles, sintering

Owning to their non-toxic and variable electrical properties, perovskite ferroelectric barium titanate ($BaTiO_3$) BT-based ceramics are of interest as the promising smart materials in commercial electrical components. However, they suffer from high sintering temperature requirement, low dielectric constant and high dielectric loss, causing a limitation for their practical utilizations, especially for the multilayer ceramic capacitors with ultrathin layers. Thus, several solutions have been proposed to overcome these limitations including an approach of reinforcing the ferroelectric matrix phase with high electrical conducting phases. In the present study, small amount of gold nanoparticles reinforced BT composites were developed by employing a solid-state sintering techniques without any binders. Apart from their environmental friendly, gold nanoparticles are thought to be reasonable candidate used for shortening the electrode distance in the nanometal/BT ceramics. These nanocomposites are expected to synergistically combine the properties of both the ferroelectric BT and the conductive gold nanoparticle, which could exhibit dielectric properties that are better than those of the monolithic BT ceramics. By employing a combination of several characterization techniques, the obtained results indicate that using different sintering temperature or gold nanoparticle amounts to produce the composites greatly affect the perovskite phase formation, densification, microstructure and dielectric properties of the materials. Microstructural investigation revealed that some gold nanoparticles were heterogeneously dispersed in BT matrix and at the matrix boundaries. The obtained results indicate that under suitable sintering condition and nanogold content, both densification and dielectric properties of the composites with fine-grained microstructure fabricated in this work were significantly improved, as compared to the unmodified BT ceramics.

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The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free 0.94Na0.5Bi0.5TiO$_3$-0.06BaTiO$_3$ ceramics

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Ta-doped lead-free 0.94NBT-0.06BT-xTa (x = 0.0 – 1.0%) ceramics were synthesized by a conventional solid-state route. XRD shows that the compositions are at a morphotropic phase boundary where rhombohedral and tetragonal phases coexist. The depolarization temperature (T_d) shifted to lower temperature with the increase of Ta content. The pyroelectric coefficient (p) of doped ceramics greatly enhanced compared with undoped material and reached a maximum of 7.14×10^{-4} C.m^{-2}.°C^{-1} at room temperature (*RT*) and 146.1×10^{-4} C.m^{-2} °C^{-1} at T_d at x = 0.2%. The figure of merits, F_i and F_v, also showed a great improvement from 1.12×10^{-10} m.v^{-1} and 0.021 m^2.C^{-1} at x = 0.0 to 2.55×10^{-10} m.v^{-1} and 0.033 m^2.C^{-1} at x = 0.2% at RT. Furthermore, F_i and F_v show the huge improvement to 52.2×10^{-10} m.v^{-1} and 0.48×10^{-10} m^2.C^{-1} respectively at T_d at x = 0.2%. F_C shows a value between 2.26 to 2.42×10^{-9} C.cm^{-2}.°C^{-1} at RT at x = 0.2%. The improved pyroelectric properties make NBT-0.06BT-0.002Ta ceramics a promising infrared detector material.

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Synthesis and properties of $YBa_2Cu_3O_{7-\delta}$ – $Y_2Ba_4CuWO_x$ ceramics composites

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Keywords: YBCO, 2411 phase, bulk, nanosized, pinning, $Y_2Ba_4CuWO_x$

YBCO is a well-known high-temperature superconductor (HTS); however, its critical current density and thus the maximum trapped magnetic field can be improved significantly by introducing the secondary phases (artificial pinning centers). In this contribution, we successfully prepared YBCO single-grain bulks with nanostructuralized $Y_2Ba_4CuWO_x$ (Y-2411W) pinning phase. Y2411W phase was prepared by solid state reaction and further refined by milling. In the next step single-grain YBCO bulks with homogenously distributed nanoparticles of $Y_2Ba_4CuWO_x$ were prepared by top-seeded melt growth. Precursors as well as the final product were characterized by XRD, SEM, EDS and PPMS. Oxygen stoichiometry was studied by STA. Bulk superconducting properties such as levitation force and trapped field ability were also measured. Obtained results are of significant importance for research and applications in the field of superconducting ceramics.

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Textured ternary PIN-PMN-PT systems and their characterization

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Keywords: piezoceramics, textured, PIN-PMN-PT, electrical properties

Ferroelectric single crystal (1-x)$Pb(Mg_{1/3}Nb_{2/3})TiO_3$-x$PbTiO_3$ (PMN-PT) and x$Pb(In_{1/2}Nb_{1/2})O_3$-(1-x-y) $Pb(Mg_{1/3}Nb_{2/3})O_3$-y$PbTiO_3$ (PIN-PMN-PT) ternary systems have been drawn attention in field of electronic device applications because of their giant piezoelectric coefficient and outstanding coupling factors of <001> direction. The Curie temperature (T_c) of PMN-PT is reported in literature between 130–170 ^oC, which is restricted to application areas. Beside this, PIN-PMN-PT ceramics have thermal stability and T_c changes from 160 ^oC up to 320 ^oC with regard to composition in morphotropic phase boundary (MFB).[1,2] However, single crystal growth techniques are required high cost equipment and single crystals show stoi-

chiometric deviations for this kind of compositions. The crystallographic textured ceramics exhibits higher electrical properties than conventional ceramics which is comparable with the properties of single crystals.[3] In this study, textured $0.26Pb(In_{1/2}Nb_{1/2})O_3$-$0.40Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.34PbTiO_3$ (PIN-5BT) and 1.5 mol. Mn % doped (PIN-5BT-1.5Mn) ceramics were synthesized by templated grain growth method (TGG) by using 5 vol % plate-like $BaTiO_3$ (BT) templates. Random and textured PIN-PMN-PT ceramics were sintered at 1150°C for 6 h. Lotgering factors of the both textured, PIN-5BT and PIN-5BT-1.5Mn ceramics were obtained as 94%, respectively. The maximum field induced bipolar strain of PIN-R, PIN-T5, PIN-1.5Mn and PIN-T5-1.5 Mn was measured as 0.16%, 0.25%, 0.12% and 0.24%at 40kV/cm, respectively.

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Photoluminescence-structure correlations in ferroelectric Eu:Ba(Ti,Zr)O_3 ceramics: study of phase transitions and polar order

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$BaTiO_3$-based ferroelectric ceramics show interesting properties such as high dielectric constant, low losses, high hydrostatic piezoelectric coefficient and PTCR effect. For these reasons, barium titanate is widely used in the electronic industry for manufacturing miniaturized multilayer ceramic capacitors, underwater transducers and self-regulating thermistors. $BaZr_xTi_{1-x}O_3$ (BZT) solid solution shows a series of phase transitions and a progressive evolution of ferroelectric order, from long-range order typical of classic ferroelectrics ($x = 0$) to short-range order typical of relaxors ($x \geq 0.25$), which consequently affects the functional properties. This material can be considered as a model system for understanding the composition-property correlations in ferroelectric ceramics. The trivalent europium ion (Eu^{3+}) is well known for its strong luminescence in the red spectral region. Even very small variations in the coordination sphere of europium ions induce major changes in the emission spectrum. Thanks to these features, Eu^{3+} is a unique and powerful local structural probe. In this framework, we used photoluminescence (PL) as a tool to investigate the phase transitions and the ferroelectric order in BZT using Eu^{3+} as active centre. Dense ceramics (relative density: 96-99%) with composition $Eu_yBa_{1-y}Zr_xTi_{1-x-y/4}O_3$ ($y = 0.01$, $x = 0$, 0.05, 0.15, 0.30, 0.50, 0.70, 1) were prepared by the classical solid-state route and sintered at 1450-1550 °C. The dielectric permittivity of the samples was measured from –150 to 150 °C and at 10^2–10^6 Hz to determine reference values of the phase transition temperatures. The study of PL spectra as a function of temperature, in the interval –100 to 140 °C, revealed strong shape and intensity variations of the emission bands in the proximity of phase transitions as well as a significant dependence of their relative intensity for compositions having $x \geq 0.30$, i.e. materials with relaxor behaviour.

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Preparation, characterisation and dielectric properties of PVDF – $BaTiO_3$ composites

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The demand for high dielectric constant materials and high energy density capacitors has rapidly increased in recent years due to the continuous and rapid development of the electronic industry and the need of storing electrostatic energy more efficiently. The combination of dissimilar materials in a composite represents an effective approach for the optimization of the dielectric properties. In particular, the addition of ferroelectric (barium titanate, $BaTiO_3$) nanoparticles with high dielectric constant ($k \approx 1000$) enables the relative dielectric constant of the polymer (usually in the range 3–10) to be significantly increased without compromising some of the most useful properties of the material, i.e. its flexibility and the high dielectric breakdown field.

Polymer composites were prepared using poly(vinylidene fluoride) (PVDF, SOLEF 6008 Solvay) as a matrix and $BaTiO_3$ nanoparticles (diameter: 100 nm) as inclusions. The $BaTiO_3$ particles were prepared by a hydrothermal-like method starting from $BaCl_2$ and $TiCl_4$ precursors. The composites were fabricated by a two-step process. Firstly, PVDF and $BaTiO_3$ particles were intimately melt-blended at 200 °C in an internal batch-mixer. Batches of about 100 g of composites containing 20–40 vol.% $BaTiO_3$ were prepared each time. Films with a thickness of 0.5–1 mm were then fabricated by compression moulding.

The composites were fabricated using bare and surface-modified $BaTiO_3$ particles. Surface modification included functionalisation with coupling molecules (silane derivatives) and coating with a thin TiO_2 shell (thickness: 20–30 nm). These engineered polymer/ceramic interfaces should facilitate the homogeneous dispersion of the inclusions and realise a more homogeneous distribution of the electric field in the ensuing composite.

The composites were characterised with different techniques. The microstructure was observed on fragile-fracture surfaces by scanning electron microscopy. The thermal behaviour was investigated by TG and DSC analyses. The amount of the ferroelectric crystalline β phase in the PVDF matrix was determined by FT-IR spectroscopy. The dielectric constant and loss tangent were measured at different frequencies by impedance spectroscopy. Simulation of the field distribution in model composites was performed by 3D finite element modelling.

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Impedance spectroscopy study on the resistance degradation of Zr-doped barium titanate dielectrics

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Keywords: barium titanate, impedance spectroscopy, resistance degradation, zirconium

In this study, a series of $Ba(Zr_xTi_{1-x})O_3$ powders were prepared for x = 0, 0.02, 0.04, 0.06, and 0.08 compositions using a solid-state reaction. It can be seen that the substitution of Ti^{4+} (0.61 Å) by 4–8% Zr^{4+} (0.72 Å) changes the room temperature crystal structure from tetragonal to orthorhombic. The $Ba(Zr_xTi_{1-x})O_3$ powders were sintered under a reducing atmosphere in a moisturized gas mixture of N_2 with 1 vol% of H_2, and the resulting average grain size ranged from 0.58 to 0.66 μm. Electrical characteristics, such as electrical resistance at high temperature (160 °C) and impedance spectroscopy were measured. The impedance data were fitted with an equivalent circuit model of three RC elements, which corresponding to the grain, grain boundary, and electrode. From the impedance spectroscopy analysis and resistance degradation data, the behavior of resistance degradation is observed to be improved with the decrease of both grain and grain boundary conductivities. However, the incorporation of Zr has an insignificant effect on the space charge layer thickness and the grain boundary potential barrier height. The insignificant or irregular variation in impedance spectroscopy and resistance degradation might be attributed by the similarity between the space charge layer thickness and the grain size because of the fine grain in this study, which means the resistance value of grain and grain boundary is not very different and the two RC responses of grain and grain boundary could not be separated easily.

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Multiferroic property of samarium doped bifeo$_3$ ceramics at morphotropic boundary by water-quenching method

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Keywords: multiferroic, samarium, bismuth-ferrite, ceramic

The bismuth ferrite ($BiFeO_3$, BFO) is a room-temperature multiferroic material with high Curie temperature (1100K) and high Neel temperature (653K). Base on the multiferroic order of BFO system, it will be applied to sensor devices and multi-storage memory devices. However, the BFO cannot be approached to single phase due to the bismuth volatility and valence electron state transition of iron. It is a hinder to measure the multiferroic property. To approach the single phase of BFO system, solid solution with rare-earth orthoferrite is the way to improve of the multiferroic property. In a specific selected of solid solution, $SmFeO_3$ (SFO) with BFO system is improved the multiferroic property at morphotropic phase boundary ($Bi_{0.86}Sm_{0.14}FeO_3$).[1,2] In this study, $Bi_{0.86}Sm_{0.14}FeO_3$ ceramics are studied with different sintering method; water-quenching (WQ), air-quenching (Q) and furnace-cooling (FC). The phase and structure are observed rhombohedrally distorted perovskite structure with orthorhombic phase. The ferroelectric remnant polarization observed with 20 μC/cm^2, 17 μC/cm^2 and 15 μC/cm^2 from WQ, Q and FC. Temperature-dependent dielectric constant is observed the ferroelectric to paraelectric transition temperature at 450 ^{o}C from WQ. The piezoelectric properties are measured with 32pC/N and 30 pm/V from WQ. Other detail information will be present with poster.

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Athermal TA_2O_5 waveguide filter for Si photonics

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Keywords: athermal, Ta_2O_5, waveguide filter, Si photonics

Athermal waveguide devices have been studied extensively recently due to their potential of providing stable spectrum response with respect to ambient temperature. This is of great importance for their applications to a wavelength division multiplexing (WDM) system.

Conventional, an athermal waveguide device can be obtained by incorporating an optical cladding on the device and using its negative thermo-optic (TO) coefficient to counterbalance the positive TO coefficient of the waveguide core. However, this approach is not applicable for Si waveguides because Si has a large TO coefficient (10^{-4}/K).[1]

In this work, Ta_2O_5 waveguide device is proposed for athermal Si photonics. The TO coefficient of Ta_2O_5 is two orders of magnitude lower than that of silicon.[2] In addition, the relatively large index contrast between Ta_2O_5 core and silica cladding limits only a small portion of light to propagate within the cladding. For the 0.5 µm by 0.7 µm Ta_2O_5 waveguide filter, the wavelength temperature shift is 0.22 pm/K, which is over 100 times lower than that of normal silicon waveguides.

The grating structure of the Ta_2O_5 waveguide filter is shown in Fig. 1. The period and duty cycle of the grating is 440 nm and 30%, respectively. The device was completed by spin coating a 2 µm thick SOG as the top cladding and cured at 250 °C for 1h. Fig. 2 shows the TE and TM transmission spectra of the device at room temperature. The FWHMs of the TE mode and TM mode are 5.1 nm and 2.7 nm. Fig. 3 shows the temperature dependent Bragg wavelength (λ_B) shift of TE mode of the waveguide filter. A total wavelength shift of 22 pm was obtained with a temperature change of 100 °C. This indicates that the Ta_2O_5 waveguide devices can be used in a practical WDM system without temperature control.

In conclusion, we successfully demonstrated an athermal waveguide device based on Ta_2O_5 material system. We believe that the proposed material system can be useful for applications in many practical WDM systems.

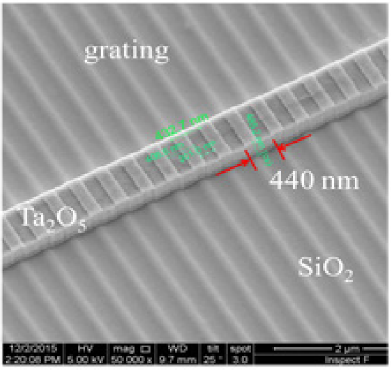

Fig. 1. The SEM photo of the Ta_2O_5 grating

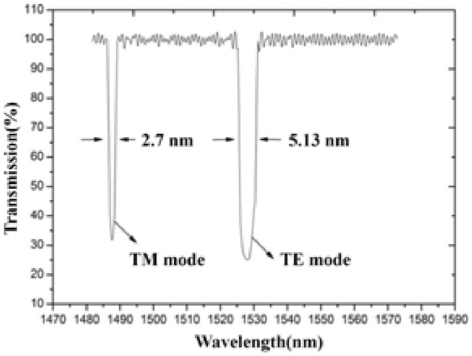

Fig. 2. The transmission spectra of the Ta_2O_5 waveguide filter

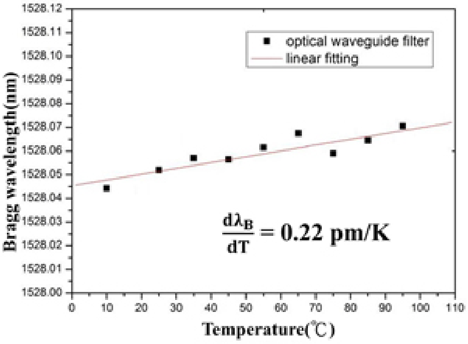

Fig. 3. The temperature dependent wavelength drift of the Ta_2O_5 waveguide filter

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Effect of chromium doping in polycrystalline CCTO

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Keywords: chromium, calcium titanate, electroceramics, non-ohmic

$CaCu_3Ti_4O_{12}$ (CCTO) is a ceramic with perovskite-type structure and has attracted much interest due to its high dielectric constant (up to 10^5) which is almost frequency-independent until the order of MHz and weakly dependent on the temperature in the range between 100 K and 400 K.[1] However, the origin of this unusual dielectric behavior is still controversial. The widely accepted mechanism is the Internal Barrier Layer Capacitor (IBLC), in which considers the material as being composed of semiconductor CCTO grains and a very thin copper-rich secondary phase observed between the grains forming insulating barriers. The main difference between the electrical properties in grains and at grain boundaries leads to electrostatic barriers, called Schottky potential barriers. The Schottky potential barriers inhibit the electronic transport and establish a large boundary polarization, resulting in a giant dielectric constant and a characteristic non-ohmic behavior on electric conduction. The dielectric behavior can be manipulated by several modifications in the chemical composition as well as preparation of the material. In this work, $CaCu_3Ti_{4-x}Cr_xO_{12}$ samples were prepared (with x = 0.00000, 0.00025, 0.00050, 0.00075 and 0.00100) by solid state reaction. The FE-SEM analysis shows that the grains have different size, from few microns up to 40 microns. At the grains boundaries it is possible to observe CuO and TiO_2 as segregate secondary phases. The X-ray powder diffraction pattern shows the CCTO and TiO_2 as recognizable crystal phases. The CuO phase was not identified by XRD technique due to its small amount in the sample. The I-V curve in the electrical characterization shows the non-ohmic behavior over all samples and the chromium doping strongly affects dielectric properties. The activation energy has a small increase with the concentration of chromium, with exception of doping 0.00075 which caused a sharp fall. However, the breakdown electric field and the leakage current had a strong increase with the dopant concentration.

Acknowledgments
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ZnO nanoparticles dielectric response determined by Terahertz time domain spectroscopy

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Keywords: ZnO nanoparticles, hydrothermal synthesis, THz-TDS, dielectric properties, far-infrared

Zinc oxide (ZnO) belongs to the II-VI group of semiconductors with a wide band gap of ~3.37eV, and crystallises commonly as hexagonal wurzite or cubic zincblende structure, which is responsible for its piezoelectric and pyroelectric properties. Its native doping due to oxygen vacancies or zinc interstitials results in n-type semiconductor properties with good electron mobility. The large exciton binding energy (60 meV) can lead to lasing action based on exciton recombination even above room temperature, promising potential ZnO applications in optoelectronic devices, such as light emitting diodes and lasers.[1] It is of interest that an increase in electrical conductivity and a decrease in thermal conductivity was observed in ZnO co-doped with Ni and Al.[2] The growing demand for materials with appropriate parameters that can be produced by low cost synthesis – by e.g. hydrothermal synthesis – attracted our attention both to bulk ZnO crystals, and more particularly to crystalline ZnO nanoparticles.

The dielectric properties of ZnO can be affected by nanoparticle morphology[3]; however, the effect of doping on these properties has not yet been clarified. For this purpose, THz time domain spectroscopy can be employed for the investigation of solid material. The complex dielectric permittivity $\tilde{\varepsilon}_S$ of sample *(s)* is frequency (ω) dependent, i.e.: $\tilde{\varepsilon}_S(\omega) = \varepsilon'_S(\omega) - i\varepsilon''_S(\omega)$, where $\varepsilon'_S(\omega)$ is the real part and $\varepsilon'_S(\omega)$ is the imaginary part or loss factor. The aim of our work was to characterize the dielectric properties of ZnO nanoparticles with different morphologies, i.e. the frequency dependence of their dielectric permittivity. The doping during hydrothermal synthesis of particles was used to obtain the changes in their intrinsic electric conductivity and in their dielectric properties. Such well-defined ZnO nanoparticles can find utilization in a variety of applications, such as gas sensors with high resolution and low noise, and in photocatalytic and thermo-solar reactors or thermoelectric devices.

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Stress release induced piezoelectricity in morphotropic phase boundary $Bi_{0.5}Na_{0.5}TiO_3$-$BaTiO_3$ ceramics

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Keywords: piezoceramics, lead-free, BNT-BT, MPB

The morphotropic phase boundary (MPB) is a compositionally-driven structural change region where the coexistence of two ferroelectric phases enhances the macroscopic properties, as in the case of the well-known, lead-based $PbZr_xTi_{1-x}O_3$ (PZT) system. Since the better properties are achieved in MPB compositions, the search for lead-free ceramics with potential high piezoelectric properties has therefore been focused on solid solutions presenting MPB. The $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$-$xBaTiO_3$ (BNT-BT) system has attracted a great deal of interest because it presents a MPB between the rhombohedral and tetragonal phases (as in the case of PZT) for $0.05 < x < 0.08$. Finding the MPB in BNT-BT system often leads up to obtain a material that shows a (pseudo)cubic X-ray diffraction (XRD) pattern. However, this singular composition exhibits ferroelectricity, which has been explained as a consequence of a field-induce phase transformation. In this work, we demonstrate that the stress release after poling, from the virgin state of the sample, is a crucial phenomenon to obtain piezoelectric response in MPB BNT-BT.

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Thermally conductive aluminum nitride thick films fabricated by granule spray in vacuum

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Keywords: insulation, low volumetric heat capacity, spray coating

A thick-and-dense film can be deposited by aerosol deposition (AD) method at room temperature. However, in order to be commercialized, it must be modified, since a lump of powder is formed at the bottleneck of a powder feeder with ease. The lump of powder hinders the aerosol from flowing in the AD equipment. Hence, granule spray in vacuum (GSV) is designed to improve the aerosol flow in this study. The lump of powder is not observed at the bottleneck, when granules are used instead of fine particles. In addition, the film deposition also becomes easy. AlN GSV films are deposited on Al substrates and their electric/thermal properties are compared to those of AlN AD films. GSV films show the thermal properties better than those of AD films. Moreover, the thermal resistance is significantly reduced by using AlN GSV films instead of AlN bulk-ceramics in thermal management systems. It is due to the removal of a thermal interface material which has low thermal conductivity. In particular, the dielectric strengths of AlN GSV films are much higher than those of AlN bulk-ceramics which are commercialized, approximately 5 times.

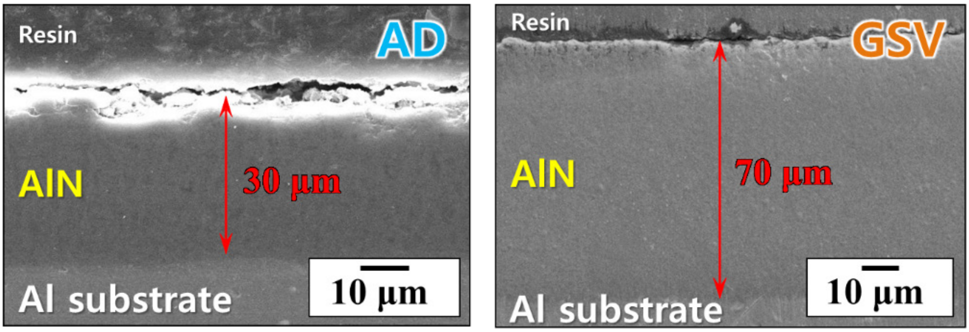

Fig. 1. Microstructure of AlN AD film and AlN GSV film

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Formation reactions and intermediate compounds during solid state synthesis of (Ba,Ca)(Zr, Ti)O_3 relaxor ceramics

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Compounds of the system $(Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O_3$ [BCZT] are under investigation because of their high potential to replace lead-based relaxor materials such as Lead-Lanthanum-Zirconate-Titanate (PLZT) and others. The highly flexible polarization of BCZT solid solutions gives rise to outstanding relaxor properties exhibiting large relative permittivities and piezoelectric constants.

The solid state synthesis of these compounds via mixed oxide route starting from oxides and carbonates of Barium, Calcium, Zirconium and Titanium needs temperatures up to 1400 °C and long reaction times to get the desired perovskite phase. In this study we follow the formation reaction of BZT ($x = 0$, $y = 0.2$), BCZ ($x = 0.2$, $y = 1$) and BCZT ($x = 0.06$, $y = 0.2$) compounds with Simultaneous Thermal Analysis coupled with Mass Spectrometry (STA-MS) and High Temperature X-Ray Diffraction (HT-XRD).

STA-MS clearly showed the decomposition of the carbonates by mass loss and the MS signal (ion current at 44 amu) which was completed between 1000 °C (BZT) and 1200 °C (BCZ). At higher temperatures only flat and diffuse endothermic DSC peaks could be observed.

With HT-XRD we were able to identify intermediate compounds of this reaction mixture and the onset temperature of the formation of the complex perovskite. In the BZT compound first $BaTiO_3$ is formed around 650 °C followed by $BaZrO_3$ at 900 °C. Also an intermediate compound with the structure of Ba_2TiO_4 appears between 900 °C and 1200 °C. The complex BZT perovskite starts to appear at 1100 °C. In the BCZ compound the formation of several modifications of $BaCO_3$ can be observed due to the low reactivity of the Zirconium Oxide. Traces of perovskite phase are observed from 800 °C onwards, but the increase of the portion of perovskite phase starts not before 1050 °C. As intermediate compounds Ba_2TiO_4 and (Ba,Ca)O can be identified.

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Dielectric tunable and ferromagnetic properties of $Ba_{0.5}Sr_{0.5}TiO_3$-$MgFe_2O_4$ composite ceramics

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Keywords: ferroelectrics, ferromagnetic, tunability, composite

$Ba_{0.5}Sr_{0.5}TiO_3$/$MgFe_2O_4$ ceramics were prepared and their dielectric and ferromagnetic properties were investigated. XRD data show ceramics consist of only $Ba_{0.5}Sr_{0.5}TiO_3$ and $MgFe_2O_4$. The permittivity of $Ba_{0.5}Sr_{0.5}TiO_3$/$MgFe_2O_4$ decreases with the increase of $MgFe_2O_4$ content when the content of $MgFe_2O_4$ is small and the sintering temperature is low. For $Ba_{0.5}Sr_{0.5}TiO_3$/$MgFe_2O_4$ composite ceramics with high $MgFe_2O_4$ content (>40%), higher sintering temperatures (≥1300 °C) result in dramatic increased dielectric constant and dielectric loss due to percolation effects. The tunability of $Ba_{0.5}Sr_{0.5}TiO_3$/$MgFe_2O_4$ sintered at 1300 °C decreases with the increase of $MgFe_2O_4$ content. On the other hand, sintering temperature has significant effect on the tunability. The tunability of 0.5BST/0.5$MgFe_2O_4$ decreases rapidly with the increase of the sintering temperature. The tunability of 0.5BST/0.5$MgFe_2O_4$ sintered at 1200 °C (21% under 3kV/mm) is even higher than that of 0.9BST/0.1$MgFe_2O_4$ sintered at 1300 °C (16% under 3kV/mm), although 0.5BST/0.5$MgFe_2O_4$ has higher $MgFe_2O_4$ content than 0.9BST/0.1$MgFe_2O_4$. This interesting phenomenon may open a new route to control the tunability of composites. For $Ba_{0.5}Sr_{0.5}TiO_3$/$MgFe_2O_4$ composite ceramics with $MgFe_2O_4$ content > 10 wt%, the Lichtenecker model and the corrected Lichtenecker model predict the relation between $MgFe_2O_4$ content and the permittivity very well. Saturation magnetization of BST/$MgFe_2O_4$ composite ceramics increase with the increase of $MgFe_2O_4$ content.

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Graphitic C/cobalt core shell composites for magneto-optical applications

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Keywords: carbon, magneto-optical, graphitization

Carbon(C) based materials, due to its uniqueness of physical properties, have attracted increasing interests for electronic applications. For example, amorphous carbon (*a*-C) thin film which is a semiconductor with a mixture of sp^2 and sp^3 bond characteristics, can change its optical, electrical, and mechanical properties by change its sp^2/sp^3 ratio.[1] In addition, the integration of ferromagnetic materials (FMs) and *a*-C can reveal interesting magneto-electronic and magneto-optical (MO) phenomena. The interfacial hybridization between FMs and *a*-C has been considered as an important role for these observed results. In addition, there are also reports that the presence of a metal can promote the formation of sp^2-bonded C nanostructures by metal-contact-induced graphitization following suitable annealing.[2] Therefore, in our work, graphitic C/Co core shell composites could be fabricated by r. f. sputtering and rapid thermal annealing (RTA). The metastable Co-C bonding in the as grown Co/*a*-C composites is decomposed and graphitic C/Co interfaces after RTA are thus formed evidenced by our high resolution transmission microscopy measurements. The x-ray absorption spectra also show a strong hybridization between graphitic C and Co. In such samples, a following strong MO effect in graphitic C/Co core shell composites was observed. One broad MO signal (feature A) below 4.1 eV was obtained, while the other (feature B) shows a peak at 5.5 eV while applied a magnetic field. We propose that the broad MO signal arises from the optical transitions between Co *d* orbitals or bands of small clusters of metallic Co and the peak at 5.5 eV could be related to C σ-σ^* gap transition. The increase in MCD intensity of feature A and the decrease in MO intensity of feature B from 15K to 300 K implies the existence of antiferromagnetic coupling between Co *d* orbits and graphitic C πorbits, therefore, inducing the strong MO effect. We expect these results would open new a perspective for C based MO materials

Acknowledgements

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The integration of functional oxide thin film with GaAs by laser molecular beam epitaxy

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Integration of crystalline oxide thin films with semiconductors has attracted considerable attention in recent years. Compared to Si, GaAs have a higher saturated electron velocity and electron mobility, transistors based on GaAs can function at a much higher frequencies. In this talk, $SrTiO_3$ films were grown on GaAs (100) substrates as an intermediate buffer layer for the epitaxial growth of oxide thin films including ferroelectric $BaTiO_3$ and semiconductor ZnO by laser molecular beam epitaxy (L-MBE). The properties of the multilayers in terms of growth modes, strain and interface structures were characterized by the *in-situ* reflective high energy electron diffraction (RHEED) pattern. The crystalline quality and surface morphology of the oxide/GaAs heterostructure were investigated respectively by a combination of X-ray diffraction (XRD) and atomic force microscopy (AFM). These heterostructure exhibit good functional properties such as ferrelectrisity and resistive switching. Furthermore, the fundamental interface properties of these heterostructure with an emphasis on the strain effect were discussed in relation with the electrical properties. The results provide an understanding of the integration of oxide/GaAs heterostructure with full control over the interface structure at the atomic-scale.

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Synthesis and electrical conductivity of $Ba_2MM'O_6$(M = La and In, M' = Bi and Sb) with double perovskite structure

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Keywords: electrical conductivity, double perovskite, Ba_2LaBiO_6

In recent years, the considerable attention has been paid to the characterization of perovskite-structured electrolytes because of their proton conductivities for the application to the intermediate temperature fuel cells which can operate at the lower temperatures below 600 °C. In such the electrolytes, the acceptor doping has been performed to introduce the oxygen vacancy which takes place the proton incorporation in the lattice.[1,2] On the other hand, the double perovskite-structured compounds with general formula $A_2MM'O_6$ have two octahedral sites which correspond to the MO_6 and $M'O_6$ octahedra; the relationship between the acceptor doping in M and M' site and the electrical conductivity has not been clarified. Thus, two types of compounds such as Ba_2LaBiO_6 and Ba_2InSbO_6 were prepared and the influence of Mg substitution for M (M = La and In) on the electrical conductivity was investigated in this study. The $Ba_2(La_{1-x}Mg_x)BiO_6$ and $Ba_2(In_{1-x}Mg_x)SbO_6$ ceramics were synthesized using the conventional solid-state reaction method, and sintered at 1200 °C for 2 h and 1550 °C for 10 h in air, respectively. The XRPD profiles of the $Ba_2(La_{1-x}Mg_x)BiO_6$ and $Ba_2(In_{1-x}Mg_x)SbO_6$ ceramics showed the single phase in the composition range of x = 0–0.15, suggesting the introduction of oxygen vacancy in the lattice. In this case of $Ba_2(La_{1-x}Mg_x)BiO_6$ ceramics, the electrical conductivity of the ceramics was improved by the Mg substitution for La. However, the electrical conductivities of $Ba_2(La_{1-x}Mg_x)BiO_6$ ceramics were lower than those of $Ba_2(In_{1-x}Mg_x)SbO_6$ ceramics. As a result, the highest electrical conductivity of 5.4×10^{-2}S/cm was obtained for $Ba_2(In_{0.95}Mg_{0.05})SbO_6$ ($x = 0.05$) ceramic at 500 °C.

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Enhancement of piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$-$LiSbO_3$ ceramics by $BaSnO_3$ addition

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Keywords: piezoelectric property, $K_{0.5}Na_{0.5}NbO_3$

Recently, K0.5Na0.5NbO3(KNN)-based piezoelectric ceramics have been studied extensively because they are considered to be one of the most promising lead-free piezoelectric ceramics. These ceramics are known to possess a high Curie temperature (Tc = 420 °C), a relatively high piezoelectric constant (d33 = 160 pC/N), and a large electromechanical coupling coefficient.[1] In addition, many attempts have been made to find alternative ways to obtain KNN-based ceramics with appropriate piezoelectric properties, and the chemical modification of KNN through forming solid solutions or the addition of sintering aids have been performed to shift the orthorhombic-tetragonal transition temperature (TO-T) from approximately 200 °C to room temperature.[2–4] Such the change in the transition temperature generally leads to the enhancement of the piezoelectric properties, resulting the presence of morphotropic phase boundary (MPB) between the orthorhombic and tetragonal phases. For example, in the KNN-LiSbO3 system, it is reported that K0.474Na0.474Li0.052Nb0 .948Sb0.052O3 (KNLNS) ceramic at the MPB region exhibits a d_{33} value of 221 pC/N.[4] Moreover, the chemical modification of KNLNS-based ceramics by ABO_3 addition has also been performed to clarify the possibility of the improvement in the piezoelectric properties. As a result, the d_{33} value of 280 pC/N was obtained for (1-x)KNLNS-$x$$BaTiO_3$ at x = 0.06.[5] In this study, the cubic-structured $BaSnO_3$(BS) addition into KNLNS was performed and the piezoelectric properties of (1-x)KNLNS-xBS was characterized. KNLNS and BS powders were prepared separately via conventional solid –state reaction method and these powders were weighed according to the stoichiometric composition of (1-x)KNLNS-xBS ($x = 0$–0.02) and fired in the temperature range of 1080–1150 °C for 3 h. X-ray powder diffraction profiles suggested the formation of MPB between the orthorhombic and tetragonal phases in the composition range of 0–0.01; at $x = 0.02$, the secondary phase was detected. With increasing the composition x from 0–0.01, the shifts of T_c and $T_{O\text{-}T}$ to lower temperatures were observed from the evaluation of temperature dependence of the dielectric constant, and the dielectric constant at room temperature increased in such composition range. The variation in the d_{33} value of the ceramics showed a similar tendency to that of the dielectric constant at room temperature; the highest d_{33} value of 302 pC/N was obtained for $x = 0.005$.

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Electrical properties of 0.5PNN-0.5PZT ceramics and their 1-3 piezocompozites

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Keywords: lead nickel niobate, electrical properties, pieozocomposite, fibrous ceramic

In this study, lead nickel niobate (PNN)-lead zirconate titanate (PZT) system was investigated. PNN was alloyed by a certain amount of PZT that formed a stoichiometric notation of $0.5[Pb(Ni_{1/3}Nb_{2/3})\,O_3]$-$.0.5Pb(Zr_{0.3}$-$Ti_{0.7})O_3$. Powder synthesis was consisted of two step calcination which is based on B-site precursor ($NiNb_2O_6$) preparation known as columbite method and conventional solid state synthesis technique in order to attain not only perovskite phase comparably but also conserving the stoichiometry. After calcination process, powders were formed as disc shaped samples by uniaxial press. In addition to bulk ceramic processing, PNN-PZT fibrous piezoceramics were also fabricated by alginate gelation technique, which reported elsewhere.[1,2] Sintering process was carried out for both bulk and fibrous ceramics at 1200 °C in a closed alumina crucible. Piezocomposites with 1–3 connectivity[3] were prepared by aligning the fibers in an ordered pattern then those were embedded into polyurethane matrix. Upon completion of curing the polymer matrix, the piezocomposites were sliced into appropriate thicknesses. Piezocomposite samples with 1–3 connectivity were polished and surface of the samples were coated with silver electrode for electrical characterizations.

Properties of ceramics were measured at room temperature as dielectric constant (K) 5530, dielectric loss (tan δ) 0.02, piezoelectric charge constant (d_{33}) 780 pC/N, saturation polarization (P_s) 36.4 µC/cm^2, remnant polarization (P_r) 28.1 µC/cm^2 electromechanical coupling (k_p) 0.64 and mechanical quality factor (Q_m) 97.

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Studies of photoluminescence and energy transfer in europium and dysprosium co-doped oxyfluoride glasses and glass ceramics

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Keywords: photoluminescence, RE ions, oxyfluoride glass ceramics, nanocrystallites, WLED

RE ions doped glass ceramics are considered as prospective materials for scintillators, lasers, communications and lighting devices. RE doped oxyfluoride glass ceramics are promising materials for lighting devices due to their advantages compared to other materials- the otherwise hygroscopic fluoride nanocrystallites are isolated in a stable oxide matrix and are characterized with low phonon energy.[1] Much effort is aimed to develop highly efficient white light emitting diodes (WLEDs) using RE ions co-doped glass ceramic materials as phosphors. White light emission from Dy-Eu co-doped glasses and glass ceramics has been reported.[2]

In the present work, series of SiO_2-Al_2O_3-CaO-CaF_2 glasses, doped with Dy_2O_3 (0–1mol%) and Eu_2O_3 (0-1mol%) have been prepared, using the conventional melt quenching method. Glass ceramics were obtained by heating the as-made glasses at temperature of 680 °C and 750 °C. Photoluminescence emission and excitation, as well as luminescence decay measurements of the samples were performed. DTA and XRD measurements were performed as well. The heat treatment temperatures were chosen on the basis of DTA data to obtain CaF_2 crystallites, XRD analysis approves the formation of nanosized CaF_2 crystallites.

Single doped samples, activated with 0.5 mol% Dy^{3+} show the highest luminescence intensity with respect to co-doped samples and samples with Dy^{3+} in higher concentrations. Luminescence excitation measurements and luminescence decay kinetics approve the energy transfer (ET) process from Dy^{3+} to Eu^{3+} ions in all samples, ET efficiency in the glasses and glass ceramics is similar. The luminescence lifetimes of Dy^{3+} ions decrease in the glass ceramics. In the glass ceramics, a partly reduction from Eu^{3+} to Eu^{2+} ions is observed. The luminescence of Eu^{2+} ions in the blue spectral range allows to obtain white light emission of the glass ceramics under UV excitation.

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Two-step sintering of KNN-based ceramics for multi-layered piezoelectric energy harvester

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Keywords: piezoelectric, $(K,Na)NbO_3$, energy harvester, multi-layered ceramic, two-step sintering

Piezoelectric materials have been applied in various electronic devices such as actuators, sensors, and transducers. Recently, piezoelectric energy harvesters (PEH) that generate electrical energy from environmental vibrations have been developed for applications such as wireless self-powered sensor nodes.[1] The standard electronic conversion circuitry and a normal battery voltage capacity of about 3V require multilayered PEH generating a large current and a low voltage. As increasing concern of the global environment issue in Pb-based piezoelectric ceramics, there have been considerable efforts to develop lead-free piezoelectric.[2] (K,Na) NbO3 (KNN) based ceramics have been considered as one of the most promising lead-free ceramics due to large piezoelectric constants comparable to Pb-based ceramics. Low temperature sintering is required for reducing the amount of noble metals in internal electrodes of multilayered ceramics. CuO-doped KNN ceramics have been sintered successfully at low temperature below 950 °C and demonstrated a high mechanical quality factor. However, CuO-doped KNN ceramics displayed inhomogeneous microstructures resulting from an abnormal grain growth (AGG). KNN ceramics with large abnormally-grown grains are not adequate for multilayered PEH. In this work, we tried to prepare CuO-doped KNN ceramics with fine grains of a few micrometers at low sintering temperature for multi-layered PEH. A two-step sintering process was tried to suppress AGG without scarifying good piezoelectric properties. Two-step sintering process was verified to suppress AGG and demonstrate high piezoelectric properties. Two-step sintering process was also applied for fabricating PEH.

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Secondary phases in the system NBT-BT(-KNN)

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Keywords: solid-state synthesis, secondary phases, electrical properties

After 15 years of investigations to replace lead-based materials in piezoelectric applications a breakthrough in still lacking. One of the most promising materials are $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)-based materials exhibiting incipient piezoelectric effect[1].

We investigated solid-state synthesis of the composition NBT-6wt% $BaTiO_3$ (NBT-6BT) and the influence of the doping with 2wt% $K_{0.5}Na_{0.5}NbO_3$ (KNN). The results show that in NBT-6BT sample minor amount unidentified Na-, Ti- and Ba-rich secondary phases is formed. When doping with KNN additional secondary phase is present, i.e. $BaTi_4O_9$ or $Ba_2Ti_9O_{20}$ as suggested by electron dispersive spectroscopy (EDS). The amount of this phase is much larger than the amount of secondary phase in NBT-6BT. In the latter, secondary phase forms a transient liquid, which results in a growth of matrix grains in the areas with the secondary phase. On the contrary, in KNN-doped sample the secondary phases are present in needle- or plate-like shape. However, none of these secondary phases can be detected by X-ray powder diffraction (XRD).

The processing of the samples (calcinations, milling, raw materials, sintering, etc.) has a great influence on electrical properties. Dielectric properties of KNN-doped sample indicate presence of an additional phase which reacts with humidity. Such behaviour deteriorates electrical properties, similar as in $K_{0.5}Bi_{0.5}TiO_3$ (KBT)[2]. Control of the stoichiometry is the key factor securing good electrical properties. Excess of alkali elements has to be avoided.

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Lead free piezoelectric system by solid state microwave synthesis

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Keywords: microwave processing, calcination, sintering, piezoelectric properties

The remarkable piezoelectric properties of (Zr,Ti)PbO_3 ferroelectrics systems make them suitable for applications in sensors, transducers and actuators, however, it is necessary to find alternative systems capable of achieving their properties without the lead presence. A promissory alternative are the based (K,Na)NbO_3 (KNN) ceramics systems due to their relatively strong piezoelectricity at high temperatures[1]. The synthesis of this lead-free piezoelectric materials is very complex due to the volatility of alkali elements and the moisture sensitivity. The microwave processing is a method which involve a volumetric heating by the absorption of electromagnetic energy and has been reported as an excellent via to improve the properties of several ceramic systems. The microwave heating mechanism of synthesis involve the energetic efficiency and enhanced reaction rates, furthermore, microwave technique is a very clean process and non-polluting method which results in improved properties[2].

In this work, the KNN based system $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.84}Ta_{0.10}Sb_{0.06})O_3$ piezoelectric ceramic have been synthetizing by the microwave solid state synthesis and their comparison with conventional mixed oxide route. The microwave calcination is being carrying out at different temperatures in air. The results obtained by X-Ray diffraction shows the formation of the perovskite structure. The structural and microstructural evolution is studied by the shift on microwave calcination temperatures and compared with the conventional synthesis process.

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Growth and characterization of GAN and InGaN nanostructures on carbon nanotubes

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Keywords: GaN, InGaN, CNT, nano-structure, MOCVD

Nanostructures have attracted significant attention for high performance electronic and optoelectronic devices because of their superior physical and chemical properties.[1] Among nanostructures, the carbon nanotube (CNT) is a particularly important material because it will be applied to many technologies, such as transparent electrode, gas reservoirs, and field emission displays. In addition, GaN-based nanostructures have studied to improve the emission efficiency of light-emitting devices such as quantum well, quantum dots, nanorods and nanowires. Although both material systems are in the commercialized-step, there are only a few reports to combine nitride-binary system and CNT. Until now, most research groups have studied on the binary InN or GaN to form nanostructure such as nanotube, nanorods, nanowires and nanocomposites on CNTs.[2,3] Due to the growth difficulties of ternary nitrides such as InGaN or AlGaN, there is no report to study on the visible green emission of InGaN on CNT template. In this study, we systematically studied the growth and optical characterization of GaN and InGaN nanostructure on CNT template.

We have successfully grown GaN and InGaN nanostructures on CNT/Si template by using MOCVD. From SEM results, we found that the bundled CNTs are embedded with discontinuous GaN hexagonal island structure. InGaN nanostructures were directly grown on the edges of CNTs and they are estimated to be polygonal crystal structure with the dimension of 100 ~ 270 nm. From high-resolution X-ray diffraction measurements, we found that $(002)_{GaN}$ was the main crystallographic plane of GaN hexagon columns, rather than $(101)_{GaN}$. In addition, two low-angle side peaks and the asymmetric $(002)_{GaN}$ peak were observed to be related a low In content InGaN nanostructure. Moreover, the selected area electron diffraction (SAED) patterns shows that the crystallites of InGaN nanostructures formed in random directions, but that single InGaN nanostructures were single crystal. We observed the strong green (~500 nm) photoluminescence (PL) and cathodoluminescence spectra from InGaN nanostructures, indicating excellent optical properties of InGaN nanostructure grown on CNT template. In addition, we found that the internal quantum efficiency of InGaN nanostructure is 11.4% by using the temperature dependent PL measurements. Based on these results, we suggest that GaN and InGaN nanostructures be successfully grown on CNT template and can improve the emission efficiency for green gap region.

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Amorphous In-Zn-Sn oxide-based thin film transistors: channel thickness dependence

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Keywords: InZnSnO, amorphous oxide semiconductor (AOS), thin film transistor (TFT)

Amorphous oxide semiconductor (AOS) thin films within the ternary oxide system comprised of In_2O_3-ZnO-SnO_2 components were investigated for possible application toward transparent thin film transistor devices. Radio frequency (RF) magnetron sputtering technique was used in the deposition of amorphous In-Zn-Sn-O (a-IZTO) films which served as an active channel layer between Cu/Ti bilayer source and gate contacts of oxide thin-film transistors (TFTs). Test device was prepared using a SiO_2/n^{++} Si substrate and adopted the so-called “bottom gate” structure. Thickness of the channel varied from 15 to 150 nm. It was found that the excellent performance was realized from thus prepared a-IZTO TFTs with field effect mobility of 25 $cm^2V^{-1}s^{-1}$, high on/off current ratio of $>10^8$, low threshold voltage of –0.1 V and a subthreshold swing of 0.14 $Vdec^{-1}$ when the device was fabricated from 30 nm a-IZTO films. TFT devices with higher channel thickness showed the degradation of TFT performance.[1] To investigate device stability, positive and negative bias stress (PBS and NBS) measurements were also conducted up to 3600 sec in the dark chamber. A small degradation was observed where threshold voltage value shifted to the positive direction while field effect mobility decreased as a function of time under positive and negative bias stress for all a-IZTO film thicknesses. This certainly indicates the viability of a-IZTO TFTs as one of alternatives replacing current LTPS TFT device. Moreover, due to its high optical transparency, a-IZTO TFT could also be used in transparent devices such as transparent displays.

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Preparation of indium oxide-coated tin oxide nanoparticle and its application to low temperature carbon monoxide sensor

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Keywords: SnO_2, In_2O_3, CO sensor, low temperature, thermal decomposition, sensitivity

Gas sensor which is composed of nanostructured oxide semiconductor with extremely high specific surface area possesses competitive advantages for achieving a high sensitivity and rapid response,[1] due to the high sensing reaction involving redox interaction between the target gas and the charged oxygen adsorbed on the surface. Generally, the metal oxides need to be heated to high temperature (~300–500 °C) to obtain appropriate sensitivity levels, resulting in high power consumption.[2] In the present study, a low operating temperature carbon monoxide (CO) sensor was fabricated from a nanometer-scale tin oxide (SnO_2) powder. The SnO_2 nanoparticles in a size range 10–20 nm were synthesized as a function of surfactant (tri-n-octylamine) addition (0–1.5 mol%) via a simple thermal decomposition method. The resulting SnO_2 nanoparticles were first screen-printed onto an electrode patterned substrate to be a thick film, and then indium oxide (In_2O_3) was coated on the surface of the SnO_2 thick film by photochemical reduction. Subsequently, the composite film was heat-treated to be a device for sensing CO gas. The thermal decomposed powders were characterized by field-emission scanning electron microscopy (FESEM), X-ray diffractometry (XRD), and surface area measurements (BET). The CO-sensing performance of all the sensors was investigated. The experimental results showed that the tri-n-octylamine addition significantly decreased the particle size of the resulting SnO_2 nanoparticle. However, the smaller particle tended to cause the formation of agglomeration, resulting in the decline of surface area and reducing the reaction site during sensing. As a CO sensing material, the SnO_2 nanoparticle (~12 nm in diameter) prepared with 1.25 mole% tri-n-octylamine addition exhibited most stable electrical performance. When In_2O_3 was photo-chemically coated onto the SnO_2 sensing material, the sensor was able to perform a superior sensing property at a relatively low working temperature < 50 °C.

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Precursor influence on morphology and photoluminescence properties for Eu-doped gehlenite glassy particles

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Keywords: gehlenite, glass, spray pyrolysis, morphology, photoluminescence

The Eu-doped gehlenite glassy particles were synthesized using spray pyrolysis. For morphology control, the porous and hollow glassy particles were synthesized using the common pore-forming agents of polyethylene glycol and hydrogen peroxide, respectively. The experimental results revealed that the hollow particles exhibited the higher photoluminescence properties than porous and solid particles. So, the hollow Eu-doped gehlenite glassy particles could be one of the potential candidates for future phosphor applications.

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Synthesis of graphene by laser scribed graphene (LSG) method

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Keywords: graphene oxide, laser scribed graphene (LSG), scanning electron microscope (SEM)

Graphene conducts electricity and heat better than anything else and has combination of unique optical and mechanical properties. Electrons have nobilities in graphene over a hundred times those in silicon.

In the present work we used a standard optical LightScribe DVD drive to directly do the laser reduction of graphene oxide (GO) films to graphene. GO was prepared by the modified Hummers' method as reported elsewhere. Briefly, 2 g graphite powders was added to a mixture of 1 g $NaNO_3$ and 46 ml H_2SO_4 and the mixture was cooled to 10 °C using an ice bath. In the next step, 6 g $KMnO_4$ was gradually added to the solution and the reaction temperature was maintained below 20 °C. The mixture was then stirred at 35 °C for 2 h. The resulting solution was diluted by adding 92 ml of deionized water until a dark brown suspension was obtained. Then, the solution was treated by adding 340 ml H_2O_2 solution. Finally, a uniform suspension of GO nanosheets was obtained by adding water to the resulting precipitate and 12 h of sonicating. The resulting suspensions were uniformly drop casted on a LightScribe DVD disk and then dried under the air at an ambient temperature. The GO coated DVD disk was placed in a LightScribe DVD drive with a wavelength of 780 nm.

Raman result confirm that the laser irradiation properly reduce GO to graphene sheets. The structure of graphene arrays were studied by SEM images the results indicated that the laser based reduction was a useful method to production graphene layers.

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New insights about dielectric relaxation in relaxor ferroelectrics

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Keywords: ferroelectric ceramics, relaxors ferroelectrics, dielectric relaxation

Relaxor ferroelectrics are characterized for a broadened and dispersive permittivity peak in their temperature-dependent dielectric spectra. Although several models have been proposed to explain the dielectric behaviour of relaxor ferroelectrics,[1–5] the identification of the nature of the dielectric response in relaxors systems still remains open and requires additional theoretical and experimental explanation. The nature of the relaxor behaviour is determined by the existence of polar nanoregions (PNRs), which possess different relaxation times (τ). The distance above which such PNRs become non-interactive regions is formed by changes in cluster size which are strongly affected by the temperature, giving rise to a distribution function of activation energy. This striking situation dominates the dynamic of the relaxors in terms of a functional behaviour of the dielectric relaxation time as function of temperature, $\tau(T)$. To elucidate the most consistent functional $\tau(T)$ constitutes a fundamental issue to understand the very attractive physical properties of ferroelectric relaxors. By using alternative model-equations of $\tau(T)$, we are able to reveal strong evidences that the 'classical' parameterization of the dielectric relaxation in relaxor ferroelectrics is not the only route to disentangle the dynamic of these materials. A model-free route solution for describing super-Arrhenius dynamics in complex systems is proposed as an effective method to elucidate the relaxation dynamics of relaxor ferroelectrics.

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Influence Sr_2TiMnO_6 addition on piezoelectric properties of $Bi_{0.5}Na_{0.5}TiO_3$-$Bi_{0.5}K_{0.5}TiO_3$ system near MPB region

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Keywords: piezoelectric property, $K_{0.5}Na_{0.5}NbO_3$,

In the various perovskite materials, bismuth sodium titanate, i.e., $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), is known to be one of the lead–free piezoelectric ceramics with rhombohedral perovskite structure at room temperature. Although the BNT ceramic has a relatively large remanent polarization (Pr), its high coercive field (Ec) has a detrimental effect on the poling treatment of the ceramics. Sasaki et al.[1] reported the piezoelectric properties of (1-x)BNT–$x$$Bi_{0.5}K_{0.5}TiO_3$ (BKT) system which exhibited a MPB between rhombohedral ($R3c$) and tetragonal ($P4mm$) in the compositions $0.16 \leq x \leq 0.20$; the highest piezoelectric constant (d_{33}) of 151 pC/N was obtained for 0.8BNT–0.2BKT (BNKT) ceramic. Recently, most of the recent works of BNKT-based ceramics have been focused on the evaluation of piezoelectric properties in BNKT–ABO_3 system to clarify the relationships between the formation of MPB and piezoelectric properties.[2–4] However, the detail on the piezoelectric properties of BNKT-$ABB'O_6$ system, where $ABB'O_6$ has a double perovskite structure, has not been clarified to date. Thus, double perovskite-structured $SrTiMnO_6$ (STM) addition was performed for BNKT ceramics and their piezoelectric properties were investigated in this study. No secondary phase was detected for (1–x)BNKT–xSTM in the composition range of 0–0.05; the diffraction peak shifts to low angle was also observed with increasing x. From the Raman spectroscopy, a shoulder peak around 320 cm^{-1}, which corresponds to Ti-O vibration mode, was observed in the compositions below 0.02, implying the coexistence of rhombohedral and tetragonal phases. As for the composition dependence of P_r and E_c values, the P_r values increased from 38 to 45 μC/cm^2 with increasing the composition up to $x = 0.005$, though the E_c values of the ceramic were almost constant (27 kV/cm). The piezoelectric constant (d_{33}) of the ceramics significantly varied for the composition x; the highest value was obtained at $x = 0.005$ (d_{33} = 204 pC/N). Therefore, it is considered that the addition of SMT is effective in enhancing the piezoelectric constant of BNKT-based ceramics in MPB region.

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Dielectric and piezoelectric properties of (1–x)$(K_{0.474}Na_{0.474}Li_{0.052})(Nb_{0.948}Sb_{0.052})O_3$–x$BaMnO_3$ ceramics

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Keywords: KNN, lead-free ceramic, piezoelectric properties, MPB, $BaMnO_3$

Piezoelectric ceramics of Pb-based material have been widely used as actuators, transducers, sensors, etc. However, the various commercial products which consist of lead-based piezoelectric ceramics may induce the continuous damage to environment.[1] Therefore, there has been significant effort in the research of new lead-free perovskite piezoelectric ceramics. The (K,Na)NbO_3(KNN)-based materials have been received the considerable attention due to their excellent piezoelectric properties and high-Curie temperature;[2] the existence of a morphotropic phase boundary (MPB) between the orthorhombic and tetragonal phases in KNN-based systems has been reported.[3] For example, Wu et al.,[4] reported the piezoelectric properties of KNN-$LiSbO_3$ system and $K_{0.474}Na_{0.474}Li_{0.052}Nb_{0.948}Sb_{0.052}O_3$ (KNLNS) ceramic in the MPB region exhibited a high d_{33} value of 221 pC/N.[5] However, the details on the $(1–x)$ KNLNS–$x$$BaMnO_3$ ((1–x)KNLNS–xBM) have not been reported to date. Therefore, in order to clarify the compositional dependence of piezoelectric properties for (1–x)KNLNS–xBM ceramics, these materials were synthesized in the present work and the relationships between crystal structure and d_{33} value were investigated. (1–x)KNLNS–xBM ceramics were synthesized by the conventional solid-state reaction method. K_2CO_3, Na_2CO_3, Li_2CO_3, Nb_2O_5, Sb_2O_5, $BaCo_3$ and MnO_2 powders were used as the starting materials. KNLNS and BM ceramics were separately synthesized and single phase of KNLNS and BM was obtained after calcining at the optimum temperature. Subsequently, (1–x)KNLNS–xBM ceramics were sintered 1095 °C to 1170 °C for 3 h in air. X-ray powder diffraction (XRPD) profiles of ceramics showed a single phase in the composition range of $x = 0$ to $x = 0.02$. Since the diffraction peak profile of KNLNS-BM ceramics are similar to those of KNN-$LiSbO_3$ ceramics with MPB region,[5] it is considered that MPB region may also be formed in the (1–x)KNLNS–xBM ceramics. The P_r values of (1–x)KNLNS–xBM ceramics increased from 18 to 31 μC/cm^2, whereas E_c values of (1–x)KNLNS–xBM ceramics decreased from 17 to 11 kV/cm. The d_{33} value of (1–x)KNLNS–xBM ceramics increased from 217 to 288 pC/N in the composition range of 0–0.005.

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Effect of LiMO$_3$ (M = Nb, Ta and Sb) additions on dielectric and piezoelectric properties of (1-x)$K_{0.5}Na_{0.5}NbO_3$ – xBa($Li_{1/4}Nb_{3/4}$)O_3 ceramics

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Keywords: KNN, lead-free piezoelectric properties, Ba($Li_{1/4}Nb_{3/4}$)O_3, MPB

Pb(Zr, Ti)O_3 (PZT) ceramics are widely used in sensors and actuators as well as microelectronic devices due to their superior piezoelectric properties. However, the use of lead-based ceramics has caused the serious environmental problems.[1] Therefore, much attention has been paid for the characterization of the lead-free piezoelectric ceramics such as $K_{0.5}Na_{0.5}NbO_3$ (KNN)- and $Bi_{0.5}Na_{0.5}TiO_3$-based ceramics. KNN is considered to be one of the most promising candidates for alternative lead-free piezoelectric ceramics because of its very high Curie temperature (T_c = 420 °C), a relatively high piezoelectric constant, and a large electromechanical coupling coefficient.[2] In addition, further improvement in the piezoelectric properties has been carried out by the chemical modification in KNN – ABO$_3$ system which leads to the formation of morphotropic phase boundary (MPB). For example, KNN – LiSbO_3 (LS) ceramics[3] exhibit the coexistence of orthorhombic and tetragonal phases, implying the formation of MPB where the piezoelectric constant (d_{33}) of 286pC/N is obtained. The Li substitution for A site in KNN is considered to play an important role in improving the piezoelectric properties with formation of MPB. On the other hand, Ba($Li_{1/4}Nb_{3/4}$)O_3 (BLN) ceramics is known as a perovskite structure in which Li^+ cation occupied the B site in the structure, though the effect of BLN addition on the piezoelectric properties of KNN has not been clarified to date. Thus, (1–x)KNN – xBLN ceramics were synthesized by the conventional solid state reaction method, using K_2CO_3, Na_2CO_3, Nb_2O_5, $BaCO_3$ and Li_2CO_3; the ferroelectric and piezoelectric properties were investigated in this study. The X-ray powder diffraction profiles of ceramics showed a single phase in the composition range of 0–0.02. From the variation in the diffraction peak intensity of (002) and (200) refrections, the coexistence of tetragonal and orthorhombic phases was suggested in the composition range of 0.005–0.02. As x increased, the piezoelectric constant (d_{33}) improved significantly in the composition range up to x = 0.02 and d_{33} of 193.5 pC/N was obtained at x = 0.01. From the results of Raman spectroscopy, the formation of MPB was also suggested in such the composition range. In addition, LiMO$_3$ (M = Nb, Ta and Sb) additions into KNN – BLN ceramics were performed to enhance the piezoelectric properties of the ceramics in this study.

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Electrical conductivity of Fe-doped $SmTiNbO_6$ ceramics with Aeschynite structure

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Keywords: $SmTiNbO_6$, electrical conductivity, Aeschynite structure

Solid oxide fuel cells (SOFCs) are considered to be one of the energy conversion systems with high energy efficiency. However, since the high operating temperature of SOFCs generally limits their technological applications, many attempts have been performed for the characterization of SOFCs which can operate at the intermediate temperature range. Accepter-doped perovskite compounds, such as $BaZr_{1-x}Y_xO_{3-\delta}$[1,2] and $BaZr_{1-x}Sc_xO_{3-\delta}$,[3] are known as the appropriate candidates for the application to the intermediate temperature SOFCs. The formation of oxygen vacancy by accepter doping allows the proton incorporation in perovskite structure which leads to the enhancement of proton conductivity. However, $BaZrO_3$ must be sintered at high temperature and it is necessary to improve conductivity at lower temperature. Therefore, we focused on the characterization of Fe-doped $SmTi_{1-x}Fe_xNbO_{6-\delta}$ ($0 < x < 0.05$) with Aeschynite structure which consists of SmO_8 polyhedra and $(Ti,Nb)O_6$ octahedra as a proton conductive electrolyte for intermediate temperature SOFCs. $SmTi_{1-x}Fe_xNbO_{6-\delta}$ ceramics were synthesized by the conventional solid state reaction method, using Sm_2O_3, TiO_2, Fe_2O_3 and Nb_2O_5. The crystal structure and electrical characterization of prepared samples were performed by using the X-ray powder diffraction (XRPD) and AC impedance spectroscopy methods. From the XRPD profiles, a single phase was obtained in the composition range of $x = 0$–0.05. The electrical conductivity was measured in the temperature range of 100–800 °C under the different atmospheres. The conductivity of $SmTi_{1-x}Fe_xNbO_{6-\delta}$ increased with increasing temperatures; the electrical conductivity of 4.60×10^{-3} S/cm was obtained for $x = 0.05$ at 600 °C.

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Fabrication of nanoparticles incorporated waveguide based transparent flexible display

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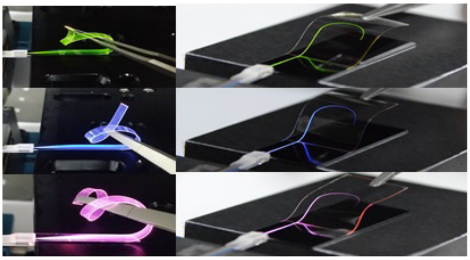
Keywords: upconversion, nanoparticle, waveguide, display

Even though upconversion nanoparticles(UCNPs) have been attractive due to their unique optical properties, great attentions have not been given to them because of their limited applications such as biomolecules and three dimensional (3D) volumetric displays.[1,2] We suggest a highly transparent and flexible display device based on core/shell(C/S) UCNPs incorporated polymer waveguide as a new application. C/S-structured Li(Gd,Y)F_4:Yb,Er/LiYF_4 UCNPs for green, Li(Gd,Y)F_4:Yb,Tm/LiYF_4 UCNPs for blue, and NaGdF_4:Yb,Tm/NaGdF_4:Eu UCNPs for red were successfully synthesized and characterized. For the fabrication of waveguide, the mixture of these blue-, green-, and red-emitting C/S UCNPs and bisphenol A ethoxylate diacrylate (n_a = 1.5647 at 632 nm) is used as core material and tetra(ethylene glycol) diacrylate (n_a = 1.5031 @ 632 nm) is used as clad materials, respectively. The display was fabricated by spin-coating and RIE process. Waveguide pattern was confirmed by SEM images. The thickness of fabricated display is so thin (~ 40 um) that it can be easily bendable. It also shows transmittance > 90% in the spectral range of 443–900 nm. The non-patterned and patterned polymer waveguide-based devices exhibited bright blue-, green-, and red-color under coupling with a 980 nm NIR laser even in a severe bending condition. Those emission colors of displays are well matched with those of UCNPs themselves.



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Transparent glass-ceramics: fabrication during heat treatment or femtosecond laser irradiation

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Keywords: glass-ceramics, heat treatment, fs laser irradiation, rare earths, luminescence

Micro/nanocrystals are formed during heat treatment[1] or laser irradiation[2] of precursor glasses. These new materials are well-known in the literature as transparent glass-ceramics. Differences in the luminescence characteristics of rare earth-doped glass samples before and after heat treatment or laser irradiation can be explained by structural changes in the environment around the optically active ions. In this work, two completely different lead-based and lead-free germanate glass-ceramic systems were examined. In PbO-PbF_2-GeO_2 glass-host compositions cubic β-PbF_2 nanocrystals are well formed, whereas quite different situation is observed for lead-free germanate samples containing BaO/BaF_2.[3,4] Single fluoride nanocrystals BaF_2 are not formed during heat treatment of precursor glasses. The presence of four crystalline phases BaF_2, BaO, $Ba_3Ga_2Ge_4O_{14}$ and GeO_2 was confirmed by X-ray diffraction. Structural aspects for germanate glass-ceramic samples fabricated under fs laser irradiation are also presented and discussed in details. Finally, the up-conversion luminescence spectra of erbium ions in two different lead-based and lead-free germanate glass-ceramic systems were studied in relation to potential temperature sensor applications.

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Multicaloric effect in $Pb(Fe_{1/2}Nb_{1/2})O_3$ ceramics

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Keywords: caloric, multicaloric effect, PFN, multiferroic, mechanochemical activation

The search for caloric materials has recently become one of the most active fields in condensed-matter science with applications in solid-state refrigeration technology. The caloric effect is related to a change of the material's entropy under the application of an external stimuli: magnetic, electric, or mechanical. Depending on the origin of the entropy change, the caloric effects can be classified as magnetocaloric (MC), electrocaloric (EC) and mechanocaloric effects.[1] Bulk caloric materials are currently not showing sufficiently large caloric temperature change (only a few degrees) for their commercial use. One idea how to overcome this problem is to prepare a material exhibiting more than one caloric effect - multicaloric material, in which the application of both stimuli can enhance the total caloric effect. Even more, different caloric modes can be applied in different temperature regions extending the operating temperature range of the cooling device. The coexistence of the MC and EC effects had been theoretically proposed five years ago[2] followed by experimental conformations.[3,4] It is very challenging to prepare efficient multicaloric materials and the search for them is not finished yet. In this work we experimentally prove that the $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) exhibits both MC and EC effects and is therefore the multicaloric material.

For the preparation of the PFN the homogenized, stoichiometric powder mixture was mechanochemically activated in a high-energy planetary mill for 30 h at 300 rpm and milled in an attrition mill for 4 h at 800 rpm. The powder compacts were isostatically pressed and sintered in an oxygen atmosphere at 1273 K for 2 h. This method yielded PFN ceramics with a theoretical density of 96% and uniform microstructure with average grain size of 2.3 μm. The dielectric permittivity and dielectric losses at room temperature and 10 kHz were measured with a HP 4284A precision LCR Meter and were 3580 and 0.038, respectively. For the indirect EC measurements, the polarization versus electric field hysteresis loops were measured by an Aixacct TF analyser 2000. At room temperature the EC temperature change was 0.81 K at 80 kV/cm. The maximum EC temperature change of 1.29 K was obtained at 80 kV/cm and 373 K. The magnetization vs. temperature at different magnetic fields was measured using a Superconducting Quantum Interference Device. The maximum MC temperature change of 0.16 K was obtained at 50 kOe and 2 K.

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Piezoelectric, ferroelectric and conduction mechanisms analyses of BCTZ ceramics for different temperatures ranges

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Keywords: BCTZ, ferroelectrics, piezoelectric, conduction mechanisms

$BaTiO_3$-based compositions have gain considerable attention due to their optimum properties produced by the substitution of the A and/or B site of the perovskite structure. In this way $Ba_{1-x}Ca_xTi_{0.9}Zr_{0.1}O_3$ (BCTZ) properties are enhanced near the morphotropic phase boundary (MPB).

Electrical characterization of BCTZ ceramics is accomplished with a set of independent piezoelectric, elastic and dielectric coefficients by means of different symmetry modes: radial, thickness and shear. An automatic iterative method developed at Spanish CSIC was implemented for all the resonances and resonator shapes needed for the determination of all piezoelectric ceramic materials including losses. Moreover, associated physical properties related to the nature of conductivity are calculated using complex impedance spectroscopy (CIS). The Impedance data obtained is associated to grain (bulk), grain boundary and interface/polarization effects.

In this work BCTZ ceramics (x = 0.10–0.18) were prepared by conventional ceramic method. Homogeneous and dense materials (up to 95% of theoretical density) were sintered at 1400 ºC (2 h). XRD analysis, ferroelectric hysteresis loops, piezoelectric and dielectric characteristics, as a function of frequency and temperature is presented. Measurements of material parameters at resonance were performed on ceramic shear plates, thickness-poled, and results were discussed in terms of the loss mechanisms of the ceramic. Besides, CIS was employed to explore dielectric relaxation as well as conductive behavior at a high temperature range.

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Gold nanoparticles decorated oxide catalyst for oxygen reduction reaction

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Keywords: SOFC, cathode, perovskite, gold nanoparticle, oxygen reduction reaction

Many researches have been investigated to improve catalytic activities of the surface for various oxide electrodes.[1] The self-regeneration and exsolution are the state-of-the-art method to form nanoparticles on the surface of perovskite type oxide. They can form well-dispersed catalytic nanoparticles on the surface, but they must be needed a reduction step at a high temperature. In the case of an electrode material for oxygen reduction reaction, a method of carrying catalyst particles on the surface by a physical mixing method and infiltration is mainly used,[2] and a surface particle forming method using physical vapor deposition (PVD) is also attracting attention. Anastasopoulos et al. reported a 30% improvement in the efficiency of oxygen reduction over conventional catalysts by using PVD method coated with 10 nm dispersed Pt and Pd catalyst particles.

The gold nanoparticles (NPs) were decorated on the surface of the PrBaCo1.9Cu0.1O5+δ (PBCCO) electrode by sputtering, and their electrochemical properties were investigated. Gold NPs were well dispersed, and the size of 10 nm was maintained even under the heat treatment condition of 950 °C. We hypothesized that the aggregation of gold NPs is inhibited by the combination of gold and copper, and the binding relationship between gold and copper on the surface was investigated by *in-situ* high temperature XPS and DFT analysis. The decoration of gold NPs on the PBCCO also decreased the polarization resistance 1.4 times less than the non-coated PBCCO electrode in air atmosphere.

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Effect of CuO to microstructure and properties of $Bi_{0.5}Na_{0.5}TiO_3$-$SrTiO_3$

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Keywords: electromechanical, doping, polarization, copper, ceramic

This report describes the sintering and ferroelectric characteristic of 0.76 $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-0.26$SrTiO_3$ (ST) (BNT-26ST) with CuO addition synthesized by using a solid-state reaction. The XRD, microstructure and density results reveal that Cu element reduces sintering temperature from 1150 °C to 1000 °C. In dielectric study, CuO addition induces the increase of relaxation behavior for 26ST ceramic in high temperature regime. In low temperature regime (< Tm ~ 150 °C), the Cu doping to 26ST accelerates the degree in freezing of dipole presumably due to the interaction between A site vacancy and nano domain boundaries. The electromechanical properties of BNT-26ST ceramics with CuO doping exhibited a significant decay in frequency dependence of polarization and strain, which might be related to formation of A-site cation vacancy.

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Structural transformation and enhancement in magnetization via sintering time variation in $Bi_{0.8}Pr_{0.2}FeO_3$ multiferroics

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Pr doped Bismuth Ferrite multiferroics; $Bi_{0.8}Pr_{0.2}FeO_3$ samples were synthesized via two step solid state reaction method with calcination at 400 ºC and sintered at 800 ºC. To study the sintering time effect on structural stability, sintering time was varied to 1 hour, 2 hour, and 3 hour. The different samples prepared showed a continual change in structure with sintering time as revealed through observed XRD patterns. Rhombohedral R3c (91.12%) + triclinic P1 (8.88%) phases were observed in sample sintered for 1 hour while with increasing time the percentage of rhombohedral phase decreases with evolution of orthorhombic Pbam phase. For the 2 hour

sintered sample, combined symmetry of rhombohedral and orthorhombic with R3c (61.06%) and Pbam (34.94%) was deduced by the best fits. With increasing sintering time to 3 hour, orthorhombic phase (59.91%) leads over rhombohedral R3c phase (40.06%). Enormous enhancement was observed in the magnetization with increasing the sintering time. Such robust change in the magnetic properties may be attributed to the increase in canting angle of spins.

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The influence of the dispersants on printing ink properties of metal oxides nanoparticles

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Keywords: metal oxides, dispersants, milling, inkjet printing

Colloidal stability of inkjet printing inks is one of the key parameters for their good printing performance. The stability of particles dispersed in water–based inks is usually achieved by electrostatic, steric, or electrosteric stabilization. Adsorption of polyelectrolytes of increased molecular weight at the solid interface of dispersed particles is responsible for electrosteric stabilization. In this work, stable homogeneous suspensions of MOx (TiO_2 and ZnO) were prepared using gum arabic (GA) and solsperse 40000 as dispersants. GA is a natural polyanionic polysaccharide with carboxylic groups as anchors, while Solsperse 40000 is an anionic phosphated alkoxylated polymer of Lubrizol. Both dispersants provide electrosteric stabilization of pigments in water based inks. GA was employed as dispersant to study the effect on the surface properties of MOx nanoparticles. GA has been used as the stabilizing agent for ink pigments for a long time. It is well known that GA can make the MOx nanoparticles have a good dispersibility and stability in GA colloidal solution for its low viscosity. The investigations on the optimum concentration of dispersants and the mechanism determining the dispersion behavior of MOx in aqueous dispersants solution were performed. Suspensions of MOx and GA/Solsperse were prepared first by dissolving dispersants in water. MOx were added in appropriate amounts. The weight ratio between MOx and GA (solsperse) was varied from 1/1 to 3.5/1. The ball milling was performed in a Retch PM 100 planetary ball mill at constant milling speed of 250 rpm using YSZ jar and balls. The effects of different milling time (15, 30, 60, 90 and 180 min) on average particle sizes were investigated. Results show improved dispersion with reduction of average particle sizes with increasing of milling time. Different ink formulations composed of MOx/dispersants (with addition of 1, 2 propylene glycol and n-propanol) were prepared and their printability properties were tested using Inkjet printer Fuji Dimatix DMP-3000. The main goal of this work is to analyse the influences of different quantity of dispersants and milling conditions on the printing quality parameters of the ink using different substrates.

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Structural and optical properties of agricultural-food waste derived glasses/glass ceramics

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Keywords: agricultural waste, food waste, glasses/glass ceramics wide semiconductor

Agricultural waste ashes and food waste are used to synthesise glass and glass ceramics. The as prepared materials are characterized using X-ray diffraction and UV-Visible spectroscopy for their structural and optical properties to check their suitability in various applications. The addition of Eggshell powder promotes the glass formation due to higher alkali content (CaO). The optical band gap of as prepared samples are in the wide semiconductor range. Probably, these as prepared glasses/glass ceramics can be used in high temperature and power generation.

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Processing of cermet nanomembranes

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Keywords: cermet, nanomembranes, sputtering, etching

Nanomembranes can be defined as quasi 2D structures, with thicknesses far below 100 nm, and large aspect ratio up to 1,000,000, considering their lateral dimensions and their thickness. Unlike thin films, nanomembranes are freestanding structures not supported by conventional substrate. They can be processed from a wide range of materials, depending of their purpose and field of application which ranges from infrared detectors, optical filters, plasmonic arrays and photonic bandgap structures, to catalytic reactors and biosensors.

Cermet is a generic name for a certain type of composites which consist of ceramic materials and metals, and in this work we present cermet nanomembranes (Cr-Si-O), processed via reactive sputtering and wet etching.

Namely, nanomembrane was deposited on the top of silicon substrate via reactive sputerring and the metal which was deposited was chromium. As chromium atoms penetrated into silicon substrate, they dislodged Si atoms from the lattice. Due to the fact that sputtering was performed in oxygen atmosphere, partial oxidation of the film occurred. The thickness of the formed composite Cr-Si-O nanomembrane was 8 nm, which approximately equals 20 atomic layers. The composition of the obtained composite layer was 52% chromium, 28% oxygen and 20% silicon, which was confirmed by EDAX analysis. The following step in the processing of cermet nanomembrane was to release it from the silicon substrate, which was

done by wet anisotropic etching of silicon. Solution of KOH and 2-propanol was used as etchant, whilst etching was performed at temperature of 80 °C for around one hour in order to completely remove Si. Removal of silicon was observed via optical microscope and SEM. Transmittance and absorbance of the nanomembrane were measured and it was proved that the nanomembrane behaves as an ideal absorber. Also, the processed cermet nanomembranes have a long lifetime.

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Sputtered thin film protective layers for the operation of OTMs in oxyfuel-like environments

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Keywords: oxygen, membranes, perovskites, dual-phase, sputtering, thin films, oxyfuel, CO_2

Oxygen transport membranes (OTM) based on mixed ionic and electronic conducting (MIEC) ceramics have attracted much interest as they can be directly integrated in a furnace for oxyfuel technology, constituting an inexpensive alternative for cryogenic air separation[1]. The absence of N_2 in this oxyfuel technology, that consists of fuel combustion by using O_2 (instead of air) in a CO_2 sweeping stream, allows more efficient combustion processes, minimizing NO_x formation, and the direct CO_2 sequestration process[2]. OTMs based on MIEC ceramic oxides present 100% selectivity, but the performance is limited by the ambipolar conductivity of the constituent material and –especially– by the stability in CO_2 containing atmospheres.

Amongst all the studied materials, BSCF is the one presenting the highest O_2 fluxes[3]. Nevertheless and despite its outstanding performance under clean environments, BSCF presents very poor permeating rates when exposed to CO_2 environments, yielding to an immediate cessation in the permeation and to the formation of carbonates eventually producing a material breakage.

A way to increase the stability of these perovskites is by CO_2 protection layers deposition[4]. Therefore, in the present work BSCF membranes performance is studied when applying protective thin-film layers by means of RF-sputtering. This technique is chosen in order to ensure the crystallinity properties together with a small thickness, necessary for maintaining the high BSCF permeation properties. First the growth of films consisting of pure ionic and nanograined dual-phase structures was studied as a function of different deposition temperatures, and then the best films were grown on BSCF bulk membranes for permeation measurements under CO_2 containing atmospheres.

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Investigation of structural and functional properties of doped $BaTiO_3$ thin films for potential application in tunable microwave devices

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Keywords: barium titanate, dielectric properties

Ferroelectric behavior of perovskites makes these materials very popular for various applications in microelectronics. Barium titanate is one of the most popular representatives of perovskites and probably the most investigated material from these group. Addition of dopants such as strontium and zirconium can change ferroelectric nature of barium titanate. Different concentration of mentioned dopants has huge influence on barium titanate structural and functional properties. Aim of this work was to approach the paraelectric state of barium titanate for potential application in tunable microwave devices such as varactors, phase shifters, etc. Barium strontium titanate (BST) is mainly used for production of tunable devices, but some other materials as barium zirconium titanate (BZT) can be also interesting for investigation. Precursor solutions were made from barium carbonate and tetrabutylorthotitanate, and as sources of Sr^{2+} and Zr^{4+} were used strontium acetate and zirconium (IV) oxychloride octahydrate, respectively. Acetic acid and 2-methoxy ethanol were used as solvents. Prepared sols were used for production of multilayered thin films with spin coating method on silicon and platinized (bottom electrode) substrates. After thermal treatment on different temperatures (750, 900, 1000 °C), prepared samples were structurally characterized by X-ray diffraction, Raman spectroscopy and scanning electron microscopy. After structural characterization samples were prepared for functional measurements and gold electrodes were deposited on top. Dielectric properties were measured with LCR meter, up to 1 MHz. We also measured ferroelectric properties.

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Aqueous TAPE casting of transparent yttrium aluminum garnet doped with neodymium (Nd:YAG) or chromium (Cr:YAG) ceramics

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Keywords: yttrium aluminun garnet, tape casting, transparent ceramics

One of the advantages of ceramic manufacturing process over single crystals is a feasibility of obtaining composite multilayered structures aimed at optimizing of the thermal properties and lowering optical losses of laser materials. According to the current knowledge the typical examples of the composite ceramic laser materials are cylindrical clad-core structures or a layered structures. This latter can be conveniently produced by tape casting and laminating. This method also, as a one of the colloidal forming techniques, is more attractive processes for manufacturing transparent YAG ceramics than dry pressing.

The main objective of this work was fabrication and characterization of YAG/Nd:YAG, Cr:YAG/Nd:YAG layered-composite ceramics with the use of aqueous-suspensions tape casting. The effect of ceramics foils preparation parameters, laminating and sintering conditions on the and microstructure and optical properties of Nd:YAG and Cr:YAG ceramics was studied. Also composite YAG/Nd:YAG, Cr:YAG/Nd:YAG ceramics were fabricated and their properties have been studied and described.

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Nonstoichiometry effects on ferroelectric and charge transport properties of $Bi_{1\pm x}FeO_{3\pm\delta}$ ceramics

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Keywords: bismuth ferrite, ferroelectric, electrical conductivity, defect, nonstoichiometry

We synthesized nonstoichiometric $Bi_{1\pm x}FeO_{3\pm\delta}$ ceramics by a conventional solid-state reaction method and studied their structural, dielectric and high-temperature charge transport properties to understand defect chemistry of the multiferroic $BiFeO_3$-based systems. Incorporation of the excess amount of Bi_2O_3 lowered the Bi deficiency in $BiFeO_3$, in which the nonstoichiometry was able to be engineered through controlling the excess amount. Polarization versus electric field (P-E) hysteresis loops and dielectric properties showed enhancement with the Bi_2O_3 addition. To better understand the defect effects on the multiferroic properties, the high temperature equilibrium electrical conductivity was measured under various oxygen partial pressures. The charge transport behavior was also examined through thermopower measurement. With those analyses, the point defect types and defect energetics in terms of thermodynamics will be discussed in details.

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The jump-like PTCR effect in metal-$BaTiO_3$ composite PTC thermistors

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A composite composed of a highly conducting phase and a high-resistivity $BaTiO_3$ phase was prepared. The high-resistivity $BaTiO_3$ was realized using a high-temperature treatment, while alloy powder was used as the conducting phase. The composite was prepared from a mixture of the constitutive phases: a highly conducting alloy powder and high-resistivity $BaTiO_3$ grains. The composition, the compacting pressure and the sintering temperature (under 1000 ^oC) were optimized in order to obtain a low-resistivity (less than 1 Ωcm) metal-$BaTiO_3$ composite with a remarkable, jump-like, anomaly (more than 10^4) in the electrical resistivity at the Curie temperature of $BaTiO_3$. It was postulated that the PTCR anomaly was obtained exclusively as a result of the disconnection of the conducting alloy network due to the volume changes associated with the phase transformation between the tetragonal and cubic $BaTiO_3$ at the Curie temperature.

Microstructural analyses, scanning electron microscopy, dilatometry and electrical measurements were used to characterize the materials that showed the PTCR (positive temperature coefficient of the electrical resistivity) effect.

T05: Ceramics for novel energy conversion, storage and use

Invited lectures

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Mixed ionic-electronic conducting membranes: fundamentals and challenges

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Mixed oxygen ionic-electronic conducting (MIEC) oxides hold promise for use as oxygen transport membranes to produce high-purity oxygen. Such membranes may further be integrated in ceramic membrane reactors for oxy-fuel combustion and syngas applications. In addition to reliability of operation under actual operating conditions, the challenge to researchers is to develop membrane materials showing fast oxygen diffusion and surface exchange kinetics. The present paper surveys theory and research on oxygen transport in the MIEC materials, with emphasis on defect chemistry and surface exchange kinetics; progress, problems and perspectives in the development of membrane materials; and identifies directions for future research.

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Design principles for perovskite photoferroics

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Photovoltaics rely on the separation of photoinduced charge carriers, which normally requires careful engineering of electron and hole attracting electrodes or p-n junctions, as in conventional solar cells. However, ferroelectrics display a spontaneous polarisation that can induce spontaneous photocurrents, allowing for greater flexibility in photovoltaic device architectures and the potential to circumvent the Shockley-Queisser.[1–3] Unfortunately most known ferroelectrics are poor absorbers of sunlight and poor conductors due to their relatively large optical band gaps.

In this talk I will discuss one strategy to induce ferroelectricity in the halide hybrid perovskites, which have recently received heightened attention due to their promising photovoltaic properties. Most perovskites are not ferroelectric, but instead show a non-polar lattice distortion called octahedral tilting. This tilting competes with the polar ferroelectric mode rendering systems paraelectric.[4,5] I will discuss i) why this tilting is amplified in hybrid perovskites and how this effects the electronic structure,[6,7] and ii) how the competitive coupling between these lattice modes can be designed to become cooperative such that the tilting can instead induce what is called improper ferroelectricity.[8–12] This will be shown using a group theoretical analysis, and demonstrated using first principles calculations.

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High-throughput screening of ceramic materials for light absorption

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Keywords: light absorption, band gap, density functional theory, high-throughput

Design novel materials for energy production in a photoelectrochemical cell, where water is split into hydrogen and oxygen by solar light, is one possible solution to the problem of increasing energy demand and storage as well as increase in pollution. A screening procedure based on ab-initio density functional theory calculations has been applied to guide the search for novel materials.

I will start describing various screening criteria and descriptors that connect the microscopic quantities calculated with computer simulations with the macroscopic properties of the device. The main descriptors used in the screening are: stability against phase separation and in water,[1] size and position of the band gap, using the GLLB-SC exchange-correlation functional.[2] These descriptors have been applied to a set of 19000 cubic perovskite structures resulting in a handful of materials for experimental investigation.[3,4] This set has also been used to identify trends that can help in speeding up the calculations for novel perovskite materials.[5,6] I will then present our results for the screening of hybrid halide perovskites, which are very promising for photovoltaics due to their high absorption properties and photogenerated charges mobility.[7]

At last, I will show the importance of the cooperative interaction in the calculation of adsorption energies on semiconducting materials.

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Prospects and challenges of solid oxide electrolysis

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Keywords: high temperature electrolysis, degradation, SOEC, multi-layer tape casting

Concerns to reduce adverse effects on the climate have led to increased focus on reducing anthropogenic CO_2 emission and consequently the amount of electricity generated globally from renewable and intermittent sources (e.g. wind and sun) is increasing. High temperature electrolysis of CO_2 and/or H_2O using solid oxide electrolysis cells (SOECs) can become a key enabling technology to reduce emissions by providing an energy efficient way to “store” electricity from periods of surplus production. The energy can, in the form of gaseous or even liquid hydrocarbons be transferred to the transport sector, where emission reduction is especially difficult. In this presentation the prospects of the SOEC technology for enabling larger shares of intermittent electricity production in the energy system will be exemplified by scenario analyses of a 100% fossil free systems.

Whereas state of the art SOFCs cells are reversible, there are important differences between SOFC and SOEC operation in terms of degradation phenomena. Highlights from the past decade of SOEC R&D at DTU Energy will be presented. Introduction of new ceramic manufacturing routes and better oxygen electrode materials has brought down the degradation rate at –1 A/cm^2 from 40%/kh to 0.4%/kh. Recent attempts to push up the maximum current density limit further by infiltration of nano-sized CGO in the Ni/YSZ structure will also be presented (so far a factor 4 reduction in degradation rate at 1.25 A/cm^2 has been observed).

Finally, a more general discussion about life time limiting degradation phenomena in SOEC operation will be given, based on own findings and literature including phenomena both at cell and stack level. Special focus will be given to mechanical issues.

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Investigation of the BZCY72-BaPrO$_3$ system for high-temperature electrochemical applications: thermal evolution of structures and electrical properties

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Keywords: $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-}\delta$, PCFC, membrane reactor, cathode, mixed conductor

The perovskite system $BaCeO_3$-$BaZrO_3$ substituted with trivalent dopants is a strong candidate for protonic ceramic fuel cell (PCFC) electrolytes and membrane reactors[1]. The composition $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-}\delta$ (BZCY72) offers a useful compromise of moderately high proton conductivity and good stability. PCFCs may operate at lower temperature, ~600 °C, than oxide-ion based SOFCs; however, decreasing the operation temperature leads to greater overpotentials at the electrode/electrolyte interface. Recently, much effort is devoted to finding materials with high mixed protonic-electronic conductivity and the requisite stability for electrodes and membrane components at the lower temperature range. Praseodymium is an interesting dopant for perovskite proton conductors since considerable electronic conductivity is generated at sufficient dopant levels[2]. Mapping the structural phase transitions and electrical behaviour with temperature and composition is critical for the development of these materials. In this work, Ba-stoichiometric and substoichiometric solid solutions between BZCY72 and BaPrO$_3$ are studied by neutron diffraction, revealing higher symmetry for low Pr contents and high temperatures, and lattice parameter contraction on heating attributable to dehydration for low Pr contents. Conductivity is p-type in dry air and N$_2$, increasing with greater Pr content. Magnetic and structural studies suggest that Pr much prefers the IV oxidation state on the perovskite B site; the positive transport species are thus suggested to exist as polarons in the oxygen band[3]. The preference for hole rather than proton or oxide-ion formation with increasing Pr content is discussed. Intermediate solid-solution members warrant further study for PCFC and membrane applications.

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Stereolithographic additive manufacturing of ceramic structures

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Keywords: additive manufacturing, stereolithography, nanoparticles paste, laser scanning, pattern exposing

Through computer aided design, manufacturing, and evaluation (CD/CAM/CAE) ceramic structures with spatially ordered micro cavities were successfully fabricated using stereolithography, an additive manufacturing technology. Titania micro photonic crystals with dendritic patterns were fabricated to control electromagnetic waves in terahertz frequency ranges. Subsequently, solid electrolyte dendrites of yttria-stabilized zirconia (YSZ) with spatially ordered pores were processed for fuel cell miniaturization. Moreover, ceramic sheets of lithium-lanthanum-titanate (LLT) with micro emboss patterns were developed for all-solid batteries. Designed models with intended 3D structures were converted into the stereolithography (STL) file format through polyhedral approximations and sliced into a series of 2D layers. The slicing pitches were defined as 10 and 50 μm for fine pattern exposing and speedy laser scanning stereolithography, respectively. The numerical data were transferred into each stereolithographic system to create bit map images for micro pattering and raster patterns for laser scanning. A photosensitive acrylic resin, including 40 vol. % of ceramic particles with 200 nm diameter, was spread on a flat metal stage using a mechanical knife edge. The thickness was automatically controlled to maintain the value given by the model slicing pitch. In the case of speedy laser scanning stereolithography, a ceramic slurry was scanned using an ultraviolet laser with a wavelength of 355 nm in order to create cross sectional planes with an edge part accuracy of 5 μm. The laser beam was adjusted to 100 μm in spot size and 100 mW in power. After the solid pattern was formed, the stage was lowered by 50 μm in layer thickness and the next cross section layer was stacked. Three dimensional structures were fabricated by stacking the two dimensional layers. In the case of fine pattern exposing stereolithography, two dimensional solid patterns were obtained on the slurry surface by light induced photo polymerization. High resolution images had been achieved by using a digital micro mirror device. In this optical device, micro aluminum mirrors with 14 μm edge length were assembled in an array of 1024 × 768 mirrors. Each mirror could be tilted independently by piezoelectric actuators. Ultraviolet light with a wavelength of 405 nm was introduced into the digital micro mirror device and the cross sectional image was reduced by 1/10 using an objective lens set; the light was focused onto a 1.3 × 1.7 mm exposing area. Using the described computer controlled layer stacking process, an acrylic resin component containing a dispersion of ceramics particles was obtained. Part accuracies of green bodies could be measured and observed by using a digital optical microscope (DOM). The formed models were dewaxed at 600 ºC for 2 hs in air with a heating rate of 1.0 ºC/min; full ceramic components were obtained after sintering. The microstructures of the sintered components were observed using a scanning electron microscope (SEM). Relative densities of these ceramic components were measured by the Archimedean method.

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Nanostructure engineering in oxide ceramics for high-temperature thermoelectric energy conversion

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Keywords: oxide thermoelectrics, phonon scattering, grain boundary, nano-inclusion

Thermoelectric energy conversion has been widely recognized to be particularly suitable for waste heat energy recuperation and energy harvesting, since it generates electricity directly from a heat flux penetrating a solid device consisting of n- and p-type semiconductors. Although thermoelectric (TE) power generation has been very successful due to its extremely high reliability in space and remote applications such as power sources for deep space probe missions, limitations in elemental abundance and thermal durability of the conventional TE materials have prevented a wide commercialization of the TE power generation.

Metal oxides are ionic compounds consisting of metal cations and oxygen anions alternately placing with the Coulombic attracting interaction between them. Since the metal-oxygen bonds are largely polarized, conducting electrons tend to localize on the positively charged metal cations, resulting in the carrier mobility generally 2–3 orders lower than those of Si and other covalent compounds. Furthermore, strong interatomic bonding predominantly by the Coulombic force in oxides coupled with the small atomic mass of oxygen leads to a high velocity of the elastic waves propagating the crystal lattice of oxides, yielding a high lattice thermal conductivity. These inherent tendencies of metal oxides had kept them away from consideration as a TE candidate until mid 90s. Nevertheless, boosted by the global environment issues and carbon dioxide mitigation problems, oxide TE materials, which are highly durable at high temperature in air, non-toxic, low cost with minimal environment impact, are becoming more and more of vital importance for recuperation of decentralized waste heat energy for higher energy efficiency.

In this paper, nanostructure engineering in TE oxides will be depicted with focuses on thermal conductivity reduction by introducing complex microstructure, and by carefully choosing the crystal structure. The former approach is exemplified by multinary-doped ZnO with a spontaneously formed microstructure in sintered bodies,[1] while the latter strategy is demonstrated by an ultra-low lattice thermal conductivity found in β-pyrochlore (defect pyrochlore) oxides having an oversized cage-like structure surrounding a small atom inside.[2,3] Current issues of TE oxides will be discussed with a future prospect of the materials and applications.

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Processes and materials for solar thermochemical production of fuels and chemical commodities

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To use heat from carbon-free sources like concentrated solar radiation to drive chemical reactions for the production of transportation fuels or of chemical commodities represents a promising way to replace established industrial processes and to avoid substantial amounts of climate relevant emissions. Recent developments offer attractive medium- to long-term prospects for the provision of chemicals like ammonia, sulfur, phosphates or cement and fuels like hydrogen and synthesis gas. The direct use of solar heat to drive endothermal chemical reactions in a temperature range between 500 and 1800 °C is possible. In the field of solar fuels production so-called thermo-chemical cycles are a viable option to produce hydrogen from water or syngas from water and CO_2 at an acceptable temperature level. The most prominent examples are cycles from the so-called sulphur family, the hybrid sulphur and the sulphur-iodine process, and redox cycles applying metal/metal oxide pairs or multi-valent metal oxides which are capable to reversible incorporate oxygen in this lattice. The present analysis gives an overview on recent developments and the state-of-the art of high temperature fuels or chemical commodities producing solar processes. It will have a look on the most important performance parameters involved and will give an outlook on further potential and necessary developments. In addition we look at variants of such processes offering the chance to use them for thermo-chemically storage of solar heat or for air separation.

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Quantification of degradation in infiltrated SOFC anodes

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Solid Oxide Fuel Cells (SOFC) are a mature technology and large SOFC stacks have been tested under operation for periods of more than 5 years showing a remarkable resilience but showing signs of degradation.[1] Nickel coarsening is one the main degradation mechanisms that affect the lifetime of the anodes and it is still yet to be fully understood. The next generation of electrodes, Ni-infiltrated anodes, have shown remarkable improvement of the electrochemical performance[2] but show a fast degradation compared with the conventional anodes.[3] In this work we present an integrated experimental/modelling approach to quantify the effect of the Ni microstructural evolution on the electrochemical performance of the next generation of anodes.

Scaffolds of scandia-stabilised zirconia (ScSZ) impregnated with different volume fractions of Ni were fabricated and characterised. Symmetrical cells were then annealed at constant temperature while recording the impedance as a function of time for several days; the polarisation of the bulk and electrode response was de-convoluted from the spectra and followed as a function of time and nickel content. The microstructure of the initial and degraded samples was precisely reconstructed with focused ion beam SEM tomography and analysed to quantify the change in three-phase boundary (TPB) density, Ni percolation and Ni particle size upon annealing. A physically-based electrochemical model, based on conservation equations, was used to establish a link between microstructural degradation and the evolution of the impedance spectra.[4]

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Manufacturing of proton conductive ceramics for hydrogen separation membranes and fuel cells

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Keywords: barium-cerate based materials, ceramic processing, tape casting

High temperature proton conducting ceramics based on perovskites of a general formula ABO_3 ($BaCeO_3$, $SrCeO_3$, $BaZrO_3$ and $SrZrO_3$), have received increasing interest as hydrogen separation membranes and as electrolytes in proton-conducting intermediate-temperature solid-oxide fuel cells and/or electrolysers (SOFCs/SOECs). These materials however still require ad-hoc investigations from the ceramic-technology point-of-view to boost their widespread deployment in the abovementioned applications.

This work aims to highlight and solve all the most critical issues linked to the ceramic process needed to obtain planar, defect free, proton conductive membranes based on barium cerate perovskites for hydrogen separation and SOFC/SOEC applications. Tape casting was exploited as industrial easy-scalable ceramic technology for both membranes and Solid oxide cells.

In particular for H_2 separation, asymmetric $BaCe_{0.65}Zr_{0.2}Y_{0.15}O_{3-\delta}$-$Gd_{0.2}Ce_{0.8}O_{2-\delta}$ membranes, constituted by a porous support and a dense active layer, were produced for the first time. The strict control of the sintering atmosphere was found to be one of the most critical parameter to obtain dense active layers. On the other hand, the possibility to produce a dense/porous/dense $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ (BCY) sandwich-structure electrolyte for SOFC/SOEC application was evaluated. The obtained samples were carefully characterized either in SOFC and SOEC mode.

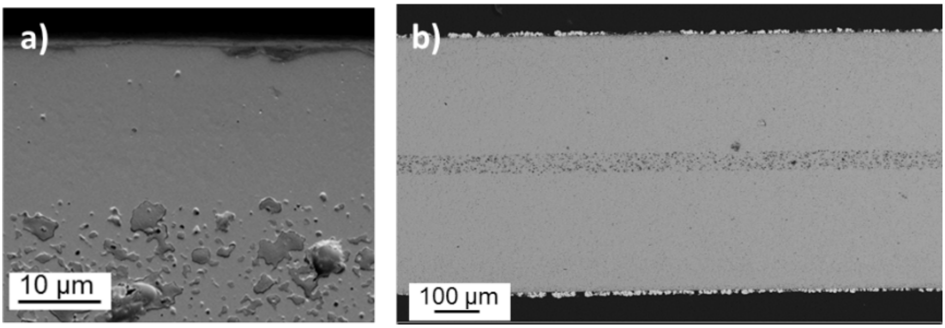

Fig. 1. Asymmetrical ceramic membrane for H_2 separation (a) and sandwich-structure electrolyte for SOFC/SOEC application (b)

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Low cost Sodium batteries based on ceramic materials – an old idea revisited

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Keywords: beta Alumina, battery, Sodium battery, NaNiCl, extrusion

During their first commercial development in the 1980s and 1990s, batteries based on Sodium and Sodium conducting ceramics had been seen as a high energy storage device for electric vehicles. As Lithum batteries proved to be a more convenient alternative for electrical mobility in the last couple of years, Na batteries effectively went to a state of scientific and commercial hibernation.

Only recently, with the advent of extremely low cost solar and wind electricity and the decentralizaion of the energy system, the demand for large scale electrical storage systems arose. Stationary power systems require very low cost. Na batteries do consist only of cheap, abundant materials, such as Alumina, Nickel, rock salt, and sheet metal, so in theory they could deliver on that promise. However, real-world Na batteries today still are manufactured with complex shapes and expensive production methods. In order to overcome these limitations, IKTS has fundamentally revisited Na battery design and manufacturing for mass production and cost reduction.

Low cost batteries for Gigawatt scale stationary energy storage can be manufactured from Na-beta-Alumina ceramics. Candidate battery cells for this applications are Sodium-Nickel-Chloride (NaNiCl) and Sodium-Sulphur (NaS) batteries. To achieve a total cost of the battery cell of under 100 $/kWh, both the ion conducting ceramic material as well as the design of the ceramic component need to be optimized for mass production. IKTS has achieved several breakthroughs in the shaping of beta-Alumina components, such as cold plastic extrusion and tape casting. These components are designed according to a set of rules derived from cost and manufacturing requirements. It is discussed, how electrochemical component design and mechanical requirements interact with shaping methods and the route to beta-Alumina phase formation. Several problems needed to be solved for high-throughput manufacturing of Na-beta-Alumina, such as the very high pH value in the feedstock, the automated shaping of tubes with one end closed and the phase stability during sintering. Material qualities with a phase content of > 96% ß“ and conductivities of > 240 mS/cm have been achieved from extrusion at IKTS.

Extruded ceramic tubes and sheets have been investigated electrochemically with very promising results. Several components have undergone electrochemical and thermomechanical testing in IKTS designed real-world battery cells based on Nickel cathodes (NaNiCl design) with capacities of well over 100 Ah.

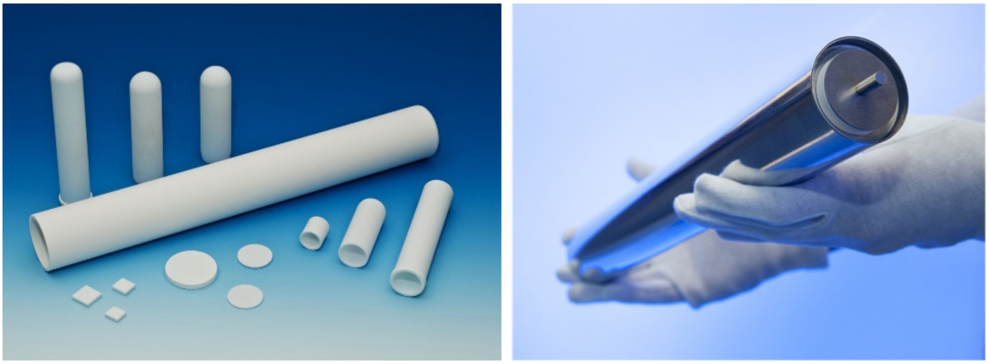

Fig. 1. Large-scale beta-Alumina tubes (left) and 100 Ah stationary NaNiCl battery cell from Fraunhofer IKTS

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Financial support for parts of the work by the Federal State of Thuringia, the German Ministry of Economics and Trade and the Fraunhofer Future Foundation is greatfully acknowledged.

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Full picture discovery for flux-grown crystals and interface designs on next-generation all-solid-state LIB

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Keywords: all-solid-state LIB, flux growth, single crystals, crystal morphology, surface/interface design

Lithium ion secondary batteries (LIBs) have been intensively developed due to strong industrial demands of high-performance electric storage devices especially for mobile electronics and green mobilities. In particular, LIBs with both higher energy and power densities compared to those of conventional ones have attracted research interests for future energy storage applications. All-solid-state LIBs are candidates for next-generation LIBs because of their safety, stability and non-flammability. In addition, high volumetric energy densities can be achieved when cathode-solid electrolyte-anode units are stacked in a multilayered manner in a single package. However, it is still difficult to achieve all-solid-state LIBs with desired properties mainly because of difficulty in smooth lithium ion diffusion, i.e., diffusion of lithium ions and electrons are interfered at interface of different materials and also inside of them. In this regards, we have tried to control and design the interface and prepare materials for all-solid-state LIBs on the basis of the crystal science and engineering[1–4]. Our research group has developed flux and its expanded methods for preparing highly crystalline materials used to all-solid-state LIBs. Flux method is a liquid phase crystal growth method in which idiomorphic highly crystalline particles can be obtained under the melting point of the target ones. Therefore outmost crystal planes are tuned by our techniques where they have desired lithium ion paths. In addition, the grown crystals are expected to have high crystallinity because diffusion and rearrangement of atoms easily occurred compared to conventional particle fabrication methods. Recently, we have developed flux method to fabricate crystal layers (films) on various substrates, which is named “flux coating method”. It has enabled us to grow crystals directly on current collector (and solid electrolytes) with good interfaces. Furthermore, we are focusing on a glass-flux method to make fine active materials/solid electrolyte interfaces. The details of crystal growth and interface design by use of our flux concept will be presented in the ECerS2017 conference.

Acknowledgements

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Oral presentations

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Three-dimensional polymer-derived ceramic composite paper electrode for electrochemical energy storage applications

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We present a rational method of synthesizing silicon oxycarbide (SiOC) supported on reduced graphene oxide (rGO) paper. We show that by controlling the amount of pre-ceramic polymer i.e., polysiloxane, it is possible to tune interlayer spacing and obtain an optimized composite electrode that may find use in electrochemical energy storage devices. In this composite configuration, the SiOC provides ample sites for reversible storage of lithium-ions while rGO acts as an electrical conductor and robust support against mechanical degradation at high currents. In this study, a reversible electrochemical capacity of ca. 600 mAh g-1 was recorded for the composite as a Li-ion battery electrode. While a specific capacitance of >75 F g-1, at a current density of >6 A g-1, was observed as working electrode in supercapacitor configuration.

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Development of porous electrodes with tailored microstructure for high temperature and pressure alkaline electrolysis cells (HTP-AEC)

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Keywords: processing, porous electrodes, electrolysis

The development of porous electrode structures with tailored microstructures is necessary to reach high current densities, of several A/cm^2 in High Temperature and Pressure Alkaline Electrolysis Cells (HTP-AEC) while maintaining high electrical efficiency (>80%). In this work we demonstrate how a porous ceramic structure can be processed using commercial $LaNi_{0.6}Fe_{0.4}O_3$ powder and sacrificial pore formers. The microstructure is optimized to accommodate a high interfacial surface area between the solid electrode and the liquid electrolyte, and at the same time allow the produced O_2 to escape through gas diffusion pores. The aim is therefore to achieve a mixed pore size distribution that can accommodate these two constraints.

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The template-assisted wet-combustion synthesis of fibrous nickel-based catalyst for carbon dioxide methanation and methane steam reforming

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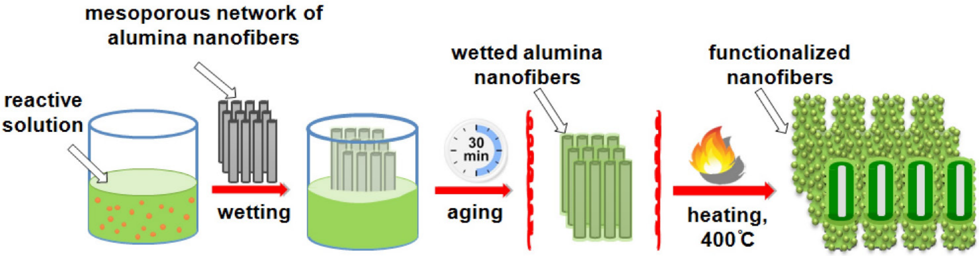
Keywords: Ni-based catalyst, combustion synthesis, carbon dioxide metanation, methane steam reforming

Template-assisted wet-combustion synthesis was used to prepare one-dimensional nickel-based catalyst for carbon dioxide methanation and methane steam reforming using highly aligned alumina nanofibers with an average single fiber diameter of 10 nm as a support. X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy, and high-resolution transmission electron microscopy demonstrated that the as-synthesized catalyst composed of double core-shell structured fibers ($NiO/NiAl_2O_4/Al_2O_3$). Due to a high temperature achieved in a short time during reaction and a large amount of gases evolved, the wet-combustion synthesis yielded homogeneously precipitated nanoparticles of NiO with average particle size of 4 nm on alumina nanofibers covered with $NiAl_2O_4$ nanolayer. To prove the role of the properly chosen fuel on the product morphology and chemical composition, Ni-based catalyst was prepared using fuel-less reactive solution. The results demonstrated that the average particle size of deposited NiO is ~40nm was obtained.

Nickel-based catalyst synthesized by wet-combustion method exhibited excellent activity in steam reforming of methane and sufficient activity in carbon dioxide methanation. The fiber-type structure of the catalyst was unchanged after the processed.



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Deciphering the influence of microstructure and crystal structure on the temperature dependent ion conductivity of Sodium-β”-alumina

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Keywords: Na-β”-alumina, microstructure, crystal structure, ion conductivity, non-Arrhenius behaviour

Na-β”-alumina is a fast sodium ion conductor at elevated temperature and thus favoured as electrolyte in Na/$NiCl_2$ batteries. Although the material is known since the 1970s, sodium ion conductivities reported in literature show a large variation[1]. While it is generally agreed that this is related to compositional as well as grain size effects, the detailed relationships are still unclear[2,3]. In addition, Na-β”-alumina is a non-stoichiometric material which makes it difficult to prepare with defined composition as sodium evaporates at the high temperatures required for sintering[4].

Based on a detailed experimental study we show that the sintering conditions affect not only grain growth, but also sodium content and crystal structure of Na-β”-alumina ceramics and explain how this affects the ion conductivity. Furthermore, the temperature-dependent conductivity data between room temperature and 400 °C feature a deviation from exponential behaviour. We discuss different interpretations of this “non-Arrhenius behaviour” as well as possibilities and limitations of extracting the contributions of grain and grain boundary conductivity from impedance spectroscopy data.

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$ZnFe_2O_4$/C nanoparticles by laser pyrolysis: new anode material for lithium-ion batteries

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Keywords: laser pyrolysis, zinc iron oxide, carbon coating, $ZnFe_2O_4$/C, composite, lithium-ion batteries

With the depletion of fossil fuels and the growing environmental concerns, lithium-ion batteries received considerable attention to contribute to the development of electric vehicles and storage for renewable energies. However, existing lithium-ion batteries cannot reach sufficient energy density to address the needs for such applications. One of the issues limiting the energy density is the low specific capacity of the graphite anode (372 mAh/g). Mixed-transition metal oxides with a spinel structure (AB_2O_4 – A, B transition metals) appear as a promising solution to replace graphite with a higher theoretical capacity (between 750 and 1000 mAh/g). Among various oxides, $ZnFe_2O_4$ is an interesting substitute for graphite, as an abundant, cheap, non-toxic and environmental-friendly material with a high theoretical capacity (1000 mAh/g). The nanostructuration of this material as well as a carbon coating around the particles can also help to maintain a mechanical stability during cycling and enhance the lithium kinetics.

$ZnFe_2O_4$/C nanoparticles presented in this work were synthesized by laser pyrolysis. In this vapor-phase process, a CO_2 laser is used to thermally decompose the precursors and synthesize nanoparticles. A solution containing $ZnCl_2$ and $FeCl_3.6H_2O$ dissolved in ethanol in a stoichiometric ratio was used for the synthesis of $ZnFe_2O_4$/C nanoparticles. Ethylene was chosen as absorbent of the CO_2 laser to allow the precursors decomposition and air as the carrier gas. To vary the carbon content of the as-synthesized nanopowders, annealings under air atmosphere were realized (Fig. 1).

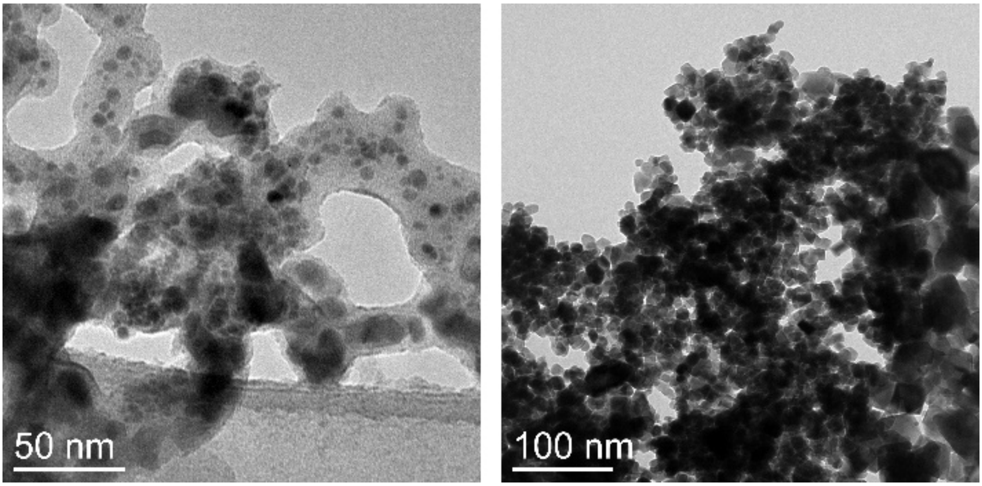

Fig. 1. Particles morphology before annealing (left) and after annealing (right)

Electrodes were then prepared using $ZnFe_2O_4/C$ (70% wt.), CMC (12% wt.) and carbon additives (VGCF 9% wt., carbon black 9% wt.) to be cycled vs. lithium metal and post-mortem SEM was done to observe the electrodes morphology after cycling.

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Pressure assisted sintering of tape casted calcium cobaltite

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Keywords: thermoelectrics, calcium cobalite, tape casting

Thermoelectric materials can convert waste heat directly into electrical power by utilizing the Seebeck effect. Calcium cobaltite $Ca_3Co_4O_9$ is a promising p-type oxide thermoelectric material for applications between 600 °C and 900 °C in air. The properties and morphology of $Ca_3Co_4O_9$ are strongly anisotropic because of its crystal structure of alternating layers of CoO_2 and Ca_2CoO_3. The electrical conductivity is for example 13.5 times higher in a/b-direction than in c-direction.[1] By aligning the plate-like grains, the anisotropic properties can be assigned to the component. Hot-pressing of tablets is a well-known technology for grain alignment of $Ca_3Co_4O_9$ and increases the thermoelectric properties in a/b-direction remarkably.[1–3] It also increases the relative density.[1–3] However, hot-pressing of tablets is limited by the tablet size. An interesting alternative for larger components is the pressure assisted sintering of panels from tape casted layers. Tape casting already leads to a grain alignment during green body forming. By combining tape casting and pressure assisted sintering (50 kN maximum force) of $Ca_3Co_4O_9$, high densities and high thermoelectric properties can be reached for large components up to 200 mm edge length.

$Ca_3Co_4O_9$ was successfully tape casted with the doctor blade technique (binder: polyvinyl butyral, organic solvent). Several layers of tape were stacked and laminated to 5 cm × 5 cm panels. These panels were sintered with different applied pressures in a LTCC sintering press with combined *in-situ* shrinkage measurement. Pressure-less sintered panels have a 2.5 times higher electrical conductivity at room temperature than test bars with randomly orientated particles. By applying a uniaxial pressure of 10 MPa during sintering, the electrical conductivity increases by the factor of 6 compared to the pressure-less sintered panels. About 40% linear shrinkage are reached in pressing direction. The Seebeck coefficient ($S_{25\,°C}$=146 µV/K) and the electrical conductivity ($\sigma_{25\,°C}$=15100 S/m) are in good agreement with the values published in literature for hot-pressed tablets.[1,3]

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High-temperature mechanical behavior of fully dense $La_{9.33+X}Si_6O_{26+3X/2}$ oxyapatite electrolyte materials for SOFCs

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Keywords: creep, mechanical properties, oxyapatite, electrolyte, SOFCs

Lanthanum silicates is considered as a potential alternative to yttria-stabilised zirconia to be used as electrolyte material in Solid Oxide Fuel Cells. While numerous studies have dealt with the influence of composition on conduction properties, very little is known about the mechanical properties of lanthanum silicate compounds. We have thus started an exhaustive study of mechanical properties of $La_{9.33+x}Si_6O_{26+3x/2}$ sintered compounds, taking benefit from our previous experience in oxyapatites preparation[1,2] and from our knowledge of oxide mechanical properties characterization[3–5].

High density (<96%) oxyapatite material, made through conventional sintering (CS) and Spark Plasma Sintering (SPS), were prepared from nanopowders synthesized through freeze-drying. Samples were then characterized mechanically at both intermediate and high temperature.

Firstly, compressive mechanical tests have been performed at solid oxide fuel cell operating temperatures (700 ºC) under different atmospheres, including air, argon and pure hydrogen. And secondly, we performed Compressive creep tests at constant speed and load at temperatures ranging from 1000 to 1300 °C. The objective was determine the effective diffusion coefficient and identify the atomic mechanisms of plastic deformation and the origin of failure of these materials at high temperature.

The experimental results have been correlated with microstructural observations by scanning and transmission electron microscopy.

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The proton in nominally anhydrous oxides: content, nature and dynamics

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The attempts to develop stable ceramic electrolyte membranes for H_2 production (electrolysers), conversion (fuel cells, CO_2 converters) or purification (membranes) led to select various anhydrous oxide frameworks (perovskites, apatites) with high ionic conduction at medium temperature (400–700 °C). The use of medium pressures (20–30 bars) allows to optimize the economic efficiency of H_2-based systems but implies high chemical resistance vs. water pressure, CO_2, etc. Different materials have been tested and some of them have recently reached the demonstrator scale. Techniques able to study H-containing frameworks are multiple (X-ray and neutron diffraction, TGA, IR & Raman spectroscopies, Elastic, Quasi-elastic and inelastic neutron scattering, PIGE/ERCS, Nuclear Reactions, etc.) but their comprehensive use limited. However, the fundamental knowledge on the proton chemical nature at the operating temperature (hydroxyl group, interstitial proton or proton gas), the exact content (differentiation between defect, surface or bulk protons), the location and the dynamics of protons remains poor and highly debated. Ion/proton dynamic and conduction take place when the species escape from the potential well, i.e. in a very anharmonic regime, very far away from the conditions of many studies. Furthermore, the unique properties of hydrogen and its low amount (i.e. a doping) in these membranes make the study difficult because of the confusion with surface species. Reasonable answers to all the above mentioned questions will be discussed at the light of recent works.

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$MgAl_2O_4$-based catalyst deposition over nickel-chromium alloy for steam methane reforming in millimetric-channel reactor

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Keywords: millistructure, catalyst slurry, dip-coating, adherence, substrate pre-oxidation

Functionalized metallic millistructured reactors-exchangers are promising solutions for intensification of steam methane reforming.[1] High temperature metals, resistant to corrosion, usually Iron/Chromium or Nickel/Chromium alloys, are used to fulfill the severe conditions occurring in this catalyst reaction (20 bars, steam/carbon molar ratio over 3, temperature between 800 and 900 °C). To perform the catalytic conversion of methane inside millistructured reactors-exchangers, thin catalyst film deposition is required. Among all the existing coating techniques (plasma spraying, CVD, sol-gel…), washcoating is probably the most described in the literature for coating structured catalysts and monolithic reactors.[2] It is a reliable technique that is easily scalable (e.g. for automotive application) and that can be adapted to several kind of substrates (ceramic, metallic). For washcoating complex geometries with limited accessibility (e.g. monolithic reactor having tortuous channels), slurry infiltration methods may be preferred. Solvent choice, solid concentration, particle size distribution, pH and additives (binders, plasticizers, wetting agents, …) are the main determining parameters.

Though $MgAl_2O_4$-based catalysts have proven to be reliable for methane conversion into hydrogen, very few studies in the literature have described its deposition on chromium oxide forming alloys.[3]

The goal of this work is to coat a homogeneous and adherent $MgAl_2O_4$-based catalyst layer by dip-coating technique onto nickel-chromium alloy foils (Inconel 625). Thermal pre-treatment in controlled atmosphere is used in order to enhance the catalyst adhesion by producing an oxide layer onto the surface. Morphology of the powder, particle size, catalyst slurry formulation, rheological properties and dip-coating parameters have been studied and optimized in order to improve the coating quality. Coating thickness, coating load and adhesion measured by weight loss under ultrasonic tests are also reported after calcinations.[4] Results obtained by application of the solution developed to washcoating of millimetric channels reactors are presented as well.

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Stability and sintering of magnesium oxide as a substrate material for lanthanum tungstate membranes

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Keywords: hydrogen, ceramic membranes, lanthanum tungstate, magnesium oxide, sintering

Hydrogen is an important resource for different applications in chemical industry, power plant technology, and mobile systems. One possibility of producing hydrogen is the water-gas-shift-reaction where hydrogen is synthesized from fossil fuels like natural gas. In order to separate H_2 from gas mixtures and achieve high purity, the use of dense mixed protonic-electronic conducting ceramic membranes shows a large potential.

Lanthanum tungstate (LaWO) with a composition of $La_{6-x}WO_{12-\delta}$ (with $d = 1.5x + \delta$ and $x = 0.5–0.6$) is a promising material for these applications due to its high chemical stability and proton conductivity. LaWO has already been investigated for structural properties, conductivity and H_2 permeation. To achieve the maximum performance of the membrane material one effective way is to reduce the membrane thickness to around 20 µm to lower the transport resistance. To maintain the mechanical stability of such a thin ceramic layer a support structure is needed. A cheap, mechanically and chemically stable material is needed for this task. Furthermore, the substrate structure has to be porous to ensure the gas transport and has to be inert towards the LaWO membrane material.

In this study we present magnesium oxide (MgO) as a substrate material for LaWO membranes.[1] For this purpose, MgO supports were prepared for sintering studies and stability tests under application conditions (H_2, CO, CO_2, H_2O). MgO powder was commercially available. The powder properties were monitored by particle size analysis and BET measurements. Stability tests were performed in two different atmospheres which represent the situations at the entrance and at the exit of a water-gas shift reactor. Sintered MgO pellets were exposed to the atmospheres for 72 h at temperatures of 600–900 °C. No reactions of the MgO with the gases could be found by XRD analysis. For the fabrication of MgO support layers the tape-casting technique was chosen. The powder properties were tailored by annealing and subsequent ball milling in ethanol. Tape-cast samples were studied for their sintering behavior using an optical dilatometer. The shrinkage rate of the MgO layer was compared to that of a LaWO membrane layer and they appeared to be quite different but still in a tolerable range. Due to this, asymmetric structures with a LaWO membrane and an MgO substrate layer were successfully fabricated by sequential tape-casting and co-firing. The two materials showed some interdiffusion during the co-firing process and consequentially the formation of a second phase inside of the MgO substrate. No crack-formation or other harmful effects of this second phase were found. Finally, the stability of the asymmetric membranes was investigated by exposing the samples to application atmospheres at 900 °C for 96 h. No reaction was visible in SEM and XRD, proving the excellent perspective of MgO in the field of hydrogen separation membranes.

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Cr/Si-poisoning of $La_2NiO_{4+\delta}$ used as air electrode in solid oxide cells

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Keywords: rare earth nickelates, SOFC, SOEC, poisoning

High-temperature steam electrolysis (HTSE) offers a way for highly efficient water splitting if thermal coupling to existing heat sources is available. HTSE technology is based on solid oxide electrolyzer cells (SOECs) which are operated at temperatures between 600 and 1000 °C. Compared to their galvanic counterpart – solid oxide fuel cells (SOFCs) – degradation rates of SOECs are currently roughly one order of magnitude higher than for SOFCs. In this work the promising electrode material $La_2NiO_{4+\delta}$ is characterized as air electrode material for high temperature fuel cells and electrolyzer cells. $La_2NiO_{4+\delta}$ is a member of the rare earth nickelate series $A_{n+1}B_nO_{3n+1}$ (A = La, Pr, Nd; B = Ni; n = 1, 2, 3 ...) which are among the most promising materials when high oxygen diffusivities, good electronic and high ionic conductivities are required.[1] In addition to their use as air electrodes for intermediate temperature SOFCs and SOECs, these compounds offer applications as ceramic membranes for selective oxygen separation, electrochemical oxygen sensors and heterogeneous catalysts.

In this work special emphasis is put on the Cr/Si-tolerance of $La_2NiO_{4+\delta}$, which is an important property for SOEC and SOFC air electrodes when applied in stacks containing metallic interconnects or glass sealings. Electrochemical properties of bulk samples are determined between 700 °C and 800 °C in synthetic air over a period of several thousand hours in the presence of a Cr-source in dry and humid atmospheres.[2] Moreover, symmetrical cells with porous $La_2NiO_{4+\delta}$ electrodes are prepared and the effect of Cr-poisoning on electrode performance is investigated both under anodic and cathodic polarization.[3] Degradation processes are continuously monitored by different experimental techniques such as conductivity relaxation measurements, current voltage analysis and impedance spectroscopy. Extensive analytical investigations are performed at several stages of the degradation process by SEM, TEM and XPS in order to determine the deposition and distribution of contaminants as well as to identify the composition of secondary phases.[4] The analytical findings are correlated with results from electrochemical measurements allowing the identification of potential degradation mechanisms.

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OTM performance optimization for oxyfuel applications by catalytic layer functionalization

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Keywords: dual-phase, composite, oxyfuel, optimization, surface modification, infiltration, oxygen permeation, ceramic membrane

Material stability along with performance is the most critical issues when Oxygen Transport Membranes (OTMs) are exposed to CO_2&SO_2-containing oxyfuel atmospheres. Under such conditions the typical mixed ionic-electronic materials used as OTMs are neither chemically nor mechanically stable. Nevertheless, recent investigations conducted on composite materials have demonstrated a good behaviour and performance of these when exposed to oxyfuel environments[1]. Amongst these materials, one of the most interesting is the dual-phase material with composition 60% Fe_2NiO_4 – 40% $Ce_{0.8}Tb_{0.2}O_{2-}\delta$ (NFO-CTO), showing an outstanding stability and a promising performance[2]. However, the obtained oxygen fluxes should be improved in order to meet the techno-economic targets.

Since oxygen permeation becomes limited by surface exchange reactions, especially at low temperatures and when reducing membrane thickness, it is possible to achieve an improvement in oxygen fluxes by surface modification. One of the most considered options is the addition of porous layers on membrane surfaces, thus allowing the enhancement in surface exchange reactions rates mainly due to the increase of surface specific area. A membrane presenting a larger active area also presents a higher number of active sites for oxygen reactions and a higher TPB length, and therefore, more sites available for O_2 molecules to be incorporated/released to/from membrane. However, the performance of these systems will remain limited by the oxygen reaction kinetics involved in the oxygen dissociation/recombination and adsorption processes. Therefore, by using suitable elements presenting redox character and adsorption properties these reactions can be boosted and thus, the oxygen permeation can be improved. Several oxides containing some lanthanides and metals meet these requirements.

Therefore, it has been considered the catalytic activation of NFO-CTO porous backbones with different elements by capillary infiltration. A first screening of the activated cases has been done by Electrochemical Impedance Spectroscopy, studying their performance under representative oxyfuel environments. The most interesting cases were later studied in oxygen permeation tests, obtaining up to 6-fold $J(O_2)$ improvements at 850 ºC with respect to the not activated case.

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Microstructural and phase evolution of atmospheric plasma sprayed manganese cobalt iron oxide protection layers in solid oxide fuel cells

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Keywords: SOFC, MCF, APS, protective coating, self-healing, $Mn_{1,0}Co_{1,9}Fe_{0,1}O_4$

Chromium containing steels are widely used as interconnects in solid oxide fuel cell stacks (SOFCs) because of their advantageous mechanical and electrical properties. The major drawback of this material is the evaporation of chromium containing species at the high SOFC operation temperatures, which lead to a strong degradation of commonly used cathode materials. Covering the interconnect's surface with a protection layer enables a strong reduction of the chromium related degradation. The use of dense layers of atmospherically plasma sprayed (APS) $Mn_{1,0}Co_{1,9}Fe_{0,1}O_4$ (MCF) showed remarkably low degradation rates within operated stacks in Jülich. Although the stacks show good performance, the APS-MCF layers undergo strong changes that are just partially described in literature,[1,2] but not fully understood yet. This study analyses the microstructural evolution and phase changes of APS-MCF layers within samples tested for annealing times of up to 10.000 hours and also within components of test stacks operated at JÜLICH. A crack healing effect is observed by annealing in air at low temperature of 500 °C. Measurements with X-ray diffraction, wet chemical analyses and thermo gravimetry support a theory describing this effect by a volume expansion that is induced by an oxidation process of the plasma sprayed MCF. Air leakage measurements reveal a strong increase of gas-tightness providing increased chromium retention. Annealing at higher temperatures of 700 °C to 850 °C leads to a segregation and a phase separation observed in electron microscopic images. Oxidation driven diffusion of Cobalt ions to the layer's surface build up a dense Co_3O_4 layer in a spinel crystal structure. This layer decelerates further oxidation of the coatings bulk. Combining these results with the performed long-term annealing tests can provide lifetime predictions of APS-MCF protective layers. Thereby a reduction of the cathode related degradation can be achieved.

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$La_{0.5}Sr_{0.5}Fe_{0.7}Ga_{0.3}O_{3-\delta}$ perovskite membrane produced by electrophoretic deposition process

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Keywords: perovskite membrane, electrophoretic deposition, oxygen semi-permeation flux, surface exchanges

Mixed ionic and electronic conducting materials with perovskite structure are of great interest for their potential application as membrane materials for oxygen separation applications.[1] However, considering industrial applications, membranes must meet several criteria: good chemical stability, suitable mechanical properties under a wide range of oxygen partial pressure at high temperature and good compromise between cost and oxygen semi-permeation fluxes (≈ 10^{-1} mol.m^2.s^{-1} at 900 °C).

The first step to improve the oxygen semi-permeation is the identification of the oxygen transport rate determining step. It depends mostly of the membrane chemical composition. Then, it is possible to increase the oxygen flux through the membrane, with the elaboration of appropriate membrane architecture. If oxygen flux is limited by surface exchange kinetics, surface properties (microstructure, chemistry, …) must be modified.[2] Numerous solutions are reported in the literature, as the coating of porous layer obtained by screen printing, or dip-coating, but also electrodeposition in the SOFC field[3]… If oxygen flux is limited by bulk diffusion, the thickness of the membrane is the most important parameter.

Oxygen permeation through $La_{0.5}Sr_{0.5}Fe_{0.7}Ga_{0.3}$ membrane is limited surface exchange kinetics. The goal of this work is to increase surface kinetics by a deposit a thin layer of $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}$. In addition to the chemical effect of cobalt containing perovskite, small grains size will be used to increase even further the surface kinetics ($d_{50} = 0.4$ µm). The deposit will be realized by an electrophoretic deposition process.[4]

Electrochemical performances of membranes have been measured using a specific device developed jointly between SPCTS and LEPMI (Grenoble). This device gives access in a single measurement to oxygen semi-permeation flux, oxygen diffusion coefficient and surface exchanges kinetics at both surfaces of the membrane.

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Overview of the electrical properties of yttrium-doped strontium zirconate as a proton-conducting component in high-temperature electrochemical devices

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Keywords: protonic ceramic cells, yttrium-doped strontium zirconate, mixed ionic-electronic conduction properties

Proton-conducting ceramic materials may be used for efficient production of pure, dry hydrogen by steam electrolysis in a high temperature range, 600–900 °C.[1] However, much investigation of the transport properties under a relevant range of conditions is still needed for development of promising devices such as protonic ceramic fuel cells (PCFCs) and protonic ceramic electrolyser cells (PCECs). $SrZrO_3$-based perovskites have emerged as strong PCEC electrolyte candidates due to their good chemical and mechanical stability. In this work yttrium-doped strontium zirconate ($SrZr_{0.9}Y_{0.1}O_{3-}\delta$) was synthesised by solid-state reaction following the ceramic method and sintered in the range 1300-1600 ºC with and without the addition of minor contents of Zn as sintering additive. The microstructural components of electrical transport such as grain and grain boundary were carefully studied in dry and wet O_2, revealing a clear effect from the sintering conditions.[2] The addition of Zn and lowering the sintering temperature improved the grain and grain boundary transport processes considerably. The ionic and electronic contributions to the electrical transport were also analysed under wet and dry oxidising and reducing conditions by impedance spectroscopy and by a modification of the electromotive force methodology.[3] All the samples exhibited a p-type electronic contribution under oxidising conditions with a dominant protonic contribution for higher values of pH_2O; oxide-ionic conductivity was negligible in wet atmospheres. Protonic transport numbers close to unity were obtained under highly reducing conditions in the temperature range 600–700 ºC for $pH_2O \approx 0.023$ atm, with an increasing n-type contribution exhibited for higher temperatures and lower humidifications.

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Chemical stability of ceramic dual-phase membrane materials for H_2-separation in water-gas shift reactors

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Keywords: dual-phase materials, mixed electronic protonic conductors, H_2 membrane, high-temperature WGS

Hydrogen can be produced by gasification of solid fuels with subsequent water gas shift (WGS) reaction to oxidize the produced carbon monoxide with steam to carbon dioxide while the steam is reduced to hydrogen. The separation of carbon dioxide using conventional techniques like physical or chemical absorption leads to high efficiency losses. In contrast, a membrane reactor containing a catalyst provides the opportunity for significantly reduced efficiency losses. The high efficiency is realized because the catalytic membrane reactor combines the two process steps of water gas shift reaction and gas separation into a more efficient single step process. The gas separation is realized by hydrogen selective membranes. The continuous removal of hydrogen provides an additional advantage because it shifts the reaction equilibrium to the product side. The WGS reaction is exothermic and the equilibrium conversion is very limited at temperatures above 450 °C but the reaction kinetics is strongly promoted in the high temperature range. As a consequence, integration of high temperature highly-permeable hydrogen membranes into the WGS reactor will enable the operation at high space velocities.

Ceramic materials gained more and more importance for the application in WGS reactors as mixed protonic-electronic conducting membrane materials. These materials offer high selectivity and are stable at temperatures of 600 °C and above. However, the aggressive gas compositions in a gasification plant, containing not only CO, CO_2, H_2, and H_2O but also inorganic contaminants from the gasified fuel, leads to very challenging conditions for the dense H_2-selective membranes. Therefore, suitable membrane materials are required not only to provide high H_2-flux but also to be stable under operating conditions.

This work deals with the development of respective membrane materials. Therefor dual-phase membranes of the type $BaCe_{0,8}M_{0,2}O_{3-\delta}$:$Ce_{0,8}M_{0,2}O_{2-}\delta$ (M=Y, Yb, Eu, Sm, Tb, Gd) were synthesised. The sintered samples were first characterized via Inductively Coupled Plasma – Atomic Emission Spectroscopy, X-Ray Diffraction and Scanning Electron Microscopy.

Besides the particle size, the thermal expansion coefficient and the conductivity in different atmospheres were measured. Subsequently, the materials were exposed to two different coal-gasification-related atmospheres (CO- and CO_2-rich streams) at 600–900 °C and afterwards investigated regarding chemical reactions of the two contained phases via XRD.

Although the materials show a very promising hydrogen flux, the chemical stability under membrane reactor conditions up to 900 °C is rather limited and leads to challenges with regard to finding more stable materials.

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Phase equilibria modelling in Bi-Sr-Co-O system involving phases with variable oxygen stoichiometry

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Keywords: phase diagram, mixed oxides, thermoelectric materials, oxygen stoichiometry

High-temperature thermoelectrics are mainly represented by transition metals mixed oxides including cobaltites. In this contribution, high-temperature phase equilibria of the partly open Bi–Sr–Co–(O) system with fixed oxygen activity, $p_{O2}/p^0 = 0.21$ ($p^0 = 101.3$ kPa), were modelled based on the experimentally determined phase diagram. Samples with different Bi : Sr : Co ratios were prepared by solid state reaction and analysed by X-ray diffraction to map the thermodynamically stable quasiternary phases and their fields of stability. For the assessment, we also used the previously reported thermodynamic data and phase equilibria for the quasibinary Bi–Co–(O), Sr–Co–(O) and Bi–Sr–(O) subsystems as well as the thermodynamic data of quaternary phases assessed from calorimetry, thermogravimetry and high temperature phase equilibria. Namely, the oxide melt is modelled based on the Redlich-Kister parameters of the corresponding quasibinary systems and the solid oxides such as the misfit phase $Bi_2Sr_2Co_{1.85}O_x$, tubular phase $Bi_{3.7}Sr_{11.4}Co_8O_x$, superconducting cuprate analogue $Bi_2Sr_2CoO_{6+\delta}$ and tetragonal 121 type phase $Bi_{0.4}Sr_{2.6}CoO_{5-\delta}$ are considered as stoichiometric concerning the cation composition, their heat capacity and entropy is determined from calorimetry (PPMS, DSC, drop calorimetry) and the enthalpy of formation is refined to reproduce their melting behaviour. The variable oxygen stoichiometry is described by fitting the partial molar enthalpy and entropy of oxygen on the thermogravimetry data. The constructed phase diagram is particularly important for designing the experiments of single crystal growth of these highly significant cobaltites.

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Effects of substrate contamination of photocatalytic TiO_2 thin films

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Although there are many reports of the fabrication and performance of photocatalytic TiO_2 thin films, there are relatively few reports of the effects of contamination from the substrates. The present work reports data for TiO_2 thin films spin coated on four different substrates that were annealed at 200°, 350°, 450°, or 550 °C for 8 h in air. The substrates used were soda-lime-silica (SLS), sodium borosilicate (SBS), fused silica (FS), or single crystal TiO_2 (T). Characterisation and testing consisted of glancing-angle X-ray diffraction (GAXRD), laser Raman microspectroscopy, atomic force microscopy (AFM), UV-VIS spectrophotometry (UV-VIS), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and methylene blue (MB) degradation.

The recrystallisation temperature of anatase depended on the type of substrate, where the films deposited on SLS were essentially amorphous at 200° and 350 °C, those deposited on SBS and FS remained amorphous only at 200 °C, and those deposited on T were crystalline at all temperatures. The XPS and SIMS data indicated that these results were due principally to the effects of the extent of sodium contamination. At the highest annealing temperature of 550 °C, the contaminants detected by XPS and SIMS were as expected: Na, Mg, Ca, and Si from SLS; Na from SBS (boron was not detectable by these techniques); Si from FS; and none from T. All of the films had consistent thicknesses of ~370 nm and transparencies in the range 70-80%. For the crystalline films, the grain sizes and surface roughnesses increased slightly (~5%) and the optical indirect band gaps decreased consistently from 3.59 eV to 3.47 eV with increasing annealing temperature. The photocatalytic performances were linked directly to the Na contamination level rather than the Si level, giving performances of the crystalline films annealed at all temperatures in the order T > FS > BS > SLS. XPS data before and after MB testing revealed that the contaminants were located on the grain boundaries and were washed out during the testing. Consequently, the effect on the band gap was an artifact of the alteration of the nanostructure and hence the performance was dependent on blockage of the active sites by the diffused contaminants.

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Development of all-oxide thermoelectric stacking device

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Keywords: processing, oxides, thermoelectric device

Due to high stability, environmental friendly impact and reasonable cost, oxides are interesting for thermoelectric devices for energy conversion at high temperature. Besides the advantages, oxides have challenges due to efficiency and processing. The efficiency of a single TE material is described by the ZT or figure of merit, which includes Seebeck coefficient, electrical and thermal conductivity. An all-oxide thermoelectric device (Fig. 1) contains an n- and a p-type conductor separated by an insulator. The direct p-n junction is the crucial part of the device having the same function as the metal current-collector being the limitation for high temperature applications for conventional devices.

Development of this new device design requires improved efficiency of the oxide materials through designed microstructure followed by an advanced ceramics processing approach. For our all-oxide device, we have selected $Ca_{0.932}MnO_3$ (CMO), $Ca_3Co_4O_9$ (CCO) and $LaAlO_3$ (LAO) as n-type, p-type and insulator materials respectively, based on coefficients of thermal expansions. Each of these three oxides were synthetized and sintered using spray pyrolysis and spark plasma sintering (SPS). The all-oxide thermoelectric device was developed using aqueous tape casting followed by co-sintering using SPS. Power output and efficiency of the device were recorded from 700 to 800 °C in air. We observed reaction layer at the p-n junction. Chemical stability and compatibility of the three materials are discussed. The work will report on the fabrication of the TE materials and device with their TE properties.

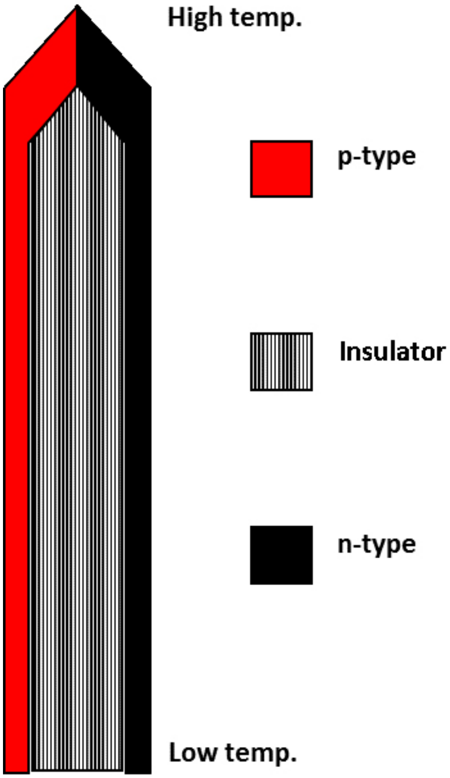

Fig. 1. A single pair of thermoelectric device

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The photoluminescent properties of rare-earth $Sm_{1.90}Eu_{0.10}Zr_2O_7$ zirconate pyrochlore

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Keywords: rare-earth zirconate pyrochlore, solid-state reaction, Eu^{3+}

Rare-earth zirconate pyrochlore materials have a chemical form of $A_2B_2O_7$, where a trivalent rare-earth occupy the A site and Zr occupies the B site ($RE_2Zr_2O_7$). They have complex crystal structures having a variety of physical and chemical properties as well as stability in extreme environments. These materials have been used as high-temperature thermographic phosphors because of their intense light emission and high-temperature stability[1]. They also exhibit excellent ionic conductivity and high tolerance to defects[2]. In this research, the zirconate type pyrochlore was chosen and synthesized by high temperature solid state reaction method under open atmosphere. The phase formation process was investigated by thermal analysis (DTA/TG) until 1600 °C. The X-ray diffraction (XRD) analysis resulted as the cubic phase structure with lattice parameters $a = b = c = 10.59$ Å and $\alpha = \beta = \gamma = 90°$. The rare-earth based zirconates, $Ln_2Zr_2O_7$ (Ln = Tb→Lu), with the ionic radius ratio, ranging from 1.44 to 1.35, crystallize in a defect-fluorite structure. Compounds $Ln_2Zr_2O_7$ (Ln = La→Gd), with the ionic radius ratio, ranging from 1.61 to 1.46, adopt the cubic pyrochlore structure[2]. At high temperature (T>1500 °C), $Ln_2Zr_2O_7$ (Ln = Nd→Gd) undergo an order–disorder transition from a pyrochlore to a defect-fluorite structure. The transition temperature depends on the nature of the rare-earth ion. Therefore, rare-earth zirconate exists only in the pyrochlore form, whereas for neodymium, samarium, and the gadolinium zirconates, a transition from a pyrochlore to a defect-fluorite structure occurs at 2300, 2000, and 1530 °C respectively[3]. The photoluminescence (PL) analysis including excitation, emission and decay time were determined by a PL spectrometer under room temperature. The sample was excited at 286 nm that is based on ligand-to-Eu^{3+} charge-transfer transitions (LMCT). The pyrochlore have emissions at 486 nm, 614 nm, 663 nm and 718 nm concerning the typical $^5D_2 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions of the Eu^{3+}-ions, respectively[4].

Acknowledgement
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Functional layers for solid oxide electrolyzers

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Keywords: solid oxide electrolyzer, functional layer, distribution of relaxation times, impedance spectroscopy

In order to increase efficiency of solid oxide electrolyzers, it is necessary to reduce electrode area specific resistances. To minimize, electrode losses, a layered cell structure is proposed, which implements thin interface layers on oxygen electrode side. This work is aimed to study how the functional layers influence the ASR of an oxygen electrode /electrolyte interface. To understand the polarization processes and their dependences on operational and material parameters, the electrochemical impedance spectroscopy (EIS) is widely used. However, a typical analysis of the spectra requires a priori assumptions of equivalent circuit. An alternative method for analyzing impedance spectra using distribution of relaxation times (DRT) is applied. In this approach each process is represented by a peak in the distribution function. The peak is characterized by relaxation frequency, area (polarization resistance) and the characteristic shape, bearing information about the electrochemical process. This allows better understanding the impact of applied functional layers.

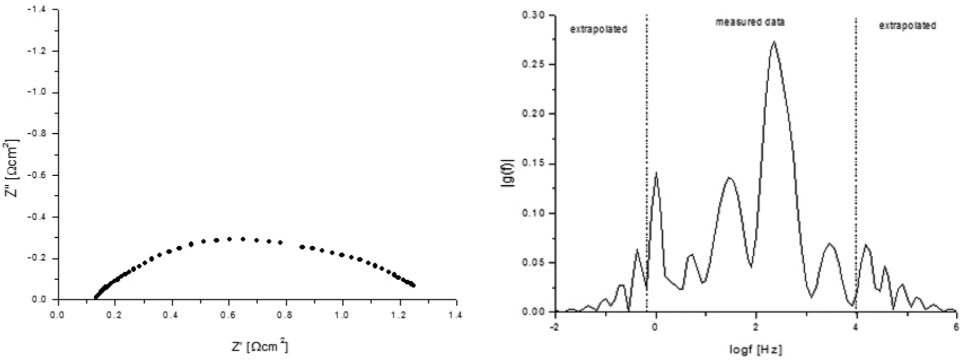

Fig. 1. Example of impedance spectrum and its corresponding DRT plot

Acknowledgement

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Mechanical properties of porous Ni(O)-YSZ solid oxide cell supports with varying Y-content

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Keywords: solid oxide cell support, Ni(O)-YSZ, strength, yttria content

Enhancing the cell strength is essential for the robustness of solid oxide cell (SOC) technologies, especially when enlarged footprints and taller stacks are needed for large-scale installations. Yttria stabilized zirconia with different stabilizer contents (3YSZ, 8YSZ) forms the structural component in most SOC cell designs. The tetragonal to monoclinic phase transformation that may occur during crack growth in 3YSZ at room temperature strongly improves its fracture toughness compared to fully stabilized cubic 8YSZ. For the SOC technology, however, it is necessary to consider effects of high temperature processing and operating conditions, as this will affect the tetragonal phase stability and transformability.

In this work, the possible improvement of the mechanical properties of SOC supports by lowering the stabilizer amount in Y-doped zirconia was studied. Four different Y contents were considered (2, 2.3, 3 and 8) and the phase stability of nanocrystalline powders with temperature and after heat treatment at 1350 °C was investigated. The results showed that a significant amount (95%) of tetragonal phase can be maintained in the 2.3Y powder even after 2h calcination at 1350 °C, whereas only 28% remains in the 2Y sample. Besides the phase stability results, fracture strength of porous Ni(O)-YSZ supports prepared using the powders both at room and high temperatures are reported.

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Long-term degradation study of anode supported flat-tubular solid oxide fuel cells

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Keywords: SOFC, current density, degradation, ASR, particle coarsening

Degradation investigation and life time prediction are crucial factors in improving durability of solid oxide fuel cells (SOFCs). We have investigated the effect of applied current density on the long-term degradation of anode supported flat-tubular SOFC. The flat-tubular SOFC was comprised of nickel oxide (NiO)-8mol%.Y_2O_3-stabilized ZrO_2 (8YSZ) anode support, NiO-Sc_2O_3 stabilized ZrO_2 (SSZ) anode functional layer (AFL), SSZ electrolyte, Gd_2O_3 doped CeO_2 (GDC) interlayer and $(La_{0.60}Sr_{0.40})_{0.95}Co_{0.20}Fe_{0.80}O_{3-x}$ (LSCF)-GDC composite cathode. Performance degradation in terms of voltage loss was evaluated during long-term operation up to 1000 h at constant current densities of 200 and 1000 $mAcm^{-2}$ at 800 °C. Electrochemical impedance spectroscopy (EIS) was performed to examine the cell polarization during long-term operation. The flat-tubular SOFC tested at high current density showed high performance degradation due to large increase in cell polarization during operation. In combination to EIS, the backscattered scanning electron microscopy results revealed that higher Ni particle coarsening and reduction of triple phase boundary length in the AFL of cell tested at high current density led to the fast performance degradation.

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Improvement of solid oxide fuel cell performance by tailoring the electrolyte-electrode interface using laser micro patterning

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Keywords: laser ablation, laser patterning, SOFC, interface, YSZ, LSM

The aim of this work is to increase the power density but also reducing size, weight and cost of Solid State Fuel Cell (SOFC) systems by the use of laser surface processing techniques. By modifying the electrolyte surface at the mesoscale, the cell power density will be improved.[1] Increasing surface corrugation directly produces an enlargement in the effective interface area between the electrode and the electrolyte. Laser processing also produces a nanoparticle coating which is deposited on the surface, generally of the same composition but different microstructure. The initial objective is to study these effects as a function of the processing parameters and surface composition, and also to demonstrate the power enhancement associated to the interface modification.

The experimental studies were performed using commercial YSZ (yttria stabilized zirconia) plates of about 150 µm in thickness, using a Q-switched diode-pumped laser (Rofin PowerLine S3 SHG) emitting at 532 nm wavelength. The currently processed area is about 60×60 mm^2. The experiments were performed using the minimum pulse width of the laser source (5 ns) in order to enhance material evaporation processes minimizing thermal effects.[2] Processing parameters such as laser power, laser focalization, machining mode (percussion, scanning,…), processing temperature and atmosphere will be experimentally determined as a function of surface parameters such as wide, depth, shape, distance between grooves, damage produced in the processed material, changes in microstructure, laser plasma plume effects, nanoparticle surface dressing, etc. Preliminary studies show groove sizes and depths in the range of 5 to 30 microns, which are in the desired patterning range.

Symmetrical cells, using LSM (lanthanum strontium manganite)/YSZ cathodes were fabricated. Electrochemical Impedance Spectroscopy (EIS) measurements were then performed on both non-machined and corrugated samples. The polarization resistance of the corrugated samples is decreased by at least 30% in comparison with the non-machined samples, measured at temperatures between 600 and 900 ºC.

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Mechanical characterisation of multi-layered ceramic systems for SOC

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Keywords: Solid Oxide Cells, mechanical properties, layered structure, cell, mechanical testing

Solid Oxide Cells technology promises to revolutionise the energy market; however, its reliability and efficiency have to be further improved. SOCs operate in harsh conditions and have to withstand considerable static and cyclic stresses, both mechanical and thermal. Thus, their mechanical stability is threatened. One fundamental aspect is the structural integrity of the cell. In fact, mechanical failure of a single cell can damage the whole stack, reducing the lifetime and the efficiency of the entire system.

This study is targeted to the ceramic layered structure of an Yttria-stabilised electrolyte supported cell. Its mechanical characterisation has been performed through destructive and non-destructive techniques (three-point bending test, impulse excitation technique, tensile test).[1] Many literature sources deal with properties of the most common electrolytes and electrodes,[2–4] yet co-sintering effects and interaction between layers are up to now not well understood. In this contribution the overall behaviour of the cell has been investigated, focusing on the role that the interface between layers plays in the changing of resulting mechanical properties. To investigate the mentioned aspects, layers were added to the electrolyte one by one. This way, individual interactions could be distinguished with the help of numerical simulations. Results obtained for consecutive samples through different techniques have been compared and discussed.

Acknowledgements

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Screen printed cathode layers with enhanced adhesion through plasma-modification of substrates surface

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Keywords: screen printing, wettability, SOFC, cathodes

Manufacturing of cathode layers in Solid Oxide Cells, requires high temperature sintering step in air (>1050 °C). For advanced SOC architectures like Metal Supported Cells, functional ceramic layers are processed directly onto a porous metal substrate, and those harsh conditions for the cathode sintering cause destruction of the metallic component. In this study, we report a vacuum plasma surface method to assist the screen printing of cathodic layers with improved adhesion at lower sintering temperatures for metal-supported fuel cells. A vacuum plasma treatment was used to chemically activate/etch the gadolinium-doped ceria (CGO) substrate to improve its wettability towards the screen printing cathodic inks. The plasma parameters such as vacuum level, Ar/O_2 flow, system power, number of plasma treatments, were optimized in order to modify the CGO surface in terms of surface energy and roughness. Scratch tests results highlight that the critical load of the sintered cathodic films is enhanced by the 50% exploiting a plasma surface treatment.

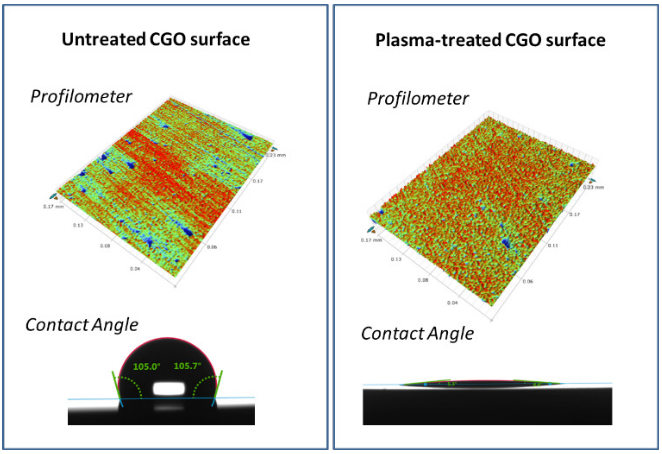

Fig. 1. Effect of the plasma treatment of CGO substrates on the surface roughness and wettability

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Recent findings on the selective thermal emission of Al_2O_3-YAG:eR solidified eutectics

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Keywords: directionally solidified oxide eutectics, selective thermal emitters, Al_2O_3, Er:YAG

Al_2O_3-Rare Earth Garnet directionally solidified eutectics (DSE) are candidate selective emitters for thermophotovoltaic (TPV) devices, by virtue of their good mechanical properties, microstructural stability at high temperatures, good thermal shock resistance and their selective thermal emission provided by the rare earth ions.[1] With the appropriate rare-earth garnet, emission bands matched to the optimum absorption of the photovoltaic cells can be chosen, and in particular $Er_3Al_5O_{12}$ has one band centred at 1.5 µm, suitably matched to InGaAs or GaSb cells.

DSE oxides can be solidified by different procedures as Bridgman, micro-pulling down or laser floating zone (LFZ) method. They can also be prepared in the form of dense solidified coatings on different substrates, thereby allowing manufacture adapted to the TPV device. As the solidified composite ceramic is translucent, its emissivity will be a volume property and light scattering can affect the thickness contributing to emission as well as its selectivity. Previous studies show that thermal emission of Al_2O_3-$Yb_3Al_5O_{12}$ eutectics[2] appears to saturate at high temperatures (1500 ºC). Here we aim at shedding light on the mechanisms responsible of this behaviour, as well as quantifying the scattering.

For that purpose we have prepared Al_2O_3-$Y_{3-x}Er_xAl_5O_{12}$ (x = 0.03, 0.3, 3) eutectics with different microstructural sizes in the form of 1mm diameter rods (by LFZ) and of flat, surface resolidified plates (using surface laser melting). We have measured the emissivity at RT on the flat plates. Specific emissivity obtained from RT measurements is mainly proportional to the Er concentration of the material. The experiments show that the emissivity at 1540 nm is already saturated for 600 µm thick samples irrespective of the Er concentration or solidification rate (coarse or fine microstructures).

The thermal emission has been measured in rods and plates, that is, heating the samples with a CO_2 laser or with electrical resistance heating respectively. Each method allows different temperature ranges. The selective emission in the NIR (bands at 970 nm and 1540 nm) in the diluted samples (x = 0.03 or 0.3) increases with temperature only slightly slower than the black body (BB) radiation in all the temperature range (700 ºC to 1600 ºC), while for the fully concentrated one, the selective emission above 1300 ºC is only slightly temperature dependent, thus deviating much faster form BB behaviour. Aided by available data and ad-hoc luminescence lifetime measurements in diluted and concentrated garnets, plausible explanations for this effect will be given and discussed.

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Synthesis, structure and electrical properties of Pr, Co-doped $SrTiO_3$ novel SOEC cathode material

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Keywords: syngas, perovskite, SOEC

Solid Oxide Electrolyzer Cells (SOECs) are very promising electrochemical devices for the production of syngas (H_2/CO) by H_2O and/or CO_2 electrolysis. The understanding of degradation processes of fuel electrode in the solid oxide electrolysis cell (SOEC) occurring during syngas production is crucial. Particular attention should be paid to the processes taking place in extreme conditions - high current density and high concentration of steam and carbon dioxide. Thus a new alternative, to the widely used Ni/YSZ, cathode materials should be found and widely investigated. The impact of the microstructure of the new cathode material on its electrical properties has a great influence on performance and stability of the cell producing synthesis gas, operating under heavy load.[1,2]

Donor and acceptor co-doped $SrTiO_3$ ceramics are known to exhibit phase stability under both oxidizing and reducing conditions. High electrical conductivity can be obtained by reduction at high temperatures and low oxygen partial pressures.[3,4]

Perovskite-like $Pr_{1-x}Sr_xTiO_{3-\delta}$ material attracted attention as a potential anode material for SOFC or cathode materials for SOECs. A high electronic conductivity under reducing atmosphere (~100 S/cm at 800 °C and 10^{-20} atm. pO_2) is reported for 20 mol% of Pr in $SrTiO_3$.[5] Co-doped $SrTiO_3$, was reported to have a very good performance as anode materials for SOFC and cathode material for SOEC. The Co acceptor doping on the B site of $SrTiO_3$ can significantly change the defect formation and charge compensation mechanisms, thus altering the electrical conduction behavior, especially the ionic conductivity and the catalytic activity.[6]

In the present study, Pr and Co-doped $Pr_xSr_{1-x}Ti_yCo_{1-y}O_{3-\delta}$ material is proposed as an SOEC cathode material. In the investigated powders, the constant 7 mol% (y = 0.07) of Co acceptor dopant amount and the various Pr donor dopant amount x = 0.1–0.3 was used in investigated samples. The powders of these were prepared by a solid-state reaction (SSR) process. The structure and morphology of obtained samples was analyzed by the X-ray diffraction technique (XRD) and scanning electron microscopy (SEM). The relative length change was examined by Netsch DIL 402 PC/4 dilatometer in temperature range from 25 ^oC to 800 ^oC while the thermal stability of samples was examined via Termogravimetry with Differential Scanning Calorimetry (TG-DSC) using Netsch STA449F1. In order to analyze the electrical properties and the possibilities to use of these materials in SOEC cathodes, the total electrical conductivity of samples was measured by DC 4-wire method in range of 500–850 °C in different gas conditions (H_2 and O_2 atmospheres). The obtained results were discussed and analyzed in comparison to the previous literature reports.

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Non hydrophobic CNT/mesoporous carbon monolith as high energy performance flow through electrodes in CDI process

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Keywords: capacitive deionisation, mesoporous carbon, carbon nanotube, energy storage and recovery

Capacitive deionization (CDI) is an energy-efficient procedure for water desalination, using ion absorption by forming electrical double layers on the surface of nano porous carbon based electrodes[1,2]. In the cell structure known as flow-through CDI, the electrodes are clamped together and the feed water flows through electrodes and the separator. These all result in CDI performance enhancement[2].

Mesoporous carbon (MC) monoliths, used as CDI electrodes were synthesized with hierarchical porosity by a hydrothermal based process. The samples were carbonized under N_2 at 600 to 900 °C. In the case of synthesizing MC/CNT monoliths, 0.5 to 2 W% multiwall carbon nanotubes were added to the solution exactly before transferring to the autoclave. The sample's microstructure, investigated by FESEM, showed interconnected uniform macro pores which acted as suitable paths for the flowing electrolyte. Furthermore FESM studies demonstrated well distribution of CNTs in the monolith matrix. Mercury porosimetry also confirmed hierarchical macro pore structure with size range of 5 to 15 µm. N_2 absorption analyses by BET and BJH methods indicated total specific surface area of about 600–700 m^2/g ,total pore value of 0.45 m^3/g and pore size distribution of 1–5 nm. The electrochemical tests of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out by a three electrode setup. Electrodes conductivity and specific capacitance increased by increasing CNT content. This trend was more obvious for the samples calcined at low temperature so that for the samples calcined at 600 °C, electrical conductivity raised about 20 times. By increasing carbonization temperature the electrical resistance reduced sharply, though specific capacitance did not increase proportionally, as these electrodes became highly hydrophobic. In this regard the electrolyte could not pass through the 900 °C samples; so despite of high electrical conductivity and high porosity these electrodes did not perform efficiently in the flow through CDI process.

The most proper electrodes with suitable electrical conductivity and water permeability, were set in a designed flow through CDI cell and different voltages were applied in order to measure cell parameters. Highest charge and discharge current of 250 mA, cell capacitance of 4 F, specific capacitance of about 80 F/gr, 1.2 mg NaCl per g electrode per min, charge efficiency of 0.85 and ion absorption of 10 mg/g, were achieved. To increase energy efficiency, the discharge current was stored in a battery which had the duty of supplying the charge step energy. The primary energy of the battery was provided by a solar panel.

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Preparation and mechanical properties of $SrTi_{1-x}Fe_xO_{3-\delta}$ (x = 0.25, 0.35, 0.5) for oxygen transport membranes

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Keywords: oxygen transport membrane, tape casting, freeze casting, fracture strength

Oxygen transport membranes (OTM) based on mixed ionic-electronic conducting ceramics allow oxygen ion diffusion through the lattice and, therefore, can be used to separate gases at elevated temperatures.[1] These membranes can achieve a remarkable competitor of existing state-of-the-art processes for oxygen production in small and medium scale.[2] Typically, such membranes have to be operated at 800–900 °C and under large pressure gradients, which challenges significantly chemical and mechanical stability of the respective brittle ceramic components.[3,4] In order to increase transport, advanced membrane modules that enable high-performance rely upon an asymmetric design consisting of a thin dense membrane layer supported by a porous substrate, where the substrate warrants the long term reliability of the mechanical integrity at process conditions.

Thus, the current work concentrates on the preparation and mechanical characterization of promising mixed conducting oxygen transport perovskite based membranes,[5,6] based on $SrTi_{1-x}Fe_xO_{3-\delta}$, (STF-$X$) with $x = 0.25$, 0.35 and 0.5. The materials were synthesized through solid state reaction process and most mechanical testing relevant dense and porous specimens were obtained by tape casting, where the mechanical stability of porous tape cast specimens was assessed via ring-on-ring bending tests serving the estimate of materials' reliabilities.

Furthermore, aiming towards an optimization of the oxygen permeation flux and mechanical stability of the supported membranes, hierarchically porous specimens were successfully obtained by freeze drying, where complementary systematic investigations of the mechanical stability aim towards a determination of the influence of the complex pore structure on the mechanical properties. Overall, the current study aids to adjust the membrane support structure regarding the process requirements. At the same time, data for mechanically derived lifetime and reliability predictions is acquired for STF based membranes.

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Development of advanced electrodes by metal oxide impregnation for microtubular solid oxide fuel cells

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Keywords: SOFC, microtubular, anode-supported, infiltration, praseodymium oxide

Microtubular Solid Oxide Fuel Cells (mT-SOFC) have attracted special interest as they are more resistant to thermal cycling and they present shorter start-up/shut-down times and higher volumetric power densities in comparison to those with the traditional planar geometry.

Standard NiO-YSZ (yttria stabilized zirconia) anode tubes used in our laboratory are fabricated by extrusion of NiO, YSZ and pore former powders, followed by dip-coating of the YSZ electrolyte. Both components are then co-sintered at 1500 ºC. Typical oxygen electrodes such as LSM (lanthanum strontium manganite)/YSZ are deposited by dip-coating and sintered at 1150 ºC.[1]

In order to increase fuel cell performance, infiltration/impregnation (generally by means of nitrates) of nanocatalyzers has been established as an important method in the development of high performing electrodes, improving their oxygen reduction or fuel oxidation properties. Infiltration can enhance the catalytic activity (via fine dispersed particles), and ionic and/or electronic conductivity (via connected particles) of fuel cell electrodes leading to a cell power enhancement.[2]

In the present work, different amounts of praseodymium oxide were impregnated into the cathode of Ni-YSZ/YSZ/LSM-YSZ anode supported microtubular cells. The fuel cell performance enhancement compared to the non-infiltrated standard was very significant, as about the same current density was obtained (above 1 A cm^{-2} at 0.5V) but lowering the operation temperature 100 ºC (800 ºC for a standard cell and 700 ºC for the Pr_6O_{11} infiltrated cell). Experiments under electrolysis mode as well as durability studies are currently being performed.

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Mixed glass former effect on ionic conductivity of lithium borophosphate glasses with So_3 addition

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Keywords: lithium-ion batteries, solid electrolyte, borophosphate glasses, ionic conductivity, mixed glass former effect

High-performance and smaller electronic devices have become a part of everyday life. In this regard, the studies about batteries focus not only on performance enhancement, but also on the utilization safety. In portable consumer electronics, generally Lithium-Ion Batteries (LIB) are used due to their promising properties such as high energy density and high cycle capacity. Glass and glass-ceramic solid electrolytes have significant advantages over liquid ones since they do not have inflame and/or explosion risk and not require separator integration.

Mixing glass formers has been reported as an effective way to increase the ionic conductivity of certain glass electrolyte systems.[1] Besides, there are several studies that suggest using SO_3 may increase the ionic conductivity of alkali phosphate ternary glass system up to two orders of magnitude.[2] However, the combination of these approaches has not been examined yet. This study aims to enhance the ionic conductivity of $40Li_2O.10SO_3.xB_2O_3.(50-x)P_2O_5$ quaternary glass electrolyte composition via mixed glass former effect and SO_3 addition. Glass compositions that contain different B_2O_3 ratios changing from 5 to 25 mol % were produced by conventional melt quenching technique at 850–1000 °C temperature range. Produced glasses were annealed at about 400 °C for 2 hours. XRD analysis results indicate that there is no crystallization observed in the samples. Ionic conductivity of the samples was measured by Electrochemical Impedance Spectroscopy (EIS) technique and qualitative chemical analyses were conducted by FTIR and Raman spectrometer methods.

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Defect engineering in development of low thermal conductivity materials

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Increasing thermal efficiency and lower emissions require gas turbine designers to further increase the combustion temperature that leads to the high temperature components such as combustion chambers, blade and vanes surfaces face more rigorous conditions. Therefore, there is urgent demand to develop new ceramic coatings with even lower thermal conductivity, higher stability and durability than currently used thermal barrier coatings coating on the surface of high temperature alloy components.

Defect engineering has attracted much attention in seeking better low thermal conductivity materials since lattice defects play a crucial role in phonon scattering and thermal conductivity reduction. Oxygen vacancies and substitutions are proven to be the most effective, while the accompanying lattice distortion is also of great importance. In this talk, recent advances of reducing the thermal conductivity of potential thermal barrier coating materials by defect engineering are comprehensively reviewed. Effects of the mass and size mismatch between the defects and the host lattice are quantitatively estimated and unconventional thermal conductivity reduction caused by the lattice distortions is also introduced. Finally, challenges and potential opportunities are briefly assessed to further minimize the thermal conductivity of thermal barrier coatings materials in the future.

In this presentation, effects of macro defects on the heat transfer in porous ceramics are also talked including the characterization method as well as modeling.

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Nickel oxide doped barium yttrium zirconate nanostructures

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Keywords: barium yttrium zirconate, nickel oxide, magnetometry, selective reduction, nanostructures

The design of high surface area, nanostructured metal-ceramic systems is important for a wide range of energy related applications, including catalysts, fuel cells, and ionic transport membranes. Yttrium doped barium zirconate (BZY) is an important material in this realm, and when doped with nickel oxide, and subsequently exposed to reducing conditions, some very interesting nanostructures form. In the present work SQUID magnetometry and transmission electron microscopy is used to describe these structures. It is shown that the nickel-oxide doped BZY may be designed so that a shell structure dominates the surface characteristics and that it ultimately leads to a barium nickel oxide phase that is selectively reduced to nickel metal. The resulting material should exhibit superb catalytic reactivity.

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Testing oxygen separation membranes based upon novel materials

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Keywords: oxygen separation membranes, testing, methane conversion, nanocomposites

Design of materials for producing syngas from biofuels by selective oxidation with oxygen separated from air using catalytic membranes reactors is important problem of hydrogen energy field. Nanocomposites based on Pr nickelate-cobaltite are promising materials due to a high oxygen mobility and relatively good chemical stability in working conditions.[1,2] This work aims at studying performance of membranes based on such nanocomposites.

$PrNi_{0.5}Co_{0.5}O_{3\delta}$ (PNC), $Ce_{0.9}Y_{0.1}O_{2\delta}$ (YDC), $Ce_{0.9}Gd_{0.1}O_{2\delta}$ (GDC) and $MnFe_2O_4$ (MF) were synthesized by modified Pechini route. PNC – YDC and MF – GDC nanocomposites were prepared using ultrasonic dispersion in isopropanol. A few PNC – YDC functional layers with various porosity, dense $MnFe_2O_4$ – $Ce_{0.9}Gd_{0.1}O_{2\delta}$ buffer layer and porous $Pt/Sm_{0.15}Pr_{0.15}Ce_{0.35}Zr_{0.3}O_{2\delta}$ or $LaNi_{0.9}Pt_{0.1}O_3/Pr_{0.3}Ce_{0.35}Zr_{0.35}O_{2\delta}/Al_2O_3$ catalytic layers were consecutively deposed on Ni/Al foam substrate. The membranes obtained were tested in CH_4 selective oxidation into syngas/oxidry reforming using specially built setup.

To measure the sample temperature, new visible spectra pyrometry technique by analysis of the working membrane images was developed. Pyrometry measurements revealed a non-uniform or Gaussian temperature profile on the surface of membranes. The oxygen permeability of membranes (the oxygen flux is up to 10 ml O_2/cm^{2}min at 950 °C under air/methane gradient) meets criteria of the practical application.[3] Syngas yield and methane conversion increase with temperature and contact time. CH_4 conversion is up to 50–60% with H_2 content in the outlet feed being up to 25% at 900 °C. H_2/CO concentration ratio is >1, which is good for the practical application. Stable performance of the membrane was demonstrated for at least 200 h time-on-stream.

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Permeability and ionic conductivity of $CaTi_{0.9}Fe_{0.1}O_{3-\delta}$

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Keywords: oxygen semi-permeation, iron-doped calcium titanate, oxygen diffusion, ionic conductivity

Oxygen transport membranes (OTM) are dense membranes that allow oxygen diffusion along a chemical potential gradient. OTMs can increase the efficiency and lower emissions of oxycombustion processes or partial oxidation of methane. The oxygen semi-permeability is proportional to the ambipolar conductivity of the OTM material. However, OTM materials with the highest conductivity also suffer from fast degradation under operation conditions. In this regard, $CaTi_{0.9}Fe_{0.1}O_{3-\delta}$ (CTF) exhibits a promising trade-off, with an intermediate oxygen flux that is compensated by its superior thermal, mechanical and chemical long-term stability[1].

In this study, we interpret the oxygen transport properties of CTF in light of the structural and electrical characterization as functions of temperature (150–900 °C) and oxygen partial pressure (1 and 10^{-27} bar). CTF is a p-type conductor, where transport is mainly due to electronic conductivity at low temperature (T <700 °C)[2]. The ionic conductivity becomes predominant for temperature above 700 °C and PO_2 higher than 10^{-5} bar, whereas n-type conductivity dominates at low PO_2 ($\approx 10^{-25}$ bar). The semi-permeation measurements confirmed these results, showing that the flux was limited by the electronic conductivity for temperatures higher than 800 °C whereas at lower temperature the ionic conductivity was limiting[3].

We also find that the ionic transport number is higher than typical OTM materials. Nevertheless, under usual operating conditions, conductivity is never solely provided by either type of charge carriers, and must be considered as mixed conductor. Ionic conductivity values determined by isotopic exchange, semi-permeation measurements, and impedance spectroscopy were compared.

We tested the stability of CTF under reactive atmospheres (CO/CO_2 and H_2O/H_2). CTF shows a remarkable stability under H_2 and CO/CO_2, with a constant flux during 1300 h. The oxygen flux decreases quickly in presence of humidity (by 66%), but recovers (by 33% in 60 h) when water vapour is removed. It is thus promising for oxycombustion process of partial oxidation of methane.

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Development of asymmetric dual phase composite oxygen transport membranes

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Keywords: oxygen transport membrane, cer-cer dual phase, asymmetric membrane, tape casting

Mixed Ionic electronic conductors (MIEC) are potential candidates for various applications including oxygen transport membranes (OTM) due to their high efficiency and infinite selectivity towards oxygen at elevated temperatures.[1] Possible applications for OTM are supply of highly pure oxygen or membrane reactors, in which the separated oxygen is directly utilized to form valuable products such as synthetic fuels or bulk chemicals. OTM transport oxygen ions by solid state diffusion through oxygen vacancies, which cannot be occupied by other ions. However, the transport is based on lattice defects and, thus, high-performance OTM materials mainly perovskites (with high defect density and mobility) suffer from limited stability in application conditions with potentially reducing and/or acidic gas atmospheres (requiring low defect density and mobility).

One approach to face the trade-off between chemical stability and oxygen flux performance are dual phase composites. In such cer-cer composites two phases are coupled to provide pure electronic and ionic conducting pathway, respectively. In this work, composites of 20 mol% Gadolinia doped ceria (GDC) as ionic conductor and $FeCo_2O_4$ spinel (FCO) as electronic conductor are investigated.[2] GDC-FCO ratio is varied proving that spinel content as low as 10 wt-% is sufficient to ensure oxygen permeability, although well below the percolation threshold. In addition, the influence of the powder synthesis route on microstructure and corresponding oxygen permeation properties is investigated and compared to state-of-the-art single phase material, i.e. $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF).

In order to increase oxygen flux further, by microstructural optimization of the membrane layout, asymmetric membranes were manufactured by sequential tape casting. Such membranes consist of a thin (~15 µm), dense membrane layer and a porous support porosity (>40%) for mechanical stability. An important issue in tape casting is the used raw materials. In order to realize cost efficient manufacturing, a reactive sintering of the membranes was developed, using commercially available CGO, Fe- and Co-oxides as raw material. Oxygen flux in such membranes is clearly limited by surface exchange, due to the low electrochemically active triple phase boundary length, at which oxygen exchange takes place. The performances of bulk and asymmetric membranes are analysed and the potential of this type of materials is discussed with regard to microstructural optimization.

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Thermoelectric properties of $(La_{0.12}Sr_{0.88})_{0.95}TiO_{3-\delta}$ between 100 and 900 °C at reducing conditions

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Keywords: A-site deficient, La-substituted strontium titanate, nanostructuring, thermoelectrics

La-doped strontium titanate (STO) is a promising n-type thermoelectric material at moderate temperatures (500–600 °C). Due to the perovskite type of structure, the material has an exceptional ability to accommodate donor-dopants and still maintain chemical stability, hence offering the opportunity to control critical properties such as electrical conductivity and Seebeck coefficient. $(La_{0.12}Sr_{0.88})_{0.95}TiO_{3-\delta}$ samples were prepared by spray pyrolysis followed by spark plasma sintering (SPS) at 925, 1100 and 1200 °C or solid-state reaction (SSR) followed by conventional sintering at 1500 °C. Thermoelectric performance was evaluated by measuring the Seebeck coefficient, electrical and thermal conductivity. The samples sintered by SPS between 1100 and 925 °C showed a low thermal conductivity ranging from 3 to 1.3 $Wm^{-1}K^{-1}$.[1] The low thermal conductivity is correlated with a low grain size combined with a highporosity. The electrical conductivity (4-point, DC) and Seebeck coefficient were measured in reducing atmosphere (humidified 5% H_2 in Ar) at temp-eratures between 100 and 900 °C. The electrical conductivity increased significantly with grain size (40 nm–4 μm) as shown in Fig. 1. At T<450 °C the Seebeck coefficient decreased with increasing grain size. The highest figure of merit, ZT=~0.2, was observed at 500 °C for the material prepared by conventional sintering.

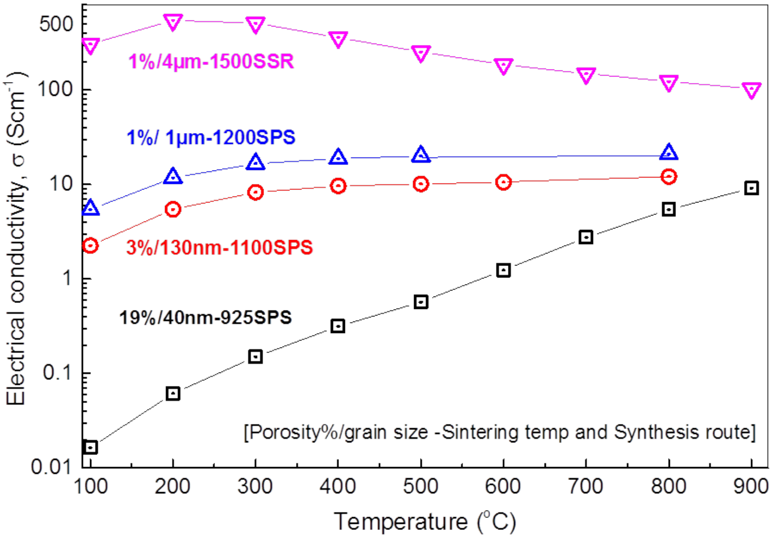

Fig. 1. Temperature dependence of electrical conductivity measured at reducing conditions for $(La_{0.12}Sr_{0.88})_{0.95}TiO_{3-\delta}$ sintered at 925 °C(SPS), 1100 °C(SPS), 1200 °C(SPS) and 1500 °C(SSR)

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Development of porous SiC using the sacrificial template technique for nuclear fusion applications

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Keywords: porous SiC, FCI, DCLL blanket, sacrificial template, thermal conductivity

One of the main technological challenges towards the attainment of nuclear fusion as energy source is the development of materials able to withstand the extreme conditions present in a future fusion reactor. In the so-called *blanket*, the energy of the neutrons produced in the fusion reaction is transformed into thermal energy, and tritium –one of the fuel elements- is generated out of lithium. In the blanket design named *Dual Coolant Lead Lithium* (DCLL) a PbLi alloy flows inside hollow channels called Flow Channel Inserts (FCIs), capturing the neutron flux energy and thus increasing its temperature up to about 700 °C. FCIs are key elements in the DCLL blanket design because they provide the necessary thermal insulation, allowing the fluid to retain the highest possible heat energy and preventing the steel structure to reach its maximum allowable temperature. The high PbLi temperatures allow high reactor efficiency, but impose a considerable thermal gradient across the FCI's walls. This gradient generates mechanical stresses that must be supported by the FCIs during operation without damage. Besides, FCIs must withstand the contact with the hot PbLi without corrosion damage, and must provide enough electrical insulation to minimize interactions of the flowing liquid metal with the high magnetic field present in a magnetically confined fusion environment. SiC is the main candidate material for FCIs. However, the relatively high thermal conductivity of SiC for FCIs application requires the development of SiC-based materials with sufficiently low thermal conductivity.

In the present research, a SiC sandwich material, formed by a core of porous SiC covered by a dense SiC layer, is proposed for FCIs. The dense coating is produced by chemical vapor deposition (CVD). According to thermomechanical calculations and FEM models, and assuming a CVD SiC dense coating of 200 µm and a porous SiC core of ≈5 mm thickness, the core material should present a thermal conductivity near 7 W/m·K at 700 °C with a mechanical strength above 50 MPa, to ensure the insulation and mechanical integrity that the application requires. The electrical conductivity should be maintained below 1-10 S/m. To develop a porous SiC with such properties, a method based on the sacrificial template technique is proposed; in order to achieve a high porous/high strength material a spherical powder with particle size about 30 times larger than the SiC powder is proposed as sacrificial phase, to achieve a sponge like microstructure. In the proposed process, a spherical mesocarbon microbeads (MCMB) graphitized powder of about 10 µm particle size is used as sacrificial template phase, which is added to a SiC powder of 0.3 µm particle size, and to Al_2O_3 and Y_2O_3 as sintering aids. The graphite phase is removed after sintering by an oxidation treatment. In this work, a description of the production method is presented, as well as the properties of the resulting SiC porous material after sintering and oxidation, like porosity, microstructure, thermal and electrical conductivities and module of rupture (MOR). In order to discuss the mechanisms taking place in the different processing steps, results from X-ray diffraction and thermogravimetric analysis (TGA) are also presented. Using this production technique, different porous SiC materials with a wide range of porosities (≈10–70%) have been produced, being possible to fabricate a candidate material to become the core of a SiC-sandwich FCI, with a porosity ≈40%, a thermal conductivity at 700 °C of ≈8 W/m·K, a MOR of about 110 MPa and electrical conductivity at 550 °C well below 0.01 S/m.

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The adsorption reaction of different shaped-alpha-bismuth oxides with iodide ions

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Keywords: bismuth oxide, flux method, morphology control, radioiodine, adsorption

Radioiodine is an inevitable product of nuclear fission, which is highly radioactive and toxic, and could present a health risk upon people. Iodide anion (I^-) is stable over the whole pH range. Thus, the selective capture of I^- from sea or lake water is required. Although silver oxide (Ag_2O) is known as a high adsorption capacity and selectivity for radioactive I^-, the high costs of silver limit its practical application. Bismuth oxide (Bi_2O_3) is a potential adsorbent for recovering I^-. Alpha-bismuth oxide (α-Bi_2O_3) is known to form Bi_5IO_7 via I^- adsorption with morphological transformation. Previous reports say that the concentration of I^- and variety of counter cation of I^- are important for adsorption reaction. However, the reaction mechanism including crystallographic information, how I^- intrude into α-Bi_2O_3 crystals and are fixed in, followed by morphological transformation, are unidentified. In this study, two kinds of shape-controlled α-Bi_2O_3 crystals by flux method were used for adsorption test and the influence of exposed crystal facet on reaction pathway is revealed.

α-Bi_2O_3 crystals with different shapes were prepared as followed: α-Bi_2O_3 crystals were grown in carbonate flux with different solute concentration by using purchased α-Bi_2O_3. The kinetics of I^- adsorption by α-Bi_2O_3 were determined using aqueous solution containing I^- with concentrations of 0.4, 0.8, and 1.2 mmol L^{-1} (the amount of adsorbent = 1 g L^{-1}, solution temperature of 10, 20, and 40 °C, pH = 6.5, stirring rate = 0, 200, and 300). The suspensions were collected for different periods while stirring. The supernatants were separated from solids and analyzed via ion chromatography (IC). Solids were analyzed via X-ray power diffraction (XRD). The morphology of reacted α-Bi_2O_3 were characterized with scanning electron microscopy (SEM).

Plate-shaped α-Bi_2O_3 crystals were obtained in low solute concentration and in high solute concentration, polyhedral ones were obtained. As a result of the adsorption test, only when polyhedral-shaped α-Bi_2O_3 crystals were used, needle-shaped crystals were obtained after immersed in aqueous solution containing I^- for 24 h. It is found that the needle-shaped crystals have Bi_5IO_7 composition determined by electron diffraction scattering analysis. From the results of time-dependent analysis, α-Bi_2O_3 crystals changed to Bi_5IO_7 crystals via three-step reaction pathways. First, partial α-Bi_2O_3 crystals reacts with I^- to form BiI_3, followed by formation of Bi_5IO_7 crystals through the reaction of BiI_3 with hydroxyl ions. Consequently, further reaction of Bi_5IO_7 crystals with remaining α-Bi_2O_3 crystals and I^- occurs to grow Bi_5IO_7 crystals itself. From the different behaviours in adsorption reaction depending on the crystal shape, the particular facet of α-Bi_2O_3 crystal which I^- diffuse into should be important to start the adsorption reaction. In addition, at equilibrium, above 80% of theoretical adsorption capacity was achieved.

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Thermochemical behavior of porous SiOC/LSMO nanocomposites with 1D nanostructures for syngas production

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Porous nanocomposites composed by a silicon oxycarbide matriz and perovskite-type oxides have been prepared with the aim of developing ceramic supported catalysts for the thermal decomposition of CO_2 and H_2O to produce CO and H_2, respectively.

The materials have been prepared through the sol-gel method by the incorporation, at different stages of the synthetic process, the precursors of La/Sr manganites (LSMO). After pyrolysis in inert atmosphere it is obtained a glass-matrix material with high surface energy and the presence of a well defined mesopore distribution. The inclusion of LSMO into the glass matrix is going to be strongly affected by the synthetic procedure. These oxides possess a hexagonal perovskite-type structure and form crystals of a few nanometer size.

The characterization of the nanocomposite material revealed the formation of 1D nanostructures composed by a carbonaceous matrix with LSMO nanocrystals growing along in parallel direction to the carbon fibre. Raman, FTIR and ^{29}SiNMR spectroscopies have been used for the structural characterization whereas textural and surface characteristics have been analyzed by SEM, TEM and N_2 adsorption techniques. Since the materials are intended to act as catalysts, we have also studied the surface of the materials in terms of their surface energy and fractal characteristics as well. We have compared the wettability of the as-prepared nanocomposite and the different phases taking part of the nanocomposite material.

The suitability of the obtained materials to be employed as thermochemical catalysts has been studied by means of thermogavimetric analysis under controlled atmosphere and through the analysis of the gases emitted during the thermochemical reaction.

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Terbium-doped perovskite-related proton conductors

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Keywords: proton conductors, perovskites, phase transformation, fuel cells

High temperature proton conducting materials have unique electrochemical properties make them suitable for numerous applications, including Protonic Ceramic Fuel Cells (PCFCs), hydrogen sensors, gas membranes or high temperature proton conducting electrolysers (PCECs) which, compared with oxide ion-conducting devices, offer higher fuel utilization and an opportunity to produce dry, pressurized hydrogen. Perovskite-type and perovskite-related materials have been widely investigated as a good oxide-ion as well as proton conductors, where the transport properties are strongly dependent on the crystal structure and particularly the defects concertation.

An evaluation of terbium content in Ruddlesden-Popper-type oxide $NdBaInO_{4+\delta}$ and its relation with phase composition, crystal structure and transport properties was performed. To determine it dense pellets of $Nd_{1-x}Tb_xBaInO_{4+\delta}$ (x = 0, 0.1–1.0) with relative density above 95% were prepared via the conventional solid-state route at 1450 °C.

Structural analysis by X-ray diffraction (XRD) performed for dried, as well as hydrated materials at room and elevated temperatures indicated that crystal structure of the studied samples can be described as Ruddlesden-Popper-related, with structural evolution from monoclinic to cubic symmetry observed for 50% Tb-doped material. Phase transportation significantly promotes transport properties of investigated material. Increase of ion conductivity by two orders of magnitude with unchanged activation energy was recoded compared with undoped sample. Electrical conductivity of the compounds conducted in dry, H_2O- and D_2O-containing atmospheres as a function of oxygen partial pressure allows establishing the H/D isotopic effect related with high temperature proton conductivity. Incorporation and removal of water molecules were also confirmed *in situ* by high temperature XRD and thermogravimetric techniques. Finally, in order to elucidate influence of Nd site substitution on transport properties, also conductivity relaxation kinetics of the Tb-doped materials was measured in different atmospheres.

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Optimization of (La,Sr)(Co,Fe)O_3 cathodes aiming on high performance and enhanced durability in metal-supported fuel cells

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Keywords: LSCF, SOFC, metal-supported fuel cell, cathode adherence, high performance cathodes

Adapted processing of (La,Sr)(Co,Fe)O_3 perovskite cathodes for metal-supported solid oxide fuel cells (MSCs) was investigated in order to develop high performance MSCs with significantly increased durability of the cathode structures. The activation and sintering procedure of the cathode was optimized to overcome the main issue of insufficient cathode adherence. Effects from different sintering approaches on the phase stability, mechanical stability, time dependent mechanical integrity, and functionality of the cell components revealed applicable processing strategies. These strategies include the implementation of a separate sintering step for MSC full-cells as well as an optimization of the current state-of-the-art *in-situ* activation process. Both strategies lead to a substantially improved adherence of the produced cathodes. Accordingly, electrochemical single cell measurements revealed a performance improvement of such produced cells in comparison to state-of-the-art cells which were *in-situ* activated at 850 °C during the startup procedure. In another approach the potential for increasing the performance by applying LSC as cathode material is the focus of investigation. The results obtained from the presented study provide the basis for further characterization of the degradation behavior in long-term measurements.

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Increased Li ion conductivity of LATP ceramics by optimized powder processing

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Keywords: Li ion conductivity, LATP, ceramic processing, separator, all-solid-state batteries

Lithium ion conducting ceramics are investigated as candidates for use as solid electrolytes in All-Solid-State, Lithium-Sulfur and Lithium-air battery concepts. $LiTi_2(PO_4)_3$ provide the prerequisite for a high Li-ion conductivity and dense microstructures for a reliable separation of the cathode and anode side. A partial substitution of Ti^{4+} by Al^{3+} can improve the conductivity up to $3.0 \cdot 10^{-3}$ S/cm for the composition $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP). However, LATP exhibits a high thermal expansion anisotropy and cracks are a result of grain growth during the sintering. At least, it was described, that the formation of microcracks can be inhibited by reducing the critical grain size (< 1.6 µm). To reduce the grain size and to achieve homogenous and crack free microstructures, the powder processing have to be optimized. In this study, the LATP powders were prepared by two different pathways: (1) melting and milling of a glass frit to a powder and (2) the wet-chemical synthesis of a calcined LATP. Both types of powder were characterized by phase analysis (XRD), particle size and shrinkage during sintering. The sintering was performed by SPS at temperatures between 800 and 900 °C. The phase composition, density, porosity, ionic conductivity, He-leakage rate and grain size of the specimens were measured. The highest density (2.82 g/cm³; 97%), ionic conductivity ($>2 \cdot 10^{-4}$ S/cm) and a homogenous microstructure was achieved at 850 °C with the material synthesized by the wet-chemical route (2). The ceramic produced from the melt of parent glass (1) showed the formation of microcracks at $T_s = 950$ °C in conjunction with the appearance of an $AlPO_4$ secondary phase (caused by Li loss during the preparation). With higher sintering temperatures coarse grains and cracks dominate the microstructure.

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Effect of particle size and hierarchical structuring on the electrochemical properties of NCM-cathode materials in lithium-ion-batteries

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Keywords: microstructure-property relationship, cathode materials, lithium ion batteries (LIBs), energy storage

In the course of energy crisis energy revolution is taking place with important changes to renewable energy sources. In this process lithium ion batteries (LIBs) are one key technology concerning energy storage and electromobility because of their high efficiency and their environmental-acceptability. Nevertheless one shortcoming of this technology is generally said the lack of long-term cyclability and poor rate capability especially at high cycling rates. Reasons are structural changes of the active material as well as inhibited mass and charge transport during cycling due to poor electronic conductivity. To improve latter and increase the reliability of LIBs, efforts must be made by modifying the cathode design to obtain hierarchically structured composites. Thereby nano-structuring is favoured because of the easier manageability compared to nanoparticles and even advantageous effects like shorter diffusion paths and improved conductivities as well as suppression of structural changes are promoted.[1]

In the following the approach of hierarchically structuring of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathode active material by an elaborated process of grinding, spray drying and calcination will be presented. Here the effects of granule size and primary particle size variation by spray drying and calcination will be presented. The relationship between process parameters, morphology and performance of the as prepared LIBs will be given by detailed material characterization in combination with electrochemical investigations. It will be shown that active material granules between 9 and 42 µm with nanostructured morphology and defined porosity have superior discharge capacities, power densities and long-term stabilities compared to bulk NCM-material. An accurate tuning of the performance at high C-rates can be reached by granule size optimization and adaption of calcination temperature.

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Characterization of solid oxide fuel cell sealants and anodes

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Keywords: solid oxide fuel cell, anode, sealant, mechanical characterization

Typically brittle sealant and anode materials are critical for the reliability of solid oxide fuel cells (SOFCs). Hence, characterization of these failure-relevant materials is crucial for the long term operation. In particular, the mechanical behaviour and elevated temperature stability which is strongly affected by creep has to be thoroughly understood and in terms of property – microstructure correlation, related to the materials' compositions, crystallization, porosity and phase stability.

Since sealant leakage can lead to malfunction of the whole system, the structural integrity of the sealant is a key issue for the operation of SOFC stacks and systems. Fracture properties and elevated temperature deformation need to be assessed, particularly for partially crystallized glass-ceramic sealants that might suffer from instability issues at operation relevant temperatures due to viscoelastic deformation of the residual glass phase. In this work, a modified sealant, which consists of a composition from the BaO-CaO-SiO_2 ternary system with Ag particles reinforcement, was characterized. Bending tests were carried out at room temperature and typical stack operation temperatures on a head-to-head specimen geometry in an as-sintered and annealed state, yielding average fracture stresses and apparent creep data. Since the sealants are exposed to a complex loading state in the stack environment, complementary torsion tests were used to investigate the shear strength. Advanced microstructural characterization was carried out to gain insight into the annealing and reinforcement filler effects. The results are compared and discussed with respect to literature data and their relevance for the application in SOFCs operating at different temperatures in the range of 600 °C to 800 °C.

Typical anode substrate materials (NiO-3YSZ and NiO-8YSZ) along with their reduced and re-oxidized state were analysed by means of fracture toughness at room temperature and 800 °C. Effects related to porosity and transformation toughening could be verified. Furthermore, creep of porous Ni-YSZ composite has been investigated under H2/Ar atmosphere at typical operating temperatures. Ni-YSZ materials with different porosities and Ni/YSZ ratios were tested in order to investigate material´s composition and porosity effects. Different loading configurations such as compression, four-point bending and ring-on-ring bending have been used to assess the differences in creep response of these materials. Interpretation and analysis of the data were based on analytical and finite element simulation. The systematic comparison and discussion of the results was aided by microstructural investigations.

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Interfaces of CaCo- and CaMn-ceramics provide high thermoelectric conversion efficiency

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Keywords: energy Harvesting, electro-ceramics, ceramic interface, microstructure

Thermoelectric materials have the option for recovery of waste heat into electricity. CaCo- and CaMn-oxide-ceramics[1,2] show large p- and n-type Seebeck coefficients and electric power output. We prepared mixtures of $CaCO_3$ and Mn_2O_3 or CoO with Co_3O_3, and added ZnO and rare earth oxides (Y, Nd, Sm). After calcination, grinding and sintering at 1000 °C for 7 h, we measured the Seebeck voltage under high temperature gradient.[3] The values for Seebeck ceoefficent (and output power) of more than -300 μV/K (8μW) for the Mn- and +200 μV/K (10 μW) for CaCo could be improved for both materials by a certain Zn-concentration, while the rare earth addition had not much affect.

The material compounds were characterized with SEM-EDX observations. The mapping could clearly identify Ca-rich and Mn- or Co-rich components, which are stable in the phase diagrams. Revising the data on a $NaTaO_3$ / Fe_3O_3 compound[4] showed that similar interfaces are present, which opens the possibility for searching new similar compounds. The explanation of the large effect of interfaces can be explained by the electric field at interfaces similar as in ferrolectrics.

These oxides are easy to handle and contacting with Cu-wires is possible. Mechanical fixation with Portland cement is also considered as an option, when the CaCo- and CaMn-ceramics is completely dry, otherwise the thermoelectric properties deteriorate. The usage of these oxide ceramics for functional materials in buildings as discussed.

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Designing the composite $SrVO_3$-$SrTiO_3$ anodes for hydrocarbon-fueled solid oxide fuel cells

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Keywords: perovskite, SOFC, anode, titanate, vanadate, electrical conductivity, polarization resistance

Perovskite-type $SrVO_3$- and $SrTiO_3$-based phases exhibit good resistivity to sulfur poisoning and do not catalyze carbon deposition, and are considered therefore as possible alternative anode materials for hydrocarbon-fueled solid oxide fuel cells. $SrVO_3$ exhibit high electronic conductivity but also a narrow phase stability domain restricted to reducing conditions. On the other hand, $SrTiO_3$ demonstrates remarkable phase and dimensional stability in a wide range of T-p(O_2) conditions but rather insufficient electrical conductivity. The present work aimed at the development of $SrVO_3$-$SrTiO_3$ composite anode materials with emphasis on a compromise between dimensional/microstructural stability and electrical properties.

Initial assessment demonstrated that $SrVO_3$ and $SrTiO_3$ form an entire range of solid solutions under reducing conditions. In all cases, exposure to air above 600–700 °C resulted in either collapse of perovskite structure (V-rich compositions) or separation of vanadium-containing secondary phases (Ti-rich composition). These phase transformations were accompanied by dimensional changes and were not reversible at temperatures below 1000 °C (probably, due to kinetic reasons).

Instability in oxidizing atmospheres complicates the fabrication of anodes in realistic conditions. Therefore, the second approach was to start from oxidized phases and to proceed via *in-situ* reduction employed for Ni-YSZ cermet anodes. V^{5+} substituted in titanium sublattice of $SrTiO_3$ acts as donor-type dopant and was found to has a limited solid solubility under reducing conditions (~30–35 at.%). *In-situ* reduction of oxidized $SrTi_{1-y}V_yO_{\pm\delta}$ at 900 °C is accompanied however by the reduction of vanadium cations, and the resultant conductivity remains too low (< 0.2 S/cm) being comparable to other acceptor-doped strontium titanates.

The next approach was preparation of composite $SrVO_3$-$SrTiO_3$ anode materials starting from oxidized phases. The precursors with nominal composition $SrTi_{1-y}V_yO_{\pm\delta}$ ($y = 0.1$–0.4) were thermally treated in air at temperatures not exceeding 1100 °C to yield equilibrated phase mixtures comprising $SrTiO_3$-based perovskite as a main phase and strontium orthovanadate $Sr_3(VO_4)_2$ as a second major phase. Transformation of strontium orthovanadate on reduction at 900 °C into highly-conductive perovskite-type $SrVO_3$ phase finely distributed in the stable $SrTiO_3$-based matrix resulted in substantial nearly instant increase of electrical conductivity by orders of magnitude reaching 10–30 S/cm for $y = 0.3$–0.4. Electrochemical activity of composite anodes applied onto yttria-stabilized zirconia solid electrolyte and infiltrated with a fraction of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ electrolyte component was evaluated by electrochemical impedance spectroscopy using symmetrical cell configuration.

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Fingerprinting compounds in Li_2O-TiO_2 phase diagram with electron energy loss spectroscopy

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Keywords: Li-ion batteries, $Li_2Ti_3O_7$, $Li_4Ti_5O_{12}$, Li_2TiO_3, EELS, TEM

Compounds in the Li_2O-TiO_2 phase diagram are materials of importance for energy applications, especially in Li-ion batteries[1]. These applications involve complex chemical reactions. It is crucial to be able to identify the metastable/stable phases forming that might cause deuteriation of the efficiencies of devices[2]. However, detection of Li is challenging. One of the most suitable methods is EELS, which is highly sensitive both to coordination and chemistry of the ions. In order to identify the thermodynamically stable phases, different synthesis routes were used for each compound. Solid state synthesis was utilized for $Li_4Ti_5O_{12}$ and monoclinic Li_2TiO_3, air-quenching from 1200 °C was mandatory for obtaining $Li_2Ti_3O_7$. Cubic Li_2TiO_3 was obtained by hydrothermal method. In order to probe the fingerprints of different compounds with unique coordination of Li and/or Ti with O, Energy Loss Near Edge Structure (ELNES) of Li-K, Ti-$L_{2,3}$ and O-K edges were determined for all compounds. The fingerprinting studies were conducted via EELS, in STEM mode. Ti $L_{2,3}$ edge showed the least dependency on both crystallography and site symmetry. Li-K edge was effected by the coordination number, with 4-fold coordination showing an extra structure in the near edge. O-K edge was effected the most by site symmetry, crystallography and stoichiometry. These fingerprints can be used as guidelines in determining the defect chemistry for energy applications in all compounds.

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Preparation of alumina supports for the fabricatıon of high flux thin membranes

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Keywords: ceramic, macroporous, supports, membrane, gas transport

Due to high energy demand in our developing world, researchers are either trying to meet this demand in new ways or redesign existing high energy consuming systems in an economical way. Membrane based separation has superior properties like low energy consumption, high purity separation and easy processing that makes it advantageous over other separation techniques. Ultrathin membranes have been developed for high flux separation, nanofiltration (NF), ultrafiltration (UF), reverse osmosis (RO), gas separation and pervaporation. Supports are significant for the fabrication of thin membranes in terms of their surface roughness and the flux[1]. Ceramic supports are mechanically/thermally/chemically stable compared to polymeric counterpart. One major drawback of macro/mesoporous ceramic supports is their high cost that prevents large scale deployment of thermally stable ceramic/zeolite/MOF membranes. Silica, zirconia, titania and alumina or their composites are generally used as the porous membrane support materials[2,3]. Ceramic supports supply not only thermal and chemical stability but also good surface morphology which leads to a smooth surface for thin membrane coating. High throughput thin membranes necessitate high flux membrane support with homogeneous surface properties and uniform pore size.

In this study, macroporous alumina supports were prepared by using vacuum assisted filtration with different α-Al_2O_3 powders (Baikowski CR-6 and Sumitomo Chemical AKP-50). Structural parameters such as pore diameter, porosity and tortuosity of the prepared macroporous supports were estimated by using He, N_2, CO_2 permeance measurements. The effect of temperature and pressure difference on the gas permeances of the prepared supports were also investigated. Supports prepared by Baikowski powder which has a larger particle size than AKP-50 powder exhibited a permeance of four times higher than that of AKP-50.

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Poster presentations

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Modeling of thermally induced delamination in glass/steel joints for solid oxide cell applications

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Keywords: solid oxide cell, interconnect steel, glass sealant, modelling, cracking

The majority of the solid oxide cell (SOC) sealants has been focusing on bonded glass seal/steel interconnect. Glass should be prepared with match thermal expansion coefficient (α) and low interfacial reaction with adjacent parts. Seal thickness can be also adjusted to improve the interfacial mechanical characteristics. In this study an analysis was performed on the stress situation at room temperature at where the residual thermal stress is at its maximum level. The developed model was used to predict the crack growth condition and life time estimation in practical situation with supports of the experimental measured data such as Young's modulus of glass seal (89.35 GPa) and steel interconnect (200 GPa), Critical fracture energy of glass (G_c=6.02±0.79 J/m^2) and joint couples as well as their thickness (50 and 300 µm for glass and steel, respectively). The normalized steady-state energy release rate was considered for the analysis and modelling the crack growth of the joint. While experimental assessments revealed that the interfacial crack deflects to the bulk glass, numerical calculations led to a diagram with "no cracking/cracking" regions. This diagram shows the maximum allowable $\Delta\alpha$ to avoid crack growth. The analysis can be regarded as the basis step for the design of multilayer glass/steel frames to increase the total resistance of the functional sealing layer against delamination. However, multilayers cannot be designed from fracture mechanics considerations alone.

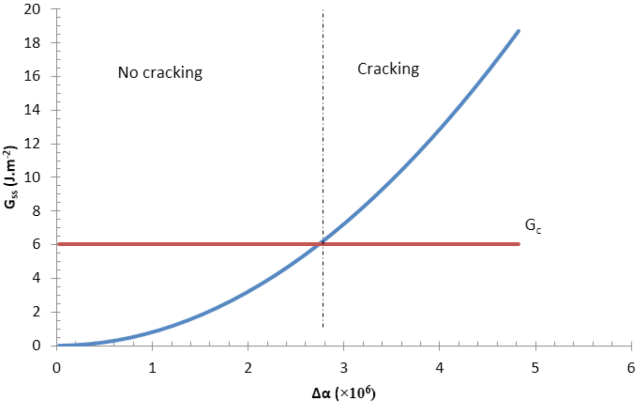

Fig. 1. Cracking diagrams showing the maximum allowable TEC mismatch for the examined steel/glass/steel tri-layers

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Ionic conductivity of Zr-rich pyrochlore $Nd_2Zr_2O_7$ based system

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Keywords: pyrochlore, ionic conductivity, interstitial oxygen conductor

Pyrochlore based materials, due to their high ionic conductivity, have been characterized as potential solid electrolytes. In this paper $Nd_{2-x}Zr_{2+x}O_{7+x/2}$ pyrochlore materials ($0 \leq x \leq 1$) were prepared by mechanical activation of the oxide mixtures, following by high temperature sintering (1500 °C, 10 hrs) of uniaxial pressed pellets. Structure and microstructural characterization of prepared ceramic samples were done by X-ray diffraction, Raman spectroscopy and scanning electron microscopy. The behavior of their TEC (thermal expansion coefficient) was investigated also. All $Nd_{2-x}Zr_{2+x}O_{7+x/2}$ are single phase materials with a relative density higher than 90%.

Electrical characterization was performed by electrochemical impedance spectroscopy as a function of temperature and oxygen partial pressure. The electrical conductivity of Zr-rich ($x > 0$) compositions is more than one order of magnitude higher than the stoichiometric composition ($x = 0$), with a conductivity value close to 0.03 S/cm at 1000 °C in air, and an activation energy of 1 eV. The oxygen partial pressure dependence shows a constant conductivity value within a large oxygen partial pressure range, typical of the ionic type conductivity. The increase of the ionic conductivity for Zr-rich compositions were interpreted by the interstitial oxygen ion formation, to compensate the Zr^{4+} in the Nd^{3+} positions. The ionic conductivity of this material was then attributed to interstitial oxygen ions migration.

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Effect of GD/SM co-doping on the electrical properties of ceria-based electrolyte materials

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Keywords: co-doped ceria, pechini method, samarium, gadolonium, solid oxide fuel cell

Ceria based materials are widely used as electrolytes for intermediate-temperature solid oxide fuel cell (IT-SOFC). ($Ce(NO_3)_3.6H_2O$, $Gd(NO_3)_3.6H_2O$, $Sm(NO_3)_3.6H_2O$ nitrate salts were used as the starting materials to form co-doped ceria electrolytes of $Ce_{0.8}Gd_{0.2-x}Sm_xO_{1.90}$

($0.5 \leq x \leq 0.15$) using the Pechini method. The samples were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). XRD patterns of the all prepared compositions indicate the formation of the cubic fluorite-type structure. The relative densities of the samples were determined above 90% after sintering at 1400 °C for 6 h. The impedance spectroscopy of the sintered pellets was performed between 300 °C and 800 °C in air and the effects of the co-dopant on the ionic conductivity of the ceria based electrolytes were investigated.

Acknowledgement
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Development of steam electrodes in water splitting reaction for high temperature proton electrolysers

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Keywords: PCEC, electrolyser, LSM, BCZY, multitube module, catalytic promotion

High temperature electrolysis technology offers high conversion efficiency of renewable and peak electricity to H_2 and may increase performance further by utilising available sources of heat and steam from solar, geothermal, or nuclear plant. In contrary to solid oxide electrolysers (SOECs), which operate at around 800 °C and H_2 is produced on the steam feed side, proton conducting electrolysers (PCECs) generate pressurized dry H_2 what significantly enhances total efficiency.

The main objective of ELECTRA project is to develop and demonstrate scalable fabrication of tubular high temperature electrolyser (HTE) cells with proton conducting electrolyte. In order to produce 250 Ln/h of H_2 from 1 kW of electrical power, a multi-tube reactor has been designed and built.

ELECTRA utilises a novel generic tubular module holding single-end closed tubes. The tubular cells are mounted with patented solution allowing then to be inserted, fasted, sealed, monitored and controlled at working conditions of individual tubes, from a cold accessible side. High-pressure steam is fed to the outside of each tube, and pure H_2 is collected inside. The electrochemical performance and system durability have been studied by electrochemical impedance spectroscopy (EIS) and gas chromatography methods. The measurements were performed in the temperature range 800 600 °C and up to 30 bar of pressure of humidified air (75% of steam).

Related to the anode development, $La_{0.8}Sr_{0.2}MnO_{3-}\delta$ (LSM) composite material has been deposited on proton-conducting $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-}\delta$ (BCZY27) electrolyte and studied in symmetric cells to investigate the anode microstructure and electrochemical performance. To enhance anode kinetic reaction, the LSM/BCZY27 60/40 vol.% composite was infiltrated with Pr, Ce, Pr-Ce 50 vol.% and Zr nanocatalysts treated at 850 °C. The R_p showed the best results ($< 0.2\ \Omega\cdot cm^2$) applying a density current of 0.5 – 5.5 mA/cm^2 range for the LSM/BCZY27 60/40 vol.% composite infiltrated with Pr-Ce 50 vol.%

Finally, ELECTRA will demonstrate proof-of-concept CO_2 and steam co-electrolysis reaction, where compared to SOECs, pressurised steam and CO_2 are fed on separate sides of the cell in the PCEC, which may be advantageous for economical syngas production.

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Two step sintering of spinel coatings prepared by electrophoretic deposition method

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Keywords: coating, sintering, $MnCo_2O_4$, IT-SOFC

Ferritic steel Crofer 22APU is one of the possible construction materials for metallic interconnects for intermediate temperature solid oxide fuel cells (IT-SOFC). During the exploitation of the fuel cells with metallic interconnect at 800 °C, an unavoidable phenomenon of chromium oxide scale formation occurs. This oxide causes a substantial increase of electrical resistance, which directly leads to higher stack losses. Another negative factor is possible vaporization of volatile chromium compounds and contamination of the cathode electrode which result in deterioration of the catalytic properties. In order to decrease the degradation, a modification of the surface of the interconnect can be applied, involving the formation of a protective and conductive manganese-cobalt spinel on the surface of the alloy. With the use of the electrophoretic method combined with a two-step heat treatment process, dense coatings can be produced, offering an effective barrier to the chromium diffusion from Crofer 22APU steel, thus substantially limiting the formation of volatile vapors from Cr scale.

In this work, a $MnCo_2O_4$ [1] spinel was used to obtain a conductive-protective coating on the interconnect made of ferritic steel Crofer 22APU. $MnCo_2O_4$ coatings, in the form of suspension, were applied on the steel surface using electrophoretic method. Deposition was performed with electric field strength of 40 V/cm in acetone and isopropyl alcohol suspension in the ratio 1:1 (v/v) and iodide. Then, a two-step heat treatment was performed. The first step consisted of reduction of the obtained coatings in reductive atmosphere (H_2/Ar) with various partial pressure of oxygen at 900, 1000, 1100 °C. The second step involved oxidizing of the previously reduced coatings. The phase composition of the coatings was determined by means of the XRD method, and microscopic observations, including the determination of the chemical composition by means of SEM-EDS.

Acknowledgement
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Sodium and potassium based geopolymers as heterogeneous catalysts in the production of biodiesel

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Keywords: biodiesel, geopolymer, heterogeneous catalyst

Many environment problems are caused when fossil fuels are used in engines. Thanks to its similar properties, a promising substitute for this kind of fuel is biodiesel (fatty acid alkyl esters), that is renewable, biodegradable and not toxic. The most used process to prepare biodiesel is by homogeneous transesterification of vegetable oils, despite the fact that it produces a high concentration of impurities in the product. The use of heterogeneous catalysts is quite attractive, their main advantage being that the purification step is minimized. Transesterification consists of a sequence of three reversible reactions, the first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides to glycerol, yielding one ester molecule for each glyceride at each step.[1] The reactions are reversible, although the equilibrium lies towards the production of fatty acids monoesters and glycerol.[1]

In this work, we investigated the biodiesel production by transesterification of soybean oil with methanol, using geopolymers as heterogeneous catalysts. Geopolymers were prepared by mixing metakaolin with an activating alkaline solution. Two types of heterogeneous catalysts were prepared in powder form: sodium- and potassium-based geopolymers. The influence of geopolymer heat treatment was also evaluated. The biodiesel was obtained in the following reaction conditions: methanol:oil ratio, 7.5:1; catalyst amount 3% of oil (w/w);

reaction temperature, 60 °C; reaction time, 1h. The reaction yield was calculated by gas chromatography measurements while X-ray diffraction (XRD), thermal analysis (DTA-TGA), and BET surface area measurements were employed to obtain more information about the geopolymer.

The results demonstrate that both geopolymers work as catalysts, and the conversion is higher when the potassium based geopolymer is used (~60% versus ~50%, potassium and sodium respectively), possibly due to the higher surface area of the potassium-based geopolymer. Moreover, the yield of reactions seems to be dependent on the geopolymer heat treatment. It should be noted that the biodiesel product still contains some Na or K impurities, so a further optimization of the material and the process is required.

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Synthesis, sintering, transport and thermal properties of $Na_2Fe_2Ti_6O_{16}$ freudenbergite

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Keywords: freudenbergite, electrical conduction, small polaron hopping, thermal conductivity

Freudenbergite compounds have a general formula of $A_2B_2Ti_6O_{16}$, where A = Na^+, and B = Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, Ga^{3+}, Ti^{3+}, Cr^{3+}, Fe^{3+}, etc.[1] They have been widely studied as components of synroc to immobilize radioactive waste.[1–5] Among them, $Na_2(Al,Fe)_2Ti_6O_{16}$ shows good leach resistance, reasonable radiation resistance, and could be incorporated into synroc to immobilize nuclear waste containing a high amount of sodium. $Na_2Fe_2Ti_6O_{16}$ has also been investigated as an ion exchanger to remove nickel from potassium solutions.[6] Recently, $Na_2Fe_2Ti_6O_{16}$ shows prospects for application as anode materials in sodium-ion batteries due to its good cycle stability.[7] The electrical and thermal transport properties of freudenbergite have not been reported yet. Such information is required to advance its application in sodium-ion batteries and other fields of research.

$Na_2Fe_2Ti_6O_{16}$ freudenbergite has been synthesized using a simple solid-state route and conventionally sintered to reach 94% density ceramics. High temperature electrical and thermal transport properties have been investigated for the first time. In the temperature range of 468 K–1000 K, the electrical conductivity of $Na_2Fe_2Ti_6O_{16}$ can be well fitted with small polaron hopping model. For a further verification of the model, we measured the room-temperature optical reflectivity and derived the optical conductivity (σ(ω)) with Kramers–Kronig analysis. A mid-infrared peak in σ(ω) confirms the presence of small polarons. From 468 K to 1000 K, $Na_2Fe_2Ti_6O_{16}$ is an n-type oxide and exhibits a temperature-independent Seebeck coefficient (~ –590 μV.K^{-1}), in agreement with the small polaron hopping mechanism. The thermal conductivity decreases with increasing temperature from 16.5 W.m^{-1}.K^{-1} (373 K) to 3.4 W.m^{-1}.K^{-1} (1000 K). $Na_2Fe_2Ti_6O_{16}$ shows a maximum figure of merit (ZT) ~ 3 × 10^{-4} at 1000 K.

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The effect of ceramic particles coated on the polyethylene separator for improving the electrochemical performance and thermal stability of lithium ion batteries

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Keywords: ceramic-coated separator, lithium ion batteries, electrochemical performance, thermal stability

Ceramic-coated separators are prepared by dip coating process for improving the electrochemical performance and thermal stability of lithium ion batteries. We coated ceramic particles (Al_2O_3 or Li_2O-SiO_2-TiO_2-P_2O_5) slurry on polyethylene separator through dip coating process after prepared slurry with a poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-12wt%HFP) copolymer. We investigated the physical properties of separators as a function of coating thickness, such as thickness, weight, air permeability, electrolyte uptake,

porosity, thermal shrinkage and morphology. Also, its electrochemical properties are performed at 25 °C using a half coin cell with $LiCoO_2$ as cathode, Li metal as anode and $LiPF_6$ in EC/DEC as electrolyte. Compared to a pristine polyethylene, thermal stability of the all ceramic-coated separators is improved. The cells are proven to have better capacity retention than for cells prepared with pristine polyethylene. In particular, the separator prepared with Li_2O-SiO_2-TiO_2-P_2O_5 slurry showed the best result in capacity retention. From this study, we supposed that the separator prepared with Li_2O-SiO_2-TiO_2-P_2O_5 slurry can be potential candidate as a separator for rechargeable lithium-ion batteries that require thermal safety and good capacity retention.

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RuO_2 nanoparticle passivated ZnO@MnO_2 core-shell nanorod arrays for supercapacitor application

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Keywords: ZnO nanorods, MnO_2, core/shell hybrid architecture, supercapacitors, energy storage

The nanostructured hybrids electrodes with different featured materials are promising for improving the energy storing capacity of the supercapacitors. Hitherto, it is challenging for the researcher to develop the high-performance nanohybrid electrode materials with controllable size, composition and morphology. Here, we have prepared the ternary core–shell composed ZnO@MnO_2@RuO_2 nanorod arrays on the flexible stainless steel mesh (SSM) through the layer-by-layer process. In the first step, the ZnO nanorods are prepared on the SSM by low temperature hydrothermal process. Later, the ZnO nanorods are decorated with the MnO_2 and RuO_2 by electrodeposition and dip and dry process, respectively. The passivation of highly conducting RuO_2 nanoparticles on the surface of binary ZnO@MnO_2 is allow the easy and fast charge transfer process to further improve the electrochemical performance of the supercapacitor. Due to enhanced electron transfer process, the charge transfer resistances of the ZnO@MnO_2@RuO_2 nanorod arrays are drastically reduced. The electrochemical test for the ZnO@MnO_2@RuO_2 nanorod arrays are performed in the Na_2SO_4 electrolyte, which gives the ultrahigh specific capacitance (more than 1000 F/g at 5 mV/s) with excellent a capacitance retention of 94% after 20000 CV cycles at 100 mV/s scan rate, indicating the excellent electrochemical features of the ZnO@MnO_2@RuO_2 nanorod arrays.

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Creep properties of fully dense $BaZr_{1-X}Y_XO_{3-X/2}$ electrolyte materials for PCFCs

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Keywords: creep, mechanical properties, Yttrium-doped Barium Zirconate, electrolyte, PCFCs

Yttrium-doped Barium Zirconate is considered an attractive alternative to Yttria-Stabilised Zirconia electrolyte material in Solid Oxide Fuel Cells. While numerous studies have dealt with the preparation of dense ceramics and with the study of influence of composition on proton conduction properties, very little is known at present about the mechanical properties of Yttrium-doped Barium Zirconate compounds. We have thus started an exhaustive study of the mechanical properties of high density (> 95%) sintered $BaZr_{1-x}Y_xO_{3-x/2}$ compounds.

Polycrystals of Yttrium doped Barium Zirconate made through conventional sintering were prepared from nanopowders synthesized through a combustion route. The samples were then characterized mechanically at high temperature[1–3].

Compressive creep tests have been performed at constant speed and load at temperatures ranging from 1100 to 1300 °C. The objective was determine the effective diffusion coefficient and identify the atomic mechanisms of plastic deformation and the origin of failure of these materials at high temperature. A gradual brittle–ductile transition was observed with increasing temperature and/or decreasing strain rate. Grain boundary sliding is the main deformation mechanism in the ductile region. The experimental results have been correlated with microstructural observations by scanning and transmission electron microscopy.

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Three phase composite PZT/Al/PU for energy storage application

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Keywords: dielectric, composite, energy, storage, density, efficiency

Piezoelectric composites are widely studied due to their good performances. Several kinds of these composites have been developed for sensing and actuation applications, however, most of them are not used for energy storage devices, because of their low dielectric properties. In this research work, a three-phase composite was developed. This latter was obtained by adding a small amount, up to 3%, of Aluminum (AL) to the PZT/PU composite. The Dielectric constant was found to be clearly increased with the increasing volume fraction of Aluminum. A comparison of piezo- and ferroelectric activities between aluminum doped and undoped composites reveal a high improvement of the energy storage density, which reaches 11J/cm^2. This novel three-phase composite can be used for multifunctional embedded capacitors applications.

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Nanostructuring of dense SnO_2 ceramics by SPS

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Keywords: tin oxide, spark plasma sintering, nanostructuring

SnO_2-based materials are widely used for catalytic and gas-sensing applications, as well as electrodes.[1,2] Most of these applications could benefit from nanometer-sized crystalline particles. Therefore, a new high yield (>90%) synthesis route at low temperature in aqueous solution has been developed. The average particle size is 4–6 nm according to TEM images and specific surface area determined by the BET method is 160 m^2.g^{-1}.

Sintering fully dense SnO_2 ceramics bodies is also complicated due to the vaporization of tin monoxide which should occur at a high rate above 1100 °C.[3] Therefore, different strategies such as addition of sintering agents or hot pressing have been developed.[4,5] However,

these techniques still require high temperatures and therefore, do not appear suitable for dense nanostructured ceramics. Spark Plasma Sintering (SPS) is now a well known technique to sinter dense ceramic bodies of oxide materials at low temperature: for instance, dense Al-doped ZnO nanostructured ceramics have been sintered at only 500 °C.[6] Therefore, the sintering of dense SnO_2 nanostructured ceramics by SPS has been studied and the key parameters have been determined. Densities higher than 95% have been reached with an average grain size of circa 60 nm.

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Synthesis & characterization of $Li_7La_3Zr_2O_{12}$ solid electrolytes for all solid-state li-ion batteries

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Keywords: all solid-state Li-ion batteries, Garnet type electrolytes, $Li_7La_3Zr_2O_{12}$, EIS

All solid-state Li-ion batteries are attracted much attention for high energy density requiring applications such as electrical vehicles since their enhanced safety compared to conventional batteries that include liquid based organic electrolytes. Extensively studied solid electrolytes in all solid-state Li-ion batteries are LISICON, Perovskite, LIPON and Garnet type of electrolytes. Among them, Garnet type Li-ion conductors are considered as an alternative candidate for replacing organic liquid electrolytes[1,2].

Cubic phase $Li_7La_3Zr_2O_{12}$ (LLZO) is relatively new composition[3]. However, low temperature stable form of LLZO is tetragonal and several attempts have been done to stabilize cubic phase at room temperature. These are either increasing sintering temperature over 1200 °C or adding stabilizers such as W, Ta, Ba, Y and Al[4]. Recently, it has been found that lowering the cubic phase stabilization temperature below 1000 °C by using solution based synthesis techniques is possible. But, there is a lack of systematic investigations of different precursors on the cubic phase stabilization during LLZO synthesis. Since the crystal structure of LLZO is similar with ZrO_2, the bonding ability of Zr sources will be more important than the other elements in the structure.

In this work, varying amounts of Al (0–40% mole) incorporated LLZO was synthesized by using nitrate precursors of Li, La, Zr and Al. In order to investigate the effect of different Zr precursors, oxychloride precursor was also used. The radial shrinkage was measured according to the pellet diameter size before and after sintering. Crystal structures of calcined powders were measured by XRD. True density and ionic conductivities of powder-bed sintered pellets using cubic phase stabilized powders was measured by Archimedes Method and AC Impedance Spectroscopy respectively. Cubic phase stabilization, types and changes of impurity phases with different Al amounts will be discussed in terms of different Zr precursors.

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Study of optical and morphological properties of vanadium dioxide nanofibers and thin films prepared by electrospinning and wet chemical coating techniques

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Vanadium oxidehave many application areas such as gas sensors, photocatalysis, solar cells thermochromics, electrochromics, optic/electronic switching devices and energy storage devices due their superior chemical and physical properties. This great interest of vanadium oxides is based on two main factors; range of oxidation states of vanadium and variability of the oxygen coordination geometries. The principal oxides of vanadium occur as single valence in oxidation states from V2+ to V5+, in the form of VO, V2O3, VO2, and V2O5. However, the vanadium–oxygen phase diagram also includes mixed valence oxides containing two oxidation states, such as V6O13 with V5+ and V4+ and a series of oxides between VO2 and

V2O3 (e.g., V8O15, V7O13, V6O11, etc.) which contain V4+ and V3+ species. In an oxide, the mixed vacancy is formed by introducing oxygen vacancy defects.

In this study, vanadium dioxide and hydrogen peroxide solutions with and without PVP polymer were prepared as a nanofiber, nanorod and thin film on smooth surfaces by electrospinning and wet chemical coating techniques respectively. Optical and morphological properties of the oxides were investigated by TEM, TEM-EDX, XRD, SEM and UV-Vis methods. To the best of our knowledge, this is the first time single crystalline V6O13 and nanorods were obtained with wet chemical coating on glass and ITO-coated glass substrates. Detail electrochemical measurement were examined of all samples on various substrates. Composition and nanostructure of the samples affect the crystallinity, stochiometry and electrochemical properties dramatically. It is worth to mention that these novel samples are good candidates for electrode of battery, supercapacitors and sensor applications.

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Nanocrystalline $TiNb_2O_7$: a new photocatalytic material

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Keywords: $TiNb_2O_7$, sol-gel, photocatalysis, nanoparticles, TiO_2, Nb_2O_5

A detailed study of a novel synthesis via colloidal sol–gel route for obtaining nanoparticulate TiO_2:Nb_2O_5 sols was performed. The H^+:(Nb^{5+}:Ti^{4+}) molar ratio was controlled in order to determine the best conditions of synthesis. Moreover, the combination of the data measured with optical techniques such as laser diffraction, dynamic light scattering and multiple light scattering with a near-infrared light allowed to follow up the evolution of the peptization process. The obtained results indicate that the colloidal sol–gel synthesis is a good procedure for obtaining TiO_2:Nb_2O_5 either as stable nanoparticulate sol or as a nanosized powder. Amorphous nanoparticles with an average size of 10 nm were obtained by controlling the synthesis variables. After calcination of the xerogels at temperatures between 500 ºC and 800 ºC, different crystalline phases were obtained, among them $TiNb_2O_7$ as the major one. Crystalline phase composition was found to have a significant influence on the photocatalytic activity. The best photocatalytic performance was observed for the material mainly constituted by the monoclinic-$TiNb_2O_7$ phase.

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Alkaline carbonates as sintering aid for $Ce_{0.1}Gd_{0.9}O_{1.95}$

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Keywords: CGO, sintering aid, ionic conductivity, electronic conductivity

CGO (Gd-doped ceria) is amongst the most studied electrolyte materials for Solid Oxide Fuel Cells (SOFC). With higher ionic conductivity when compared to zirconia-based electrolytes, the main drawbacks of this material are the onset of electronic conductivity when exposed to reducing conditions, and the usually demanding firing temperatures (>1400 °C) to reach full densification. Lowering the SOFC operating temperature is the simplest solution for the first problem. Sintering aids or chemical routes to obtain reactive powders are the best known ways to avoid the second drawback. In this work emphasis will be in the first approach, following previous activity in this direction.[1,2]

Pellets of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) were fabricated via liquid phase assisted sintering at 900–1100 °C by adding different contents of $(Li_{0.52}Na_{0.48})_2CO_3$ (NLC) as sintering aid. The effects of this sintering aid on the structure and microstructure were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. Complementary impedance spectroscopy measurements performed between 200 and 750 °C included simple tests in air or as a function of the oxygen partial pressure (pO_2) down to about 10^{-20} atm.

XRD analysis of as-prepared powders indicates that the carbonates do not incorporate into the cubic structure of CGO. Densification results showed that with small additions of NLC the densification could reach 93–96% at 1000 and 1100 °C. Electron microscopy revealed a dense well defined microstructure. A slight improvement of electrical properties was also seen with respect to conventional CGO pellets fired at 1500 °C. A small increase in conductivity under low pO_2 also suggests that the sintering aid might partly block the electronic conductivity of CGO. These results indicate the potential of this route to produce a competitive electrolyte for low temperature.

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Broad band plasmonic nanomaterials included ZnO film for high performance polymer photovoltaics

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Keywords: ZnO, polymer solar cell, photovoltaic, surface plasmon, nanomaterials, composite

Metal oxides including ZnO have been commonly used as electron transport materials (ETMs) for the fabrication of polymer photovoltaicls for their high electrical conductivity and carrier mobility.[1–3] Recently, researchers have tried to improve the light absorption capability of photovoltaics by introducing metallic nanomaterials into either electron or hole transport layer to further raise up the power conversion efficiency (*PCE*) of photovoltaic devices. In this paper, we report the use of broad band plasmonic nanomaterials to improve the electrical conductivity and carrier mobility of ZnO film as well as the light absorption efficiency of the polymer photovoltaics. We adopt gold nanorod-in-shell (Au NR-in-shell) nanomaterials to be embedded in ZnO film to serve as a new ETM in the fabrication of polythieno[3,4-b]-thiophene/benzodithiophene:[6,6]-phenyl C_{71} butyric acid methyl ester (PTB7:$PC_{71}BM$) photovoltaics. In the presence of Au NR-in-shell nanomaterials, there are large improvements in the short circuit current density (J_{sc}) and fill factor (*FF*) of devices. The enhanced J_{sc} and *FF* are attributed to the combination of the enhancement in light-trapping, series resistance, carrier lifetime, and device mobility, leading to a realization of a *PCE* of 9.01% from 7.94%. Our approach shown here can pave a key step for the further development of high performance optoelectronic devices.

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Material characteristics and electrochemical performance of the $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-δ}$ electrolyte for solid oxide fuel cell

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Keywords: solid oxide fuel cell, electrolyte, bismuth oxide, solid state reaction, defect

Bismuth oxide-based materials exhibit high oxide-ion conductivity due to their high concentration of oxide vacancies and have been proposed as potential electrolyte materials for SOFC and oxide sensors. In this study, $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-δ}$ ($0.12 \le x \le 0.24$) oxygen ion conductors were synthesized by the solid-state reaction method. The phase, microstructure and electrochemical performance of samples were detected by XRD, SEM, TEM and AC impedance. Small amount of the $CaZrO_3$ and $Ca_{0.15}Zr_{0.85}O_{0.85}$ second phases were observed on the grain boundary of the cubic fluorite structure $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-δ}$ matrix. The lattice parameter *a* of the Bi0.85-xCa0.15ZrxO1.5-δ is in the range of 5.512~5.525 Å. Since the ionic radius of Ca2+ (0.99 Å) and Zr4+(0.79 Å) is smaller than the ionic radius of Bi3+ (0.96 Å), therefore, the addition of CaO and ZrO2 tends to reduce the lattice parameters. However, the lattice parameter a and unit volume of $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-δ}$ δ as x≥0.21 are apparently higher than that of $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-δ}$ δ as x≤0.18. It is found that the diffraction peaks belong to $Ca_{0.15}Zr_{0.85}O_{1.85}$ second phase is apparently observed as x≥0.21. Therefore, it is suggested that the doping amount of Ca2+ and Zr4+ in $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-δ}$ structure decreased due to the formation of second phases of $CaZrO_3$ and $Ca_{0.15}Zr_{0.85}O_{1.85}$. The conductivity of all Bi0.85-xCa0.15ZrxO1.5-δ samples increases as the temperature increases. The Bi0.70Ca0.15Zr0.15O1.5-δ sample has the highest conductivity of 0.05 S/cm at 750 °C. The typical impedance spectra of $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-δ}$ samples show that the main resistance come from the charge transfer polarization at low temperatures and the grain boundary resistance dominated as temperature increased above 600 °C due to the second phases of $CaZrO_3$ and $Ca_{0.15}Zr_{0.85}O_{1.85}$ appeared on the grain boundary. The result of Temperature-Programmed Reduction curves of the $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-δ}$ samples in 5% H_2- 95% Ar atmosphere show that

all $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-\delta}$ reduced in the temperature range of 300–380 °C. It is still a challenge for $Bi_{0.85-x}Ca_{0.15}Zr_xO_{1.5-\delta}$ to be applied as the electrolyte of SOFC due to reduction problem in low partial oxide pressure atmosphere. A high protection layer is needed if Bi_2O_3-based materials used as the electrolyte of SOFC.

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Synthesis and characterization of composite cathodes with mixed conductivity for protonic ceramic fuel cells

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Keywords: Solid Oxide Fuel Cells, mixed conductivity, composite

Research into clean-energy sources has grown in recent decades. Fuel cells are of particular interest due to their high efficiency and low pollution when compared to technologies based on fossil fuels.[1] Protonic ceramic fuel cells (PCFCs) based on $BaCeO_3$ are recognized as the most promising for operation at intermediate temperatures (450–650 °C). Partial substitution of cerium with zirconium is one of the best ways to optimize transport and mechanical properties, as well as improve stability in CO_2 H_2O, H_2S and SO_x-containing atmospheres.[2] Composite cathodes with mixed conductivity have shown an improved performance in PCFCs.[3] In this work, a composite formed by $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ (BZCY72) and $LaNi_{0.5}Cr_{0.5}O_3$ (LNC) was investigated. BZCY72 and LNC powders were obtained by the Pechini method and mixed mechanically in the weight ratios of 25/75 and 50/50 BZCY72/LNC. The compositions were pressed and sintered at 1400 °C. The sintered composites were characterized by X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM / EDS) and impedance spectroscopy. XRD results showed that the 25/75 and 50/50 composites presented BZCY72 and LNC phases, and a small amount of a third phase, resulting from the decomposition of BZCY72. The EDS mapping of the two studied compositions showed percolation of the BZCY72 phase for two compositions studied. The conductivity measurements in several dry gases and atmospheres humidified with H_2O and D_2O showed the presence of electronic and protonic conductivity for these composites.

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Production and characterization of waste glass based lightweight aggregates with colemanite

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Keywords: aggregates, colemanite, lightweight pellets, fluxing agent

The growing market in the building-block industry lead to an increasing demand for lightweight aggregates. Producing lightweight aggregates reduces the bulk density and make easier to work and transport the related products. Also, these products improve technical specifications (e.g. good thermal and acoustic insulation, lightness of concrete).[1,2] On the other hand, lightweight aggregates are defined as materials lighter than water and distinctly more porous than sand, gravel and ground rock, which are commonly referred to as dense aggregates.[3] In addition to that, another valuable point of producing lightweight aggregates reduce the consuming of natural mines. In this study, the possible usability of waste glass for the production of lightweight aggregate has been studied. To develop new receipt of lightweight aggregate from waste glass (WG) and Colemanite (C) was added to new formulation to form highly porous micro-structure and to achieve expending capability of aggregates at the 750–850 °C temperature. For these purpose, different mixture and various sintering temperature was investigated in laboratory scale. The characterization analyses of microstructure by electron microscope (SEM), density and mineral phase analysis (XRD) revealed that both a glassy phase matrix on the surface and interconnected/isolated closed microporous inside the aggregates were occurred with the addition in different amount of Colemanite which is known as a flux agent.[4]

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Valorisation of fired ceramic wastes as a replacement materials in production of AAC

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Autoclaved aerated concrete (AAC) is a highly porous and well-known walling materials with its good fire resistance, low density, low shrinkage and low thermal conductivity when compare with the other building materials. It usually produces by using lime, silica sand, ordinary Portland cement, gypsum and Al metal powder (first to form hydrogen gas and after pores inside). On the other hand, some wastes or natural raw materials like pozzolanas can also be uses as a raw or replacement materials. This paper is focused on to study the suitability of fully replacing fired ceramic sanitary ware wastes (CSW) replaced to silica sand in standard receipt. CSW were taken from Ege Ceramic Company which was located in Manisa/Turkey. The products produced both standard (S) and with CSW receipts were characterized by thermally, mechanically and density. The result shows that CSW can easily be used in place of silica sand in production of AAC because of similar technical properties was observed (Table 1). In addition to that using CSW decreases both thermal conductivity and density of the samples but compressive strength of the samples are nearly same.

Table 1. Thermal, density, compressive and A factor values of standard (G2/035) and with CSW replacing sample of AAC

Properties	**S (G2/035)**	**With CSW**
Thermal conductivity (W/mK)	0.088	0.082
Density (Kg/m^3)	377	373
Comprehensive strength (N/mm^2)	2.15	2.09
A factor	945	939

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Room-temperature sodium/sulfur battery using β″ alumina solid electrolyte

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Keywords: β″ alumina, solid electrolyte, room temperature, sodium/sulphur battery

Use of conventional energy resources such as fossil fuels has caused global environmental pollution. To reduce this, intensive efforts have been dedicated to the development of clean energy technologies, including solar, wind, and others. However, due to their dependence on specific natural environments, the combination of these technologies with large-scale energy storage systems is in high demand. One of the most desired energy storage systems is a large-scale secondary battery storage system whose secondary battery has a low cost and high energy density. The Na/S battery is a typical secondary battery whose characteristics are in good accordance with these requirements.[1] Sodium and sulfur are highly attractive electrode materials, with many advantages such as abundance in nature, high capacities, and low cost. A high temperature Na/S battery has a high theoretical energy density of 760 Wh kg-1. These advantages have led to worldwide commercialization of high temperature Na/S batteries. However, the high temperature Na/S battery requires an operating temperature of over 300 °C to secure liquid states for both the cathode and anode, and so a portion of the generated electricity is continuously consumed to heat the battery, which decreases the energy efficiency of the device. In addition, physical contact between the cathode and the anode due to failure of the solid electrolyte can cause a fire or an explosion. In order to overcome these drawbacks, our group has investigated room temperature Na/S batteries with solid-state electrodes, using sodium for the anode and sulfur for the cathode.[2] Room temperature Na/S batteries are safe and have a higher theoretical energy density of 1230 Wh kg-1 based on the final discharge product Na_2S. However, these Na/S batteries have a low first discharge capacity and poor cycling properties. In this work, a room temperature Na/S battery has been designed to improve the cycling performance using β″ alumina solid electrolyte with a S/C composite and liquid electrolyte. The resulting Na/S battery shows a high first discharge capacity of 855 mAh g^{-1} and coulombic efficiency close to 100%, as well as stable cyclability.[3]

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Electrical characterization of $Ba_5(Zr,Ti)Nb_4O_{15}$ hexagonal perovskites

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Keywords: proton conduction, hexagonal perovskites, Pechini method, solid oxide fuel cells

Among the common materials used to produce solid oxide fuel cell's (SOFC's) electrolytes and electrodes are oxides with perovskite structures. Nowadays, there are many different studies on this field, where developing new proton conduction materials to improve SOFC's performance is one of them. Present work evaluated the viability of compound $Ba_5Nb_4O_{15}$ (BNO) as a candidate to produce SOFC's elements. This compound presents a hexagonal perovskite structure and recent papers point that this structure can shows some indication of proton conduction. At present study, it was evaluated BNO synthesis through an alternate method to solid-state reaction, based on Pechini method and using different oxides as precursors. The addition effect titanium and zirconium on structure and electric properties was also studied. Synthesized powders were pressed and sintered at temperatures of 1400 °C and 1450 °C. Sintered samples were characterized by X ray diffraction, scanning electron microscopy, porosity and apparent density and by electrical conductivity measurements. BNO phase was successful obtained in all synthesis, although non-stoichiometry phases were present on Pechini sample after calcination at 900 °C. After sintering at 1450 °C, Rietveld refinement pointed out these phases were no longer present. To improve densification samples, the synthesized powders were milled to reduce the size of agglomerates and bulk porosity achieved after sintering was less than 5%. Electrical conductivity measurements in humid (H_2O) atmosphere and heavy water (D_2O) atmosphere of sintered samples showed an indication of proton conduction in this structure. Addition of titanium and zirconium dopants produced grain refinement, but it was not efficient to improving electrical conductivity.

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Advanced ceramic and their composites based on zirconia for energy application

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Keywords: advanced ceramic, yttria stabilized zirconia, porous carbon, thermo-mechanical properties, energy application

The employment of advanced ceramic materials in energy production, distribution, storage and conversion, plays a key role in the development of sustainable and clean energy. Thus the elaboration and exploration of ceramic matrix composites became necessary in order to enhance the thermo-mechanical properties of ceramic, which suggest further energy application in fuel cells, photovoltaic, wind energy, supracapacitors, hydrogen storage material, high temperature superconductors.[1] The focus consists on determining the variation of the toughness, hardness, thermal conductivity, coefficient of thermal expansion and the microstructure for yttria stabilized zirconia and zirconia matrix based composite with porous carbon, CNTs and graphene additives. The microstructural, chemical, and thermo-mechanical behaviours of different zirconium dioxide (ZrO_2) powders have been investigated by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS) and X-ray Spectroscopy (XPS). Furthermore the zirconum dioxide (ZrO_2) based powders have been sintered with sub-micro size structure by using Spark Plasma Sintering (SPS).

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SnSb alloys as anode materials for Li-ion and Na-ion batteries

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Keywords: Li-ion batteries, Na-ion batteries, tin, antimony, anode

In recent years, Na ion battery has drawn much attention as an alternative large scale energy storage device due to the relative abundance of sodium to lithium in earth. Sn and Sb have been investigated as anode materials for Li-ion and Na-ion batteries in last few years, and the results show that Sn based anode materials demonstrate relatively high capacity, while the Sb based anode materials present better cycling performance. SnSb alloy anode material has also been studied, in the hope that SnSb alloy can have high capacity from Sn and high cyclic stability from Sb. In this study, SnSb alloys with extra Sn or Sb are prepared via simple ball milling and their Li and Na electrochemical behaviors are systematically investigated with different starting materials and process variables. Further, the effective way to improve the Li and Na electrochemical performance with SnSb alloy anode is also discussed.

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IIon-exchange property of lepidocrocite-type layered titanate

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Keywords: lepidocrocite-type layered titanate, ion-exchange

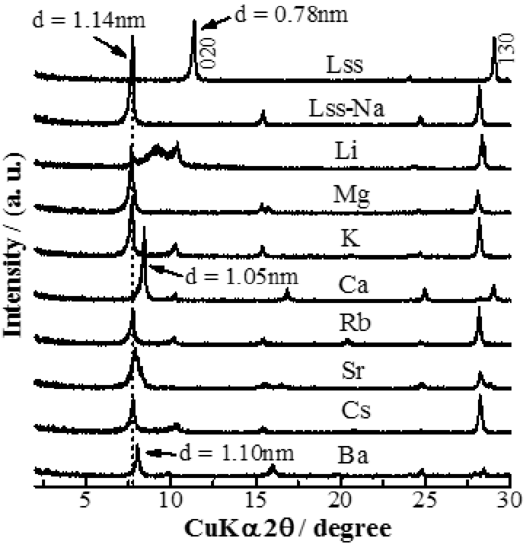
Ion-exchange and intercalation are low energy and eco-friendly reaction because these reactions are conducted at relatively low temperatures. Layered inorganic materials can improve ion-exchange or catalytic properties by ion-exchange, thus, layered inorganic materials have been expected to be promising materials in chemical industry. In this study, lepidocrocite-type layered sodium titanate ($Na_{0.70}K_{0.05}Ti_{1.75}Li_{0.25}O_4$, Lss-Na) was prepared and its ion-exchange property with various cations was investigated.

Lepidcrocite-type layered potassium titanate ($K_{0.75}Ti_{1.75}Li_{0.25}O_4$, Lss) was stirred in aqueous NaCl solution at room temperature for 4 days to for ion-exchange of interlayer potassium ion. After drying at room temperature for 2 days, Lss-Na was obtained. The ion-exchange properties of Lss-Na against metal cations was examined using metal chloride under the same conditions. The structure of the samples were estimated using XRD and DTA-TG, and the adsorption amount of various metal cations in the samples were determined by ICP.

Fig. 1 shows the XRD patterns of Lss, Lss-Na and ion-exchanged samples. The interlayer space (d) increased from 0.78 nm (Lss) to 1.14 nm (Lss-Na) by ion-exchange. This suggests that the interlayer space of Lss-Na was hydrated. Li^+, Ca^{2+}, and Ba^{2+} exchanged samples shows the decreased interlayer space comparing Lss-Na. From the ICP analysis, the chemical formula for Lss-Na is estimated to be $Na_{0.70}K_{0.05}Ti_{1.75}Li_{0.25}O_4$. Assuming that the ion-exchangeable interlayer cations is $Na_{0.70}K_{0.05}$ in Lss-Na, the uptake degree of the samples were calculated (Table 1). Lss-Na especially uptook Ca^{2+} ion: the 92% interlayer cations were exchanged by Ca^{2+}.

Table 1. The uptake degree of ion-exchanged samples

Ion	Li^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Uptake degree	24%	27%	0%	11%	17%	92%	17%	50%



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Anode ceramic material for sodium battery

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Keywords: solid state battery, sodium battery, ceramic anode

At the present times, there is an urgent need to develop high-capacity, operationally safe, mechanically robust, and cost-effective rechargeable battery systems to enable a widespread deployment of all-electric vehicles, renewable energy and smart grid infrastructure of our future. The state-of-art rechargeable batteries use two primary types of electrolyte solutions, aqueous and organic, to support the migration of the working ion. Batteries based on aqueous electrolytes are safe in operation, but have low voltage and energy capacity. In contrast, those based on organic electrolytes exhibit 2–3 times higher voltage and energy density than the former, but are unsafe in operation, particularly at high charging/discharging rates. The all-solid-state Li^+ and Na^+ rechargeable batteries have been considered the next-generation energy storage devices because the use of solid inorganic electrolytes and electrodes exclude leakage, volatilization, or flammability.

This work focuses on the optimization of the synthesis parameters to obtain the very promising anode material $Na_2Ti_3O_7$ (NTO) for an all sodium solid state battery. The reaction mechanism to produce the pure phase was carefully studied. Moreover, the possibility to combine NTO material with an electrical conductive phase to improve the electrical performances of the anode was evaluated.

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Microstructure and ion conducting properties of Al-substituted $Li_7La_3Zr_2O_{12}$ ceramics sintered at high temperature

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Keywords: Li^+ ion conductor, garnet oxide, sintering, microstructure, AC impedance measurement

Al-substituted $Li_7La_3Zr_2O_{12}$ (Al-LLZ) ceramics show high lithium ion conductivities over 10^{-4} S cm^{-1} at room temperature and chemical stability against Li metal, and thus have attracted attention as solid electrolytes for all-solid-state batteries(1). Interestingly about dense Al-LLZ ceramics (density: >90%), wide range values of the activation energy for ionic conduction (E_a) from from 25 kJ mol^{-1} (2) to over 40 kJ mol^{-1} (3) have been reported. However the determining factors of E_a have remained unclear.

In this study, two dense Al-LLZ sintered ceramics with different microstructure were prepared to investigate the relationship between microstructure and conducting properties. One ceramic was composed of the grains with a few micrometers to about 20 μm and the observed fracture mode was dominantly intergranular. The other ceramic was composed of the smaller grains with mainly about 1 μm and the observed fracture mode was almost completely transgranular. In addition, SEM observation suggested that these two ceramics did not have remarkable grain-boundary phases like an amorphous phase.

Conductivities were determined by a conventional AC impedance measurements at the temperature range of 25–80 °C. The former ceramic with larger grains showed the total conductivity of 3.6×10^{-4} S cm^{-1} and the E_a of 32 kJ mol^{-1}. The latter with smaller grains showed 4.4×10^{-4} S cm^{-1} and 26 kJ mol^{-1}. In other words, the ceramic in which grain growth was suppressed and transgranular fracture occurred exhibited the low E_a even compared to many literatures. To investigate a contribution of grain-bulk and grain-boundary resistances for this highly conducting Al-LLZ, AC impedances of the ceramic with Au electrodes were measured up to the higher frequencies of 100 MHz at the low temperature of –20 °C. A specially adjusted measurement system was utilized to accurately measure small impedances at high frequencies. As a result, one depressed inseparable arc, which was converged to the origin at high-frequency end, and a liner spike at lower frequencies were observed. This result indicates that the present Al-LLZ ceramic do not have much larger grain-boundary resistances compared to grain-bulk one and these resistances cannot be intrinsically separated against well densified LLZ ceramics at temperature above –20 °C.

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Mechanical characterization of substituted $Li_7La_3Zr_2O_{12}$ using nano- and microindentation

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Keywords: solid electrolytes, battery, mechanical properties, nano and microindentation

Conventional lithium ion batteries (LIB) are based on liquid electrolytes due to their very high ionic conductivity; however, they suffer from serious drawbacks related to their flammability and leakage. Solid state Li ion conductors, such as garnet type materials, are expected to possess a higher thermal stability, larger chemical stability compared to metallic Li anodes[1] and supress detrimental dendrite formation[2]. Mechanical boundary conditions and operation as an electrolyte could induce microcracking, structural and mechanical failure that terminates the battery life. Therefore, the reliability of solid electrolytes is important to warrant long-term reliability of solid state batteries. However, literature quoting mechanical properties is limited, hence, studies on the relationship of mechanical behaviour and operation conditions is required.

The current work presents a mechanical assessment of Ta-substituted $Li_7La_3Zr_2O_{12}$ based on nano- and micro-indentation characterization, yielding elastic modulus, hardness and fracture toughness with their actual dependency on the apparent penetration depth. Hence, results are discussed with particular emphasis on the effect of local deformation behaviour of these ceramics. The indentation tests were based on different procedures using either constant loads or loading cycles, revealing different sensitivities for local/global behaviour related to grain, grain boundary, pores and micro-cracks as well as softening due to surface deterioration via the impact of environmental moisture. The interpretation of the results was also supported by complementary optical and electron microscopy as well as roentgenographic assessment.

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Facile synthesis of BiOBR/rGO composite with enhanced photocatalytic efficiency under visible light

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Keywords: BiOBr, reduced graphene oxide, visible-light active photocatalyst, rhodamine B, nitrogen gas

The high efficiency visible-light active BiOBr/rGO composite photocatalysts was successfully prepared via a simple precipitation method at room temperature. The precursors were prepared by dissolving Bi)NO3(3.5H2O and KBr in glycerol and distilled water, respectively. Various mounts of reduced graphene oxide)rGO; 0.1–2 wt%) were added into the mixed solution precursors, and stirred at room temperature to get precipitated powder without further heat treatment The obtained products were characterized for phase, morphology, optical properties and surface area by X-ray diffraction, filed-emission scanning electron microscopy, transmission electron microscopy UV-Vis diffuse reflection spectroscopy and Brunauer–Emmett–Teller, respectively. The photocatalytic efficiency of prepared BiOBr/rGO composites for decomposition of rhodamine B dye and nitrogen oxide gas under visible light irradiation were examined. It was shown the enhancement in photocatalytic activity of BiOBr by compositing with rGO, in which the highest activity for degradation of rhodamine B and nitrogen oxide gas were obtained from samples containing 1 and 0.25 wt% of rGO, respectively.

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Ceramic functionalized flow batteries electrodes for urban electric micro-vehicles

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In the frame of the SPECTRA (Smart Personal $C0_2$-free TRAnsport) project, which proposes a new perspective combining electric micro-vehicle[1–3], infrastructure recharge and intelligent management of urban mobility, design and fabrication of new electrodes for flow batteries has been developed. Economically convenient and technically competitive mobile cell storage solutions must ensure not only response time and storage capacity suitable for meeting both the generation and grid needs, but must also show mechanical instability[4,5] to afford embedding in the stack and mobile working condictions.[6]

In this work, the fabrication of ceramic functionalized flow batteries electrodes (CF-FBE) has been carried out. CF-FBE based on carbon nanofibers (CNFs) provided by Grupo Antolin and either silicon carbide (SiC) or alumina (Al_2O_3) has been developed to improve performance on working conditions. Obtained results about electrode fabrication have been discussed in the present document and related with the electrode performance and corrosion resistance.

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On the electrical performance of zirconia based composite electrolytes

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Keywords: zirconia, composite electrolytes, alkali metal carbonates, impedance spectroscopy

Composites consisting of mixtures of oxide-ion conductors and alkaline metal carbonates are new types of electrolytes that may find application in Low Temperature/Intermediate Temperature Fuel Cells (LT/IT-SOFCs). The attention given to this class of materials is related to their high ionic conductivity (>0.1 S/cm at T>500 °C) with respect to standard ceramic electrolytes, allowing low operating temperatures.

Zirconia-based materials are well-known electrolytes for solid oxide fuel cells (SOFC), although with moderate ionic conductivity. The use of such oxides as matrix of a composite electrolyte could combine the excellent mechanical performance of zirconia with the high ionic conductivity of the salt mixture. However, the reactivity between doped zirconia and alkali-metal carbonates is known. Doped zirconia like PSZ (partially stabilized zirconia) or TZP (tetragonal polycrystalline zirconia) also show a tendency to degradation, with phase changes induced by thermal treatment and/or exposure to water vapour.

The present work aims to assess the performance of composite electrolytes based on pure monoclinic zirconia, the stable room temperature polymorph of this oxide. This solution is feasible since the sintering temperature can be kept below the critical monoclinic to tetragonal phase change, where a large volume change is known to occur often determining the failure of the ceramic.

In this context, zirconia-based composite electrolytes with sodium and lithium carbonates (NLC) were prepared in a two-step method. This consists of the preparation of the ceramic skeleton using a small amount of NLC as sintering aid, and posterior impregnation with the carbonate mixture. The skeleton and the composite were investigated by impedance spectroscopy from 300 up to 600 ºC. These composite materials were also characterized by X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS).

Distinct composites based on zirconia sintered under various conditions, originated a wide range of microstructural characteristics. Impedance spectroscopy revealed a strong relationship between the performance of the ceramic phase alone and after impregnation.

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Lead free BS-PT ceramics for energy harvester applications

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Lead and lead free piezoelectric ceramics can be used for various energy related devices due to their piezoelectric properties.[1] In general piezoelectric materials were easily respond to environmental mechanical energy. Piezoelectric materials can generate high voltages and low currents corresponding to the mechanical energy. Also some time, lead and lead free piezoelectric ceramics can dissipate mechanical energy by converting them to the electrical energy. [2] As a result, piezoelectric materials can be applied to the shock absorber system or energy harvesting system at the same time. In general, shock absorber system or energy harvesting system require complicate circuit to dissipate or store maximum energy. Therefore, recently, these kinds of piezoelectric energy systems have been attracted much attention. these kinds of converting force can be explained by the piezoelectric effects (from mechanical energy to electrical energy) or inverse piezoelectric effects (from electrical energy to mechanical energy), respectively.[3]

In this study, a passive damping system based on multilayer $(Bi,Sc)O_3$–$(Pb,Ti)O_3$ piezoelectric ceramics was investigated by employing weight impact system. The ceramics were prepared by employing a traditional solid-state reaction. A drop weight of 0.75 kg was applied to the area of 10×10 mm^2. Furthermore, measured and simulated output energies were compared and analyzed. The generated power was calculated through the output voltage and current, where as the simulated power was obtained by employing the energy absorbing impedance-matching method. Both the calcination and sintering conditions of $(Bi,Sc)O^3$-$(Pb,Ti)O^3$ ceramics significantly affect the grain size and density, which effects are closely related to the microstructure, piezoelectric, and other properties of the ceramics. Optimizing the calcination temperature improved the piezoelectric coefficient from 388 to 440 pC/N, while improving the relative dielectric constant at 100 Hz from 1401 to 1479. We believe that the optimized calcination process can enhance the ezoelectric properties of (Bi,Sc)O3-(Pb,Ti)O3 ceramics by a very large margin.

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Synthesis and characterization of $Pr_2Ni_{0.9}Co_{0.1}O_{4+\delta}$

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Keywords: rare earth nickelates, freeze drying, conductivity relaxation

Research and development in sustainable energy technologies have gained increasing importance over the last years. Especially electrochemical cells and systems can be expected to play a key role in many different fields of technologies. Rare earth nickelates with K_2NiF_4-structure are among the most promising materials for many of these applications, e.g. electrode materials for solid oxide fuel cells and electrolyzers, electrochemical oxygen sensors, ceramic membranes for selective oxygen separation, or heterogeneous catalysts, because of their favorable properties, such as high oxygen diffusivity, as well as good electronic and significant ionic conductivity.[1] Currently though, the limitation of the oxygen exchange kinetics by the rate of the surface exchange process represents a drawback for technological applications.

The present work reports on the synthesis and characterization of the novel K_2NiF_4-type material $Pr_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ (PNCO). Ni in $Pr_2NiO_{4+\delta}$ is partially substituted with Co in order to increase the surface exchange coefficient of oxygen. For the preparation of larger quantities of chemically homogenous, single phase PNCO powder, a freeze drying method based on aqueous acetate precursor solutions was developed. The metal cation solutions were mixed, shock-frozen in liquid nitrogen, and freeze-dried. During a calcination step, the complex oxide was formed. X-ray powder diffraction (XRD) and Rietveld refinement showed that the material was single phase with K_2NiF_4-structure. The powder was characterized by dilatometry, differential scanning calorimetry (DSC), and thermogravimetriy (TG). In pure Ar, a transition from the orthorhombic to the tetragonal structure modification occurred, which was also reported for unsubstituted PNO.[2,3] For oxygen exchange and electrical conductivity measurements, a dense PNCO sample was obtained by sintering a pellet at 1300 °C. By this procedure it was possible to produce a phase-pure PNCO pellet with 99% of the theoretical density, which will be used for studies of the oxygen exchange kinetics by means of the dc-conductivity relaxation method.

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Hybridization of phosphate or phosphate compound and mesoporosu silica for acid-durable adsorbent for rare earth metal cations

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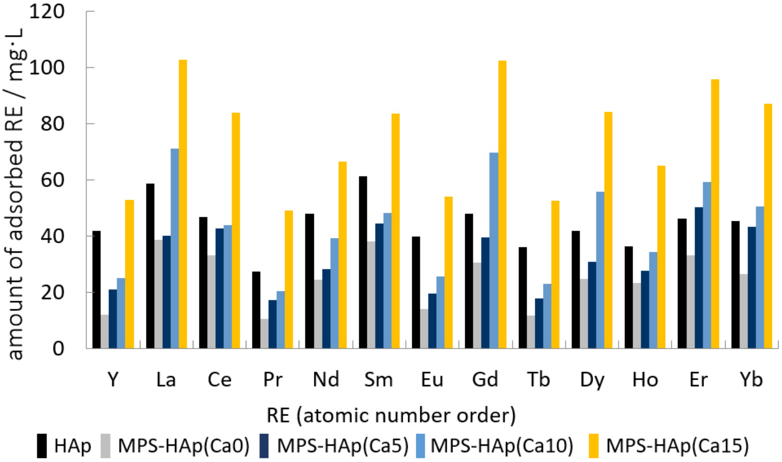
Mesoporous silica is strong candidate for adsorbent, filter, catalyst support and so on due to its strong durability for acidic condition. Especially, mesoporous silica with hexagonal 1-dimensional pore array is an attractive material because homogeneous pore size and array may provide possibility for molecular sieve. However, surface of mesoporous silica has low activity for some sorts of adsorption, reaction and so on due to OH group on the silica surface show only week acidity. Therefore, phosphate group or phosphate compounds (hydroxyapatite) was hybridized with the mesoporous silica, and adsorption of rare earth metal cations were examined under coexisting circumstance of the rare earth cations.

Typical preparation of mesoporous silica (MPS) was performed by $Si(OC_2H_5)_4$, $C_{16}H_{33}N(CH_3)_3Br$ and $C_2H_5NH_2$ with heating at 70 °C. The hybridizations of phosphate were examined by three ways, synthesis by reflux of MPS with H_3PO_4 (designated as MPS-HP), that from reflux solution of Na_2SiO_3 and Na_2HPO_4 (MPS-NaP), and that from Na_2SiO_3 and $PO(OC_2H_5)_3$ (MPS-EtP).

For preparation of MPS-hydroxyapatite, Ca-substituted MPS (prepared by $Si(OC_2H_5)_4$ and $Ca(NO_3)_2·4H_2O$) was used for the hybridization. The Ca-substituted MPS was then put into NH_4H_2PO4 aqueous solution (designated as MPS-HAp). The prepared hybrids were characterized by XRD, SXRD, FT-IR, NMR, microporosimeter and XPS for structure of the hybrid, and ICP for adsorption of rare earth metal cations.



XRD patterns (omitted in this paper) confirm that the hexagonal structures were partially kept during the hybridization. For the hybrid with phosphate, the maximum phosphorus amount was around 2.9 mol%. On the other hand, for MPS-HAp, the maximum amount of HAp is around 21 mass%, which corresponds to around 8.8 mol% of phosphorus. Fig. 1 shows rare earth adsorptions under coexisting circumstance of 13 rare earth metal cations to MPS-HAp at pH = 0. For MPS and phosphate hybrids, the adsorption amount per phosphorus is around 0.3, whereas approx. 0.9 for MPS-HAp. Such difference may result from difference mechanisms for rare earth adsorption as follows, coulomb force to phosphate for MPS-phosphate and ion exchange of Ca by rare earth for MPS-HAp. The acid durability will be reported in the day.

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ZnO/TiO$_2$ nanolaminate films prepared by atomic layer deposition as ultralong-life anode material of lithium ion batteries

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Keywords: atomic layer deposition, ZnO/TiO$_2$ stacks, anode, lithium ion batteries, ultralong-life

Rechargeable lithium ion batteries hold huge potentials for energy storage due to their high energy density and excellent cycle life. However, current commercially used graphite anode exhibits the low theoretical capacity of 372 mAh g^{-1}, which is unable to fill the increasing demands of the ever-enlarging market. Therefore, transition metal oxides (TMOs) with higher theoretical capacities have been widely researched as anode materials, such as Fe$_3$O$_4$, SnO$_2$, NiO, Co$_3$O$_4$, and ZnO. Among these oxides, ZnO has attracted a great deal of attention due to its high theoretical capacity of 978 mAh g^{-1}, natural abundance, easy preparation, low cost and environmental friendliness. However, it was found that ZnO suffers from severe capacity degradation and inferior rate performance, which can be attributed to the low electronic conductivity of ZnO and the severe volumetric changes during charge/discharge. Moreover, it has been revealed that the lithium embrittlement of ZnO is much worse than that of SnO$_2$, leading to the electrochemically driven solid-state amorphization and pulverization of ZnO. Therefore, various approaches have been attempted to improve the electrochemical performance of ZnO anode, including construction of nano-structured materials, metal doping and decoration with highly conductive matrix.

In this work, we have designed ZnO/TiO$_2$ nanolaminate films by atomic layer deposition (ALD) as anode material for lithium ion batteries. ZnO/TiO$_2$ nanolaminate films with 144 nm thickness were fabricated on copper foils by depositing cycle unit of 5 nm ZnO/1 nm TiO$_2$ repeatedly using ALD. The ultrathin TiO$_2$ films inserted into ZnO films were designed to buffer the volumetric changes during charging-discharging process. It was found that the pulverization of ZnO/TiO_2 has been effectively inhibited compared to the pure ZnO film anode after cycling process. Accordingly, the electrochemical test demonstrated that the reversible capacity and the rate performance of ZnO films anode have been greatly improved by inserting TiO_2 thin films, which could maintain a reversible capacity of 53.61 uAh cm^{-2} at 200 mA cm^{-2} and 47.23 uAh cm^{-2} at 500 mA cm^{-2} after 100 cycles. Its excellent high rate capability and long cycle stability can be attributed to the fact that TiO_2 thin film can buffer the volume change and prevent from the pulverization of ZnO. Constructing nanocomposite films might open up new opportunities for ZnO based anode materials for lithium ion batteries.

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Preparation and photocatalytic properties of pyrochlore-type $AgMO_3$ (M = Nb,Ta)

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Keywords: hydrothermal reaction, ion-exchange, photocatalytic

Pyrochlore-type oxides are formed by composing many metal element having the general chemical formula $A_2B_2O_6O`$ or $A_2B_2O_7$, (space group Fd-3m, No. 227) and the A and B atoms are generally alkaline metal, alkaline earth metal, rare-earth metal, or transition metal elements. We attempted preparation of pyrochlore-type $(K,H)MO_3 \cdot nH_2O$, (M = Nb,Ta) and ion-exchange of K^+ ion with Ag^+ ion. The crystal structures of the mother compound and their ion-exchange compound were refined with Rietveld method and their photocatalytic properties were checked.

Pyrochlore-type $(KH)NbO_3 \cdot nH_2O$ was synthesized by hydrothermal reaction method. The starting compound Nb_2O_5 (5g), 30ml of KOH solution were put in to Teflon autoclave and heated up to 220 °C for 2 days. In the case of $(KH)TaO_3 \cdot nH_2O$, the starting compound was an amorphous Ta_2O_5 and the reaction temperature was 200˚C . The ion exchange reaction was performed with excess $AgNO_3$ at 300 °C. The products were identified by X-ray powder diffraction and thermal stability was checked by TG-DTA. The photocatalytic activity of the products was checked by using phenol degradation under UV-light irradiation.

The refinement of pyrochlore-type $(K,H)NbO_3 \cdot nH_2O$ was successful and the *R* factors were $R_{wp} = 5.27\%$, $R_p = 2.44\%$ and lattice parameter was $a = 10.6409(2)$ Å. The ion-exchange reaction of $(K,H)NbO_3 \cdot nH_2O$ with excess $AgNO_3$ was not successful and the product had fluorite-type structure. Structural change from fluorite-type to perovskite-type at 600˚C showed by TG-DTA. The Ag/K ratio of the fluorite-type compound was 0.53. The *R* factors for fluorite-type $(K,Ag,Nb)O_{2-x}$ were $R_{wp} = 2.32\%$ and $R_p = 1.51\%$ and the lattice parameter was $a = 5.20392(9)$ Å. Fig. 1 shows time dependence of phenol degradation for pyrochlore-type $(K,H)NbO_3 \cdot nH_2O$, $(K,H)TaO_3 \cdot nH_2O$, $AgTaO_3$, fluorite-type $(K,Ag,Nb)O_{2-x}$, and perovskite-type $AgNbO_3$.

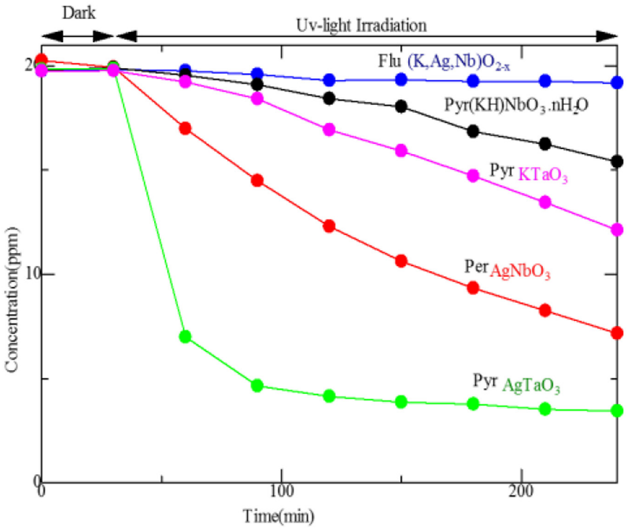

Fig. 1. The time dependence phenol degradation for pyrochlore-type $(K,H)NbO_3 \cdot nH_2O$, $(K,H)TaO_3 \cdot nH_2O$, $AgTaO_3$, fluorite-type $(K,Ag,Nb)O_{2-x}$ and perovskite-type $AgNbO_3$

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Synthesis and electrochemical properties of layered double hydroxide film composed of period-four transition metals and its hybrid with conductive polymer

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Keywords: Layered Double Hydroxide, conductive polymer, electrochemical properties

Layered Double Hydroxide (LDH) is a kind of layered material composed of metal hydroxide layers and intercalated anions. Generally Mg, Co, Zn and Al are used divalent and trivalent metal cations, which can be replaced by some transition metal. In our laboratory, metal hydroxide-conductive polymer hybrid is gaining attention, which is beneficial to improve the electrochemical performance of the hybrid materials by synergistic effect. In this study, we first prepared the LDH structure with Co-Al, Ni-Al, Co-Fe and Ni-Fe composition. On this basis, we used electrochemical method to prepare LDH–polyaniline hybrid films and its performance were tested.

The CoAl-LDH structure were prepared by hydrothermal method (The preparation of Ni-Al, Co-Fe and Ni-Fe were the same method). The electrodeposition was then carried out at a constant current. The sample films were characterized by XRD, FT-IR, SXRD, FE-SEM and XPS. The electrochemical properties were tested by cyclic voltammetry and charge/discharge cycles test.

Fig. 1 shows XRD patterns of Co-Al, Ni-Al, Co-Fe and Ni-Fe LDH film. In the spectrum, we can find LDH diffraction peak. Therefore SXRD patters were measured for confirmation of LDH formation. Fig. 2 shows SXRD patterns of formed LDH structures. From the patterns, CoAl-LDH and NiAl-LDH show better crystallinity than others. The LDH composed of Fe^{3+} seems to include impurity phase. By comparison to Fig. 1, the diffraction peaks of layered structure are apparently large. Such difference may result from perpendicular orientation in the film sample. Fig. 3 shows SEM images of CoAl-LDH. We find that most of the particles seem to be vertical growth in the substrate surface and particles are roughly uniform distribution. The result of electrochemical properties and hybridization with polyaniline will be reported in the day.

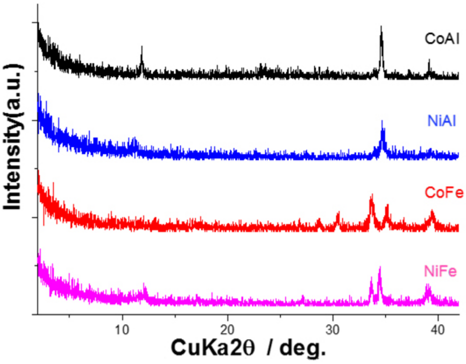

Fig 1. XRD patterns of CoAl, CoFE, NiAl and NiFe

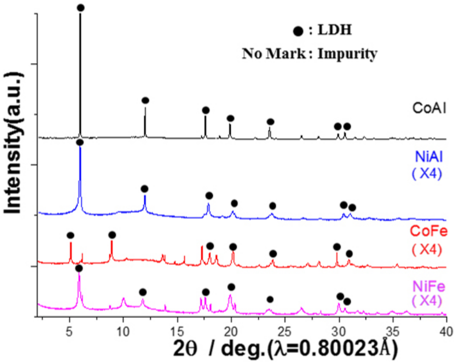

Fig 2. SXRD patterns of CoAl, CoFe, NiAl and NiFe

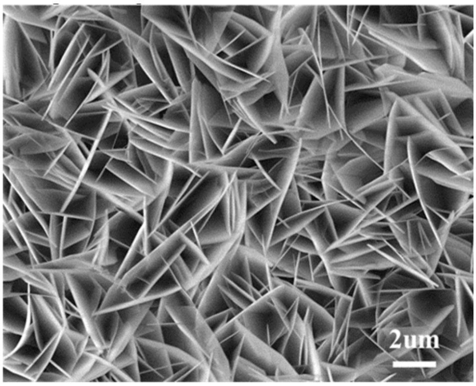

Fig 3. SEM images of CoAl-LDH

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Mechanical properties of LLZO solid electrolytes for battery application

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Keywords: solid electrolyte, battery, elastic modulus, strength, fracture toughness

Beneficial volumetric storage and stability aspects led to increased interest in solid state Li based electrolyte materials are for battery application as. Especially $Li_7La_3Zr_2O_{12}$ (LLZO) with 2 mol% Al doping, 40 mol% Ta doping is a promising material in this respect because of its high Li-ion conductivity as well as chemical stability. Mechanical behavior is important due to its relationship to reliability, rendering micro- as well as macromechanical behavior into the focus of the current work. Local properties are assessed using nanoindentation yielding local elastic modulus, hardness and fracture toughness, whereas the global behavior in terms of specimens' elastic modulus and fracture stress are characterized via ring-on-ring tests. Fracture stresses are analyzed via Weibull statistics yielding the characteristic strength and Weibull modulus. The aspect of environmentally assisted subcritical crack growth is discussed based on the variation of the loading rate during strength testing. Results are discussed in terms of their relationship to microstructure and local as well as geometrical imperfections. The interpretation of the results is supported by complementary optical and electron microscopy as well as roentgenographic assessment.

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Controlled architecture of magnesium/aluminium layered double hydroxide (LDH) crystals

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Keywords: layered double hydroxide, morphology control, intercalation, ion exchange

There have been increasing attention to layered double hydroxides (LDHs), also known as hydrotalcite-like compounds and anionic clays. They are represented by a general formula of $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]_x^{+}[A_{nx/n}]_x^{-}mH_2O$ consisting of octahedral brucite-like host layers (M^{2+}/M^{3+}: divalent and trivalent metal cations), charge-balancing anions (A_n^-) and interlayer water molecules. Their ion exchange properties, especially selectivity and capacity, have been widely studied by many researchers for various combinations of metal cations. However, morphol-

ogy control of LDHs for high ion exchange capacity has not been established. This study report the controlled growth of three-dimensional architectures of LDHs composed of magnesium and alumina in host layers (Mg/Al LDHs) by using magnesium oxide and aluminum oxide as sources. The effects of ingredient aluminum oxide with various crystal structures and sizes on the morphology, specific surface area and ion-exchange capacity of resulting LDHs were investigated.

A typical synthetic procedure of LDHs with three-dimensional architectures was as followed: aluminum oxides with amorphous phase, θ-phase or α-phase and magnesium oxide with stoichiometric composition were immersed in an aqueous solution. These solutions were stirred for 10 h at each temperature at 80 °C, and subsequent precipitated powders were collected and filtered. After drying at 60 °C, X-ray power diffraction (XRD) analysis was carried out and their morphologies were characterized with scanning electron microscopy (SEM).

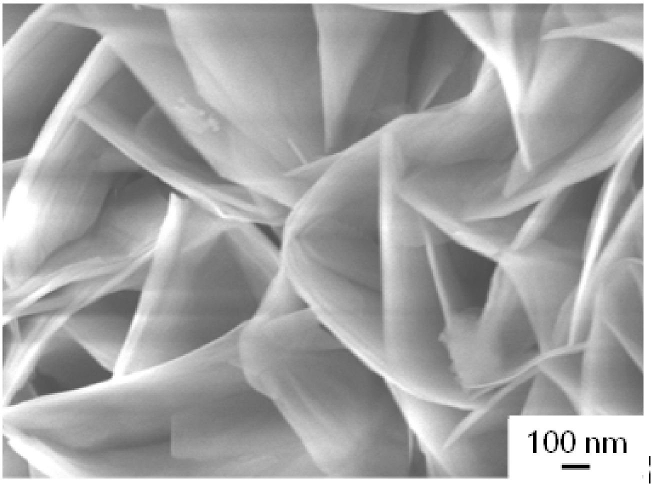

Fig. 1. SEM image of Mg/Al LDH crystals obtained from aqueous solution containing θ-Al_2O_3 and MgO as sources at 80 °C

Successful formation of Mg/Al LDHs with three-dimensional architecture was confirmed from XRD and SEM analysis only when θ-phase aluminum oxide was used among various ingredient aluminum oxides. With respect to the morphological feature, plate-shaped crystals with diameter of 1.0 µm were connected to each other and construct secondary particles with diameter of 10 µm (Fig. 1). From the time-dependent analysis, it was found that the plate-shaped LDHs were formed on the surface of aluminum oxide through the precipitation with magnesium ions and hydroxy ions, followed by intrusion into the center of aluminum oxide. The ion exchange capacity will be discussed in comparison with conventional synthetic LDHs.

Acknowledgement
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Enhanced visible-light photocatalytic acitivity of Fe_2O_3-coated TiO_2 powders prepared by atomic layer deposition

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Keyword: visible-light photocatalytic activity, Fe_2O_3 coating, commercial TiO_2 powders, atomic layer deposition

With the rapid development of modern industry, environmental pollution has become a serious issue. TiO_2, as an efficient and safe photocatalytic material, can only absorb ultraviolet light. In order to make full use of visible light, the doping and modification of commercial TiO_2 powders (P25) have drawn great concerns. Among various approaches, the semiconductor/semiconductor hetero-junction is perceived as the most effective way to improve the TiO_2 visible light response. Atomic layer deposition (ALD) is a kind of novel thin film coating preparation method with large area uniformity, excellent three-dimensional conformality, simple and precise control of film-thickness, and low processing temperature due to self-limited surface chemisorptions mechanism.

In this work, Fe_2O_3-coating on commercial TiO_2 powders (P25) was prepared using $Fe(Cp)_2$ and O_3 by thermal ALD. The effect of different ALD cycles on the visible-light photocatalytic properties of P25 has been investigated carefully. The XRD patterns indicate TiO_2 anatase structure without other secondary phase. The HRTEM image shows lattice fringe phase of TiO_2 nanocrystalline with untrathin surface disorder region, possibly originating from the Fe_2O_3 or Fe-doped TiO_2. XPS and ICP analyses confirm the slight Fe amount existence in TiO_2 powders. The UV-visible absorption spectra of Fe_2O_3 coated TiO_2 indicate some absorption in the visible light region with reduced the bandgap from 3.35 eV to 3.05 eV. Fe_2O_3 coated TiO_2 powders exhibit significant photodegradation of methyl orange (MO) under visible light irradiation. 400-cycle Fe_2O_3-coated P25 has optimal photocatalytic acitivity with ~72% degradation of MO in half an hour. The catalyst loading amount and recyclability has also been examined. The possible photocatalytic mechanism of Fe_2O_3-coated TiO_2 powders is proposed.

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T06: Ceramics and glasses for healthcare

Invited lectures

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Expanding applications of bioactive glasses in tissue engineering and wound healing

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Keywords: bioactive glasses, tissue engineering, ion release, vascularization

Due to its excellent bioactivity, bioactive glasses are being highly considered for tissue engineering scaffold development. Usually in combination with biopolymers, bioactive glasses can form composites for applications in soft tissue engineering and wound healing.[1] The ability of bioactive glasses to enhance vascularisation via the action of dissolution products (biologically active ions) will be discussed based on *in vitro* and *in vivo* studies. 45S5 Bioglass® scaffolds with a highly interconnected porous structure can be fabricated by the traditional polymer replica technique. A possible disadvantage of such scaffolds is their high brittleness and low resistance to fracture. To increase the low mechanical properties and to impart malleable behaviour, scaffolds are coated with a biopolymer. In this investigation, scaffolds were coated with gelatin by dip coating and vacuum infiltration, amongst other investigated methods. The coating and infiltration of scaffolds by biodegradable polymers will be presented as a suitable approach to enhance the structural integrity of scaffold and to impart functionalities, including incorporation of inorganic particles, e.g. mesoporous particles, as drug carriers.[2] The *in-vitro* characterisation of bioactive glass based scaffolds will be discussed highlighting the effects of bioactive glass dissolution products (metallic ions) on cell behaviour in relation to osteogenesis and angiogenesis.[3] *In-vivo* investigations to determine the vascularisation potential of new bioactive glass scaffolds will be discussed in relation to the current main challenge of tissue engineering, namely that the biomaterial construct support vascularisation. In the emerging field of bioactive glasses for soft tissue engineering, an overview of their applications in contact with soft tissues will be presented with focus on our current work on dressings for wound healing and on hydrogel-bioactive glass composites for biofabrication.

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Engineering bioactive glasses with well-balanced overall properties

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Keywords: bioactive glass, scaffolds fabrication, sintering, osteoinduction

Bioactive glasses (BGs) elicit special responses when in contact with biological fluids.[1,2] The leached ionic species exert an osteoinduction role, stimulating the recruitment of immature cells to develop into preosteoblasts, promoting healing in bone fractures and defects filled with BG bone grafts. The bone-like hydroxyapatite (HA) layer formed at the surface of BGs *in vivo* leads to strong bonding to living tissues. Another crucial requirement for the successful engineering of bone tissues is the 3D structure of bone graft (scaffold) as it provides a suitable environment for osteogenic cells to migrate, proliferate, differentiate, and promote new bone formation. All these relevant features strongly depend on a number of interrelated factors that need to be well balanced, including the chemical composition and structure, which determine the biocompatibility, the degradation rate, and the easiness of processing (shaping and sintering) the material. BGs with high alkali contents create high pH environments, become cytotoxic and are difficult to process. This presentation deals with the development, characterization and processing of a series of alkali-free bioactive glass compositions that offer a set of well-balanced overall properties. Porous scaffold are easy to process by additive manufacturing. BGs are biocompatible and degrade with time into non-toxic products and exhibit fast *in vitro* mineralization.[1] The BG compositions also foster early cellular differentiation and proliferation and alleviate the oxidative stress *in vitro*,[3] and excellent osseointegrative and osteoconductive properties when implanted *in vivo*.[4] These distinctive features are very promising for demanding applications in healthcare and tissue engineering and bone regeneration and the supporting evidences will be disclosed.

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Resorption of calcium phosphate materials: considerations on the *in vitro* evaluation

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Keywords: dissolution, precipitation, calcium phosphate, mechanics, physico-chemistry

Calcium phosphates (CaPs) are currently used as bone grafts thanks to chemical similarities with the mineral fraction of bone. Depending on their composition and their processing route (e.g. sintered ceramics or cements), CaPs can be more or less soluble under physiological conditions. A deep knowledge of resorption phenomena could allow tailoring CaP based bone graft according to the patients' needs. Literature is quite abundant concerning the evolution of calcium phosphates after immersion in model fluids. However, results vary considerably according to the test conditions. A comparison of the information provided appears therefore difficult, due to the large variability of tests performed. Thus, the present study is aimed at underlining the importance of choosing appropriate immersion conditions and of paying a particular attention to the influence of the set-up. The influence of the immersion conditions is demonstrated, as well as the possible presence of artefacts induced by the experimental protocols. In addition, the interest to follow-up at the same time and at the local scale physicochemical, microstructural and mechanical properties is discussed. For each of the aforementioned points, evidences are provided through the results obtained by immersing DCPD and β-TCP samples in different 'model' solutions (TRIS and PBS) for different times.

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Design and processing of novel biomedical-grade nanocomposite ceramics: tailoring composition, microstructure and properties

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Keywords: ceramic nanocomposites; biomedical applications, microstructural tailoring, composition-structure-properties relationships

With the increase of life expectancy, the need for artificial biomedical devices having improved performance and durability is increasing as well. This implies new challenges for the materials used in these applications, since improved mechanical properties (strength, toughness and wear behaviour) and longer term biocompatibility are required.

In this frame, tetragonal zirconia polycrystals (TZP) and zirconia-based composites have shown their feasibility as biomedical materials and especially oral implants, as these ceramics match biocompatibility, mechanical specifications and aesthetic properties, as required for dental applications.

However, a major concern in the processing of these composites relates to the ability of keeping a homogeneous microstructure and a fine zirconia grain size, necessary to produce reliable biomedical devices with the expected performances.

This work deals with a novel approach concerning both the materials design and the elaboration process of nano-composite ceramics, allowing an effective tailoring of the powder characteristics, final microstructure and properties with the aim of fabricating biomedical devices characterized by a perfect reliability and a lifetime longer than 60 years. By this approach, a careful control and optimisation of the main ceramic processing steps is carried out, leading to robust relationships among composition, architecture and performances in terms of mechanical behaviour and durability. In particular, attention will be paid to the synthesis of zirconia-based composite powders, by exploiting a simple but reliable powder coating method, able to assure the required microstructural features in final materials. In addition, the thermal pre-treatment of composite powders will be optimized, in order to tailor some features (e.g. nucleation extent stage and crystallization degree) prior sintering, which will be then carefully controlled in order to obtain fully dense materials, in which a perfect tailoring of the microstructural parameters (grain size, distribution, morphological development of secondary phases) will be achieved.

By this strategy, strong, tough and stable ceramics are successfully produced, making them promising candidates for structural biomedical applications.

Acknowledgements

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Bone in-growth: the next step in ceramic orthopedic implants

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Dense structural oxide ceramics are widely preferred as a favorable material in tribological applications for arthroplasty. Their hardness, strength, wear resistance, and biocompatibility make them suitable for artificial joints. Pure aluminum-oxide and zirconia-toughened alumina (ZTA) ceramics are in use for several decades now. The most commonly used ceramic material today is a zirconia and platelet toughened alumina (ZPTA) known under the trade name BIOLOX®delta. Several million parts of this material have been implanted worldwide and it has shown a significant improvement over pure alumina in terms of safety and wear.

However, the biological and chemical “inertness” constrain the connection of the implant to the surrounding bone. This is one of the reasons why ceramic orthopedic implants are usually backed with metal shells to facilitate fixation in the bone structure. Therefore, the aim of today’s ceramic implant development is modifying the ceramic surface in a way that allows direct-to-bone implantation. To omit the metal backing would allow larger bearing diameters and wall thicknesses while at the same time saving bone substance.

In order to facilitate structural interconnection of the bone with the ceramic implant several routes can be followed. There are additive and subtractive technologies that allow texturing the surface of the ceramic body in a way that will allow mechanical interlocking with the bone scaffold. Additionally, chemical modification of the surface can further improve bone cell adhesion. Following the above different routes, it can be demonstrated that a material commonly known as “bio-inert” can be bio-activated allowing osseointegration.

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Tuning nanoceramics for angiogenesis and its potential in cancer therapy

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Angiogenesis is the formation of new blood vessels from existing blood vessels and is critical for many physiological and pathophysiological processes. In this study we have shown the unique property of redox active ceramic nanoparticles (Re-NPs) to induce angiogenesis, observed using both *in vitro* and *in vivo* model systems. In particular, Re-NPs trigger angiogenesis by modulating the intracellular oxygen environment and stabilizing hypoxia inducing factor 1alpha endogenously. Furthermore, correlations between angiogenesis induction and Re-NPs physicochemical properties including: surface valence state ratio, surface charge, size, and shape were also explored. High surface area and mixed valence states make these nanoparticles more catalytically active towards regulating intracellular oxygen, which in turn led to more robust induction of angiogenesis. Role of these nanoceramics in potential cancer therapy will be highlighted.

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The prospects for bio-glass implant coatings

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Keywords: bioactive glass, implant coatings, magnetron sputtering

The ability of certain silica-based glass formulations to bond to hard and soft tissues was discovered in the late sixties by L.L. Hench.[1] Due to their highest indices of bioactivity, silicate bioactive glasses (SBGs) are the suitable candidates capable to stir the quest for a new generation of osseous implants with superior functional performances. Although frantic researches in the past were dedicated to the fulfilment of this conceptual desiderate by employing well-established and novel physical and chemical deposition technologies, reliable metallic implants coated with SBG are not yet available for medical practice. In the recent period, tremendous efforts have been dedicated to delineate new derivative glass formulations[2] capable to expand the functionalities of SBGs to low dimensional objects for drug delivery or regenerative bone scaffolds fabricated by additive manufacturing, robocasting or 3D printing, and finally coatings for fast and safe osteointegration of metallic implants. For instance, the ability to match the CTE values of SBG and Ti, by designed oxidic substitutions, without affecting the osteointegration capacity, reopens the question of manufacturing durable SBG implant coatings, capable to realize the rapid transition to real-life applications.

The presentation will provide an overview about the advantages, drawbacks and peculiarities of one of the most promising technologies for functionalization of implants with SBG coatings: radio-frequency magnetron sputtering (RF-MS). Beside its renowned remarkable advantages (e.g., ability to generate highly adherent, pure, uniform and compact coatings, or to enable facile engineering of coatings' features by varying the process parameters), RF-MS is one of the fewest deposition methods that can successfully be scaled-up to industrial level (as demonstrated in electronics industry). The progresses achieved so far in the realm of RF-MS SBG sputtered coatings will be reviewed to highlight the potential of this technique. Simple, inexpensive, yet scientifically more accurate *in vitro* bioactivity screening tests have been used to probe the SBG coatings performance. It is postulated that only an exigent *in vitro* testing can filter the best implant solutions and boost their safe translation to clinical applications. Furthermore, solutions to tackle the current technical obstacles will be debated, paths for potentially extending the applicational range of RF-MS will be presented, whilst insights on the chances to surpass the current knowledge boundaries in the field will be revealed and inquired.

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Nature-inspired innovative processes to generate smart materials for regenerative medicine

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Introduction. Tissue regeneration requires the use of scaffolds acting as an instructing guide for cells, so that substantial mimicry of compositional, morphological and structural features of natural tissue is highly desired. However, this target is very hard to achieve, when human tissues with high compositional and structural complexity such as bone have to be regenerated. In this respect, even though hydroxyapatite (HA) is the best-in-class for bone regeneration, the thermal treatments compulsory for scaffold consolidation destroy all the fine compositional and nanostructural cues triggering and directing the cell fate towards tissue regeneration and vascularization. In this respect, nature-inspired synthesis approaches are rapidly gaining ground in material science, for the development of biomaterials with unique composition, structure and performance. Biomineralization and biomorphic transformation processes[1,2] are relevant examples of this concept.

Materials and methods. Biomineralization process are carried out in aqueous environment where collagen fibrils were dispersed at body temperature in the presence of Ca, P and Mg ions, and under pH control. The process was directed to generate bone-like and functionally graded scaffolds with high mimicry of mineralized and non-mineralized regions present in osteochondral tissues.

Biomorphic transformation process, starting from natural sources, such as wood, implies a sequence of heterogeneous reactions at the interface between a natural porous template and a reactive gas, concluded with a low temperature phosphation process that avoids the use of sintering for physical consolidation. The 3-D structure is maintained throughout the whole transformation process, leading to bioactive apatite with hierarchical organization.

Results and Discussion. Hybrid composites with highly porous structure and outstanding mimicry of newly formed bone tissue are the product of biomineralization process. In particular, the heterogeneous nucleation of nearly amorphous apatitic phase occurred onto the assembling collagen matrix, exhibiting multiple ionic substitutions and crystal orientation inducing specific chemotactic and topotactic interaction with cells, all features at the basis of regenerative ability demonstrated in the pre-clinical and clinical tests.

Biomorphic 3-D hierarchically organized porous ceramics consisted in highly biomimetic, multi-substituted nanocrystalline apatite phase, directly nucleated in the 3-D state to form a scaffold exhibiting bone-mimicking structure with open and interconnected porosity and hierarchical organization at the multiscale. Such features determined very high mechanical strength and damage-tolerant mechanical behaviour, thus resulting into high mimicry of bone tissue. *In vitro* tests in static and dynamic conditions showed high biocompatibility and bioactivity, as well as overexpression of the most relevant genes involved in bone formation.

Conclusions. These results confirm that the adoption of nature-inspired processes is an elective approach to obtain highly bioactive materials with innate cell-instruction ability, thanks to biomimetic features that are not achievable by the traditional ceramic processing. Therefore, these new approaches promise to be a breakthrough in the synthesis of bioceramics with boosted bioactivity, potentially opening to frontier applications in regenerative medicine.

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Oral presentations

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Osteogenic differentiation of human dental pulp stem cells on bone-apatite like coatings obtained by Pulsed Electron Deposition

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Keywords: bone apatite, hydroxyapatite, Pulsed Electron Deposition, human dental pulp stem cells

Introduction. In orthopaedics and dentistry, novel approaches for fabricating biomimetic and mechanically robust bioactive coatings are desirable in order to further improve the clinical results of coated implants compared to uncoated ones[1]. Here, we report the first deposition of bone-apatite like (BAL) coatings directly from a biogenic apatite target, by the novel pulsed electron deposition (PED) technique[2]. The osteogenic potential of BAL coatings was investigated *in vitro* by evaluating the adhesion, proliferation and differentiation of human dental pulp stem cells (hDPSCs) on BAL coatings.

Experimental methods. Bovine tibial shafts were deproteinized using sodium hypochlorite and machined into cylindrical targets. Sintered HA targets were used as control. BAL and HA coatings were deposited at room temperature by PED in the Ionized Jet Deposition (IJD) version. After deposition, part of the samples was annealed at 400 °C for 1h. Sample composition, microstructure, morphology and mechanical properties were investigated by SEM-EDS, ICP-OES, FT-IR, XRD, AFM, contact angle measurements and nanoindentation. hDPSCs were plated on the samples and cultured in both osteogenic and non-osteogenic medium. At day 21 the expression of typical osteogenic markers was evaluated.

Results and discussion. As deposited amorphous BAL coatings showed chemical composition very close to the one of biogenic target. Upon annealing at 400 °C, also the crystallinity resembled that of biogenic apatite. Further, mechanical properties increased with annealing up to value comparable with those of commercial sprayed HA coatings. hDSPCs showed a better proliferation on BAL_400 than on other coatings. Interestingly, cells reached the osteogenic commitment on BAL_400 without the need of an osteogenic medium. In particular, immunofluorescence and western blot analyses revealed the expression of typical osteogenic markers, i.e. Runx-2, Osx, osteopontin and osteocalcin, thus suggesting that BAL_400 itself can promote the osteogenic commitment of the cells.

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Photolymerization to prepare polymeric-ceramic composites for bone regeneration

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The life expectancy in the worldwide has been increased in the last. Consequently, traumas and bone pathologies are frequently found in older population. For this reason, the treatment and regeneration of bone defects caused by traumas, tumors, infections, disorders from skeleton development or progressive distorting illness, is a challenge with great social and economic impact, which the modern science have to affront.

Polymeric-ceramic composites are an encouraging suggestion. Ceramic materials such as calcium phosphates and silicates biodegrade in Ca^{2+}, PO_4^{3-} and SiO_3^{2-} ions. These ions promote bioactivity and osteinduction, which are mandatory requirements in an ideal implant for bone regeneration. The disadvantage of ceramic materials is their brittleness. However, these ceramics materials can be embed in a biocompatible polymer matrix which improves their mechanical properties.

Photopolymerization has been selected to prepare these composites because it is a cost-effective method in comparison with other techniques and allows obtaining complex structures. Moreover, photopolymerization is initiated by Ultra Violet-Visible (UV-Vis) aided by a photoinitiator. UV-Vis aids to sterilize the composite during the synthesis process. Some ceramics can be used as photoinitiators.

PEGDMA is an excellent candidate for photopolymerization. Moreover, has been choice due to their mechanical properties but also because of its swelling behavior. These swelling properties make possible PEGDMA be used as drug delivery system. For example, antibiotics can be delivered *in situ* to avoid infections.

In this study, polymeric ceramic composites have been prepared using ceramic porous particles of β-TCP, where Ca^{2+} has been partially substituted with Mg^{2+}, and wollastonite. These particles have been embed in a PEGDMA matrix. Gel fraction, swelling and mechanical properties of the composites have been studied. Also, *in vitro* studies in simulated body fluid (SBF) have been carried. Moreover, composites have been evaluated as delivery systems to avoid infections. Finally, ceramics have been evaluated as photointiators.

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Seeding of lithium disilicate glass–ceramics for enhanced fracture toughness

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Keywords: sol-gel, toughness, SPS, biomaterials

Lithium disilicate glass-ceramic materials are a type of glass-ceramic materials, which has as major phase Li_2O-$2SiO_2$. Lithium disilicate glass-ceramic has been the model system of many theoretical studies with regard to nucleation and crystallization mechanism and a nucleating agent was suggested as necessary component to promote nucleation and volume crystallization in the base glass after suitable heat treatment. Recent compositional modifications to lithium disilicate base glasses have yielded translucent glass-ceramics that are characterized by high strength, excellent chemical durability, and aesthetic appearance of natural teeth. Therefore, these types of materials are preferred for dental applications such as veneers, crowns, bridges and implants.

In recent years, the glasses prepared through a sol-gel route are found to have advantages over conventional glass melting method such as: better homogeneity, higher level purity, lower stoichiometric losses and less contamination from crucibles. On the other hand, it is generally accepted that the sol-gel route enables to provide transparent bulk materials.[1]

In the present work, lithium disilicate glass–ceramics were prepared by two different methods. The first is the conventional melting of oxide powders and heat treatment to obtain final glass- ceramic material. The second method, consisted of a sol-gel process for the preparation of crystalline lithium disilicate ($Li_2Si_2O_5$) phase from tetraethylorthosilicate (TEOS) and lithium nitrate ($LiNO_3$) precursors. The obtained $Li_2Si_2O_5$ sol-gel phase powder was mixed in different proportions as seeding agent with the other as prepared conventional glass powder. The aim was to obtain better mechanical properties of the final glass- ceramic material promoting a preferential growing process of some of the lithium disilicate grains within the composite matrix. After mixing the powders, they were pressed into pellets and densified by Spark Plasma Sintering (SPS) method. Several heat treatment schedules were implemented and characterization techniques as XRD, SEM and Vickers hardness test were used to essay the final glass- ceramic samples and to reveal the effect of the seeding sol-gel material addition. Results indicate that growing of lithium disilicate giant sized grains within a smaller component matrix could enhance both fracture toughness and strength properties of the material.

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Spark plasma sintering of 13-93 bioglass composites reinforced with *in situ* reduced graphene oxide

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Keywords: 13-93 bioglass, spark plasma sintering, graphene, mechanical characterization

13-93 bioactive glass has a fairly large window between glass transition and the onset of crystallization which greatly promotes its full densification by viscous flow sintering without crystallization occurring. This has facilitated the fabrication of porous bioactive scaffolds from this glass composition by a variety of shaping methods, including robocasting.[1] Robocasting, also known as direct-write assembly or direct-ink writing, is an extrusion-based additive manufacturing technique and, as such, it can produce scaffolds with customized external shape and predefined, reproducible internal architecture.

As a consequence of this greater control over pore architecture, robocast 13-93 bioglass scaffolds exhibit much higher mechanical strength than 13-93 scaffolds made by conventional techniques.[2] However, the intrinsic poor toughness of 13-93 bioglass still limits the mechanical performance of 13-93 robocast scaffolds for load bearing applications.

Graphene, a monolayer of carbon atoms arranged in a honeycomb lattice, has shown impressive thermal, mechanical, and electrical properties, and is a promising alternative as a reinforcement to tailor the material structure at nanometre scale in order to obtain stronger and tougher engineering ceramics.[3]

The current study reports the use of graphene-like nanoplatelets to enhance the fracture toughness of 13-93 robocast bioglass scaffolds. 13-93 robocast scaffolds with a fixed three-dimensional design and different loadings of graphene oxide (GO) were sintered by spark plasma sintering (SPS) at a relatively low temperatures, during which *in situ* partial thermal reduction of GO took place. The resulting robocast 13-93 bioglass scaffolds reinforced with reduced graphene oxide (rGO) were subject to an ample study covering aspect of processing, sintering, microstructural characterization, and mechanical performance.

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Flash sintering of TCP

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Keywords: flash sintering, tricalcium phosphate, β→α phase transition, bioceramics

In this work, sintering behavior of tricalcium phosphate (TCP) ceramics under the effect of an external electrical field (in flash sintering configuration) was analyzed to obtain dense bio-resorbable components. The aim was to understand the physical condition leading to the flash phenomenon and to study the effect of consequent reduction in sintering time and temperature on the undesired β→α-TCP phase transition occurring at high temperature.

TCP powders were synthesized by conventional solid state reaction and then shaped into cylindrical green body by uniaxial cold-pressing. Their sintering behavior was studied by dilatometry under different E-field at constant rate heating. The presence of α-TCP and the microstructure were investigated by XRD and SEM techniques.

It is shown that a flash phenomenon takes place at furnace temperature below 1000 °C. In addition, although β→α transition occurs at ~1150 °C for pure TCP, the detection of both polymorphs within the sintered bodies indicates that higher temperature is reached in the material, which is very likely associated to Joule effect induced by the current flow along the sample.

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Translucent zirconia-silica glass ceramic for dental restoration: structure related mechanical strength

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Keywords: glass ceramic, ZrO_2-SiO_2, translucency, dental application, mechanical strength

ZrO_2-based full ceramic have been widely accepted as a promising dental ceramic because of their excellent mechanical properties and good biocompatibility. However, the aesthetics of ZrO_2-based full ceramics needs to be improved because of the opacity.[1] Glass ceramic, such as lithium disilicates, is widely used due to its excellent translucency, allowing for more flexibility to adapt to the colour of the surrounding teeth. However, glass ceramics generally have flexural strength and fracture toughness, generally less than half of the full ceramics. This limits the application of glass ceramics on long bridgeworks. Nanocrystalline materials (NCM) shows significantly enhanced properties and thus have been the subject of considerable research over the past three decades[2]. Among the different types of NCMs, tough and high-modulus nanocrystalline glass ceramics (NCGC) has potential applications in load bearing parts as a biomaterial. Thus, a ZrO_2 based glass ceramic which possess an excellent combination of high strength and translucency would be a promising alternative ceramic in dentistry.

This study aims to obtain ZrO_2-SiO_2 glass-ceramic that possess high mechanical strength as well as excellent translucency by controlling the content, size, and connection of nanocrystalline ZrO_2. Toward this end, homogenous nano-powders with three different compositions were synthesized by sol-gel method, followed by spark plasma sintering. Highly-translucent nanocrystalline glass ceramics (NCGC) were obtained. Tetragonal ZrO_2 was the only crystalline phase in all the glass ceramic samples. Samples with high zirconia content showed that the structure of the skeleton was predominately built by nano-sized ellipsoidal ZrO_2 particles bonded by grain boundaries, with amorphous SiO_2 filling the voids between the ZrO_2 particles. One of the compositions achieved a flexural strength of 1014 MPa. To our knowledge, 1014 MPa is the highest flexural strength value of glass ceramics ever reported, which is much higher than transparent zirconia and alumina ceramics. In conclusion, the ZrO_2-SiO_2 NCGC developed in this study showed promising potential for use in dental restoration.

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Development and characterization of multi-element doped hydroxyapatite coatings for orthopaedic applications

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Keywords: bioceramic coatings, hydroxyapatite, biocompatibility, corrosion

Nowadays, intensive efforts are being made to develop such coatings that possess antimicrobial and biocompatible properties at the same time in order to prevent post-operative infections. These coatings can be silver (Ag), zinc (Zn), strontium (Sr) and magnesium (Mg) doped hydroxyapatite. Among all of the antimicrobial materials, Ag is the most economic and most effective in action against various sorts of bacteria. The main advantage of silver compared to other antimicrobial materials is that bacteria will not become resistant to silver and the effect of silver ions is continuous and prolonged. One major advantage of hydroxyapatite coatings loaded with silver and other biocompatible minerals is that they promote bone growth, accelerate the wound healing process owing to the Zn content, thus increasing the biocompatibility ability of the implant materials. In our research work, the coatings were prepared by pulse current deposition method. The hydroxyapatite layers were doped with mineral elements either with co-deposition or with surface post-treatment with solutions containing the necessary components. The basic electrolyte solution contained $Ca(NO_3)_2$, $NH_4H_2PO_4$ and H_2O_2 at pH of 4.3 and the electrodeposition process was carried out at 70 °C. Since the as-deposited calcium phosphate coating was mainly in Monetite phase, after deposition, the samples were immersed into 1 M NaOH solution to achieve phase transformation into Hydroxyapatite. The biodegradable properties of the layers were evaluated by electrochemical tests in simulated body fluid (SBF) at temperature of 37 °C. Electrochemical Impedance Spectroscopy (EIS) measurements were performed also to test the samples' corrosion stability. All the electrochemical tests were carried out using a classical three electrodes cell with platinum as counter electrode, saturated calomel electrode SCE as reference electrode and the samples as working electrode. The surface morphologies and grain size of samples were also observed by SEM measurements[1–3].

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Cleaning with photons: challenges and opportunities of photocatalytic water and air sterilization

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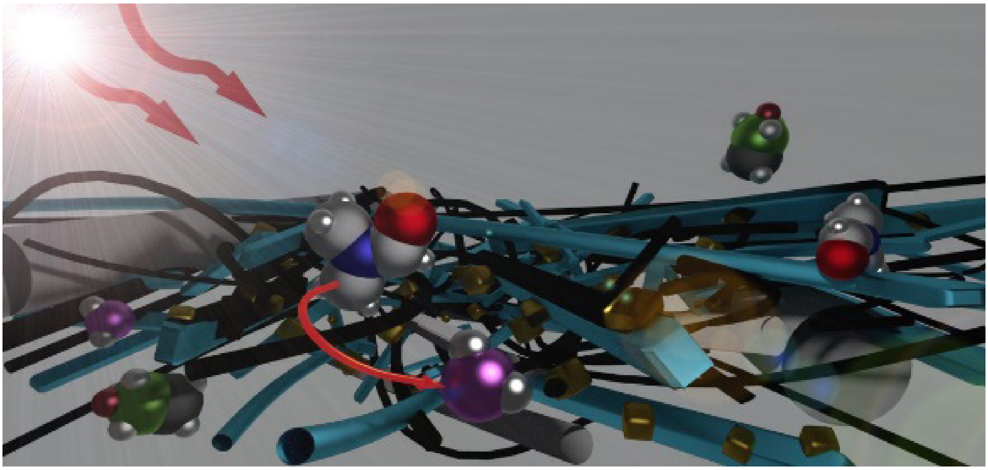
Keywords: micropollutants, ceramic filter, reactive oxygen species, advanced oxidation processes

The discovery of photocatalytic water splitting and photocatalysis dates back to the 1970s. Since then, several semiconductor nanoparticles have been found to have remarkable photocatalytic activity to eliminate health-threatening bacteria, viruses, worms and persistent, bioaccumulative organic water pollutants as pharmaceuticals, pesticides and endocrine disruptors. Surprisingly, despite significant research efforts, studies have mainly remained in the stage of laboratory experiments and only a limited number of products using this technology can be found on the market. Materials and devices with sufficient efficiency, stability and low cost are yet to be demonstrated. Among the known semiconductor photocatalysts, titanium dioxide (TiO_2) is the most popular owing to its excellent chemical stability, low toxicity and low cost.



I will discuss the main technical barriers impeding the commercialization of this technology and show several strategies as potential countermeasures to improve the photocatalytic efficiency of titania based solar environmental purification systems. As an example, the first prototype of a low cost, durable and easy to operate solar-thermal water purification device will also be presented, which allows the production of bio-hazard-free drinking water from contaminated water resources.

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Novel nanocomposite ceramic scaffold fabricated via 3D printing for cancer therapy application

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Keywords: ceramic, magnetite, scaffold, cancer therapy, biomaterials

Cancer is the second advance cause of mortality in the world. The method approaches include surgery, radiation, and thermal therapy practiced depending on tumefaction type and level of cancer syndrome. Through chemotherapy cases usually, encounter dangerous side effects due to a lack of tumor-specific uptake occurring in injury to normal organ tissues. Magnetite ceramic is a bioresorbable material that has been widely employed in the biomaterials domain and cancer therapy plans. The association of nano-magnet or blending of it is with silicate ceramics like bredigite or akermanite ceramics has allowed a variety of nanocomposite materials including significantly developed mechanical and biochemical properties before-mentioned strength, arrangement, porosity, degradation speeds, and bioactivity that are necessary for tissue manufacturing.[1,2] These features are immediately associated with the structure and their range of porosity, as well as the dimension of their pores and their interconnectivity.[2,3] In this study, the 3D printing (3DP) stands out, where the composition of ceramics is achieved layer by layer, according to a planned computational design which gives a comprehensive direction of structure and scaffold geometry. The aim of this research was to develop, for the first time, three-dimensional magnetite-bredigite scaffolds containing various amounts of magnetite nanopowder. Morphology of bioactive surface of scaffolds was investigated. Furthermore, the effects of scaffold composition on the bioactivity, and biodegradability were also evaluated. Indeed, the micro-pore size of the scaffolds decreased with progressing bredigite content proving that the sinterability of the scaffolds was developed. The nanocomposite scaffolds revealed higher bioactivity and biodegradability with increasing magnetite content as a biological features. In this work, the optimum sample depending on magnetite content which shows a potential candidate for bone tissue engineering.

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Bioceramic with self-powered fluidic delivery and lubrication

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Keywords: bioceramic, hierarchically organized nanochannels, self-powered fluidic supply and lubrication

Most living organisms are able to efficiently supply fluid and nutrients to every part of the body by employing hierarchically organized capillaries with gradient channels. Inspired by nature, such as bone with both sufficient mechanical strength and permeability, we developed a ceramic nanocomposite platform with capillary networks and capable of self-powered and self-regulated fluidic transport. The creation of a graded micro- and nano-channel network in hydroxyapatite bioceramic was made possible via two phase-transition mechanisms, one being polymer-ceramic phase-segregation and the other being liquid-vapour and solid-liquid phase transitions, both of which are pressure-temperature dependent. The pressure dependences were exploited in making the gradient channels that favour directional liquid transport. We directly observed cellular uptake of nutrient in this new nanostructured ceramic material by tracing radioactive fludeoxyglucose. We also measured its mechanical strength for load bearing and found it be similar to human bone. This approach of building into a ceramic composite a 3D network of capillaries for self-powered and directional fluidic transport opens new possibilities for ceramic applications in bone implants and in drug, lubricant, and coolant deliveries.

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The phase-partitioning-dependent residual stress evolution in 3Y-TZP ceramics affecting ageing and fracture behaviour

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Keywords: zirconia, phase transformation, X-ray diffraction, annealing, ageing, fracture

Yttria-stabilized tetragonal zirconia (3Y-TZP) is today's ceramic material of choice in dentistry owing to its improved aesthetic appearance compared to metals, excellent biocompatibility and mechanical properties. The mechanical performance and the susceptibility to controversial low-temperature degradation (LTD) ageing process is governed by stress- and moisture-induced tetragonal-to-monoclinic (*t–m*) transformation, respectively. However, *t–m* transformation not only depends on factors such as grain size and yttrium concentration/segregation, but also on the internal residual stresses that evolve during sintering-related phase-partitioning and during mechanical and thermal handling procedures.

We have investigated the influence of the phase partitioning of 3Y-TZP ceramics on the stability and the structure of transformable yttria-lean tetragonal phase (YLZ) and un-transformable yttria-rich phases (YRZ; *t*``– and *t*`–prime) and on the formation of residual stresses in YRZ, further affecting the ageing kinetics and fracture mechanics. The results obtained, by employing XRD (MAJ equation and Rietveld refinement), FIB-SEM, Vickers indentation and flexural strength measurements, indicate that the formed YRZ phases are under compressive stresses in the 3Y-TZP matrix, since a systematic relaxation after ageing and/or annealing was observed. The observed relaxation puts additional perspective on the understanding of the *t–m* transformation mechanism ultimately governing both the ageing and fracture behaviour in 3Y-TZP.

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Micro-patterning of calcium phosphate bioceramics with femtosecond laser

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Keywords: CaP ceramics, laser patterning, physico-chemical surface characterization, biological assessment

The bioactivity of synthetic bone implants is highly impacted by their surface topography, especially by the presence of micro-patterns likely to influence cell behaviour.

In this study, laser machining technology was employed in order to produce controlled regular micro-patterns on dense calcium phosphate surfaces, without any contamination. The choice of the source was directed towards a femtosecond pulsed laser, with 1030 nm wavelength and 270 fs pulse width, in order to limit the thermal impact of such a process and thus to avoid the unwanted phase transformations potentially induced by the temperature elevation. Beta tricalcium phosphate substrates with perfectly controlled micro-patterning and without any secondary phase were obtained by controlling the process parameters (laser power, scanning speed, pulse frequency). An accurate optimization of the process parameters allowed obtaining micropatterns with several complex designs. The microstructural characteristics were investigated by microscopy (optical, confocal, scanning electron) and the phase identification was performed by X-Ray Diffraction and Raman spectroscopy. This work allowed highlighting the effects of the process parameters on the patterning.

The influence of surface micro-patterning on bone marrow stem cell behaviour was highlighted *in vitro*. In particular, an elongation of the cells shape was observed along linear grooves made by laser machining, whereas cells appeared more spread on smooth surfaces with same chemical composition. These results show that linear patterning should promote cell migration. The effects of the micro-patterning design and particularly the presence of angular shapes, on cell adhesion, proliferation and differentiation are currently evaluated *in vitro*.

To conclude, femtosecond laser machining technique seems to provide an interesting alternative to conventional ceramic surface treatments of calcium phosphates. This technology, which allows a minimization of the thermal impact, appears promising and can now be envisaged for the surface treatment of calcium phosphate ceramics or even calcium phosphate coatings used for bone tissue engineering.

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Evaluation of prospective perovskite mediators for magnetic fluid hyperthermia

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Keywords: AC magnetic field, Lanthanum strontium manganese oxide, LSMO, perovskite, peroxide sol-gel, microwave, induction heating, magnetocaloric effect, specific absorption rate

Contemporary modalities for 'Magnetic fluid hyperthermia' (MFH) involve the use of a colloid of magnetic nanoparticles (MNPs), which in the presence of an AC magnetic field induce a temperature increase of between 41 °C to 46 °C, selectively damaging cancerous tissue.[1] The majority of materials investigated for MFH until recently were iron-based[2] as they are biocompatible with high Specific absorption rates (SARs), but, their high Curie temperatures (T_cs) mean that an applied field may lead to overheating of local tissue. Initial research to reduce the T_c to within the therapeutic range showed that the perovskite Lanthanum strontium manganate ($La_{1-x}Sr_xMnO_3$, LSMO) was promising as a prospective mediator[3] and is the focus of our work. MNP clusters were synthesised and characterised *via* SEM, IR spectroscopy and XRD with Rietveld analysis in order to confirm the crystalline phases, crystallite size and morphology. The magnetic properties (magnetic susceptibility, T_c and magnetocaloric effect (MCE) were assessed using magnetic heating experiments and the Superconducting quantum interference device (SQUID). Initial characterisations of LSMO synthesised using a modified peroxide sol-gel method at a range of dopant levels confirmed $La_{0.65}Sr_{0.35}MnO_3$ to give the optimal induction heating results (T_c of 89 °C, T_{max} of 46.7 °C and SAR of 56 W g_{Mn}^{-1}.[4] We also observed an increase in orthorhombic crystal structures with increasing strontium dopant. Other dopants (Ba and Ca) were also evaluated, with magnetic heating observed for materials with larger A-site dopant radii relative to La^{3+}; and reduced magnetic heating effects observed for smaller A-site dopant radii.[5] Subsequent work has dealt with the optimisation of LSMO (decreasing aggregate size, increasing SAR) using a variety of synthetic approaches, including a microwave assisted method where SARs as high as 175 W g_{Mn}^{-1} were achieved. The enhancement of magnetocaloric effect was ascribed to a greater core ferromagnetic contribution as a result of the improvement in the degree of crystallinity and magnetic susceptibility of the samples.

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The potential of high borate glasses for transarterial embolization

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Keywords: borate glass, gallium, therapeutic inorganic ions, transarterial embolization

Introduction: Research into borate glasses has been significantly dwarfed in comparison to other oxides; an estimated 15.5% of oxide glass research was dedicated to borates during 1850–2013, while approximately 70% accounted for silicates1. Nonetheless, borate glasses have (i) displayed promising therapeutic potential and (ii) the ability to modulate material properties by compositional modifications. Within this study, a high borate glass system was investigated as a novel resorbable material for transarterial embolization (TAE) purposes, serving as a delivery platform for the therapeutic inorganic ion gallium, while also providing for indication specific characteristics, i.e. a resorbable imageable material.

Materials and Method: Six glasses (70B-20Sr-10-x(Ga)Na (x = 0, 2, 4, 6, 8, 10, mol%) were melted and processed to a particle size distribution of 45–150 μm. Structural analysis of each composition was done via magic angle spinning nuclear magnetic resonance spectroscopy. Glass transition temperatures (Tg) were determined by differential scanning calorimetry and radiopacity was verified using computed tomography at 120 kV. Ion release kinetics for each element in each composition was determined by ICP-OES (up to 30-days). The theoretical mass loss was calculated from cumulate ion release and theoretical glass composition.

Results: Initial substitutions of Ga2O3:Na2O resulted in destabilization of the network. However, at ≤6:4 Ga2O3:Na2O ratio, network stabilization occurred with an (i) increase in Tg, (ii) a decrease in total ion release at 30-days of extraction, and (iii) a reduction in mass loss. Maximum mass loss was observed to be 66% reducing to 39%, at the highest Ga_2O_3 loading. Ga release followed a similar trend with the highest release at 6:4 ratio and a decrease thereafter. ^{11}B MAS NMR showed that increasing Ga_2O_3:Na_2O caused a linear increase of B[3] at the expense of B[4] groups. The data indicates the potential formation of GaO_4– tetrahedral, causing network stabilization to occur. Radiopacity increased from 3236 to 4943

HU, higher than a clinically used commercial control (Contour™), which has been recorded to be 2520 HU[2].

Conclusion: A maximum mass loss of 66% was obtained and Ga ion release was maintained for up 30 days. A clinically relevant radiopacity was obtained, which would aid by providing spatial and temporal distribution of materials in target tissues. All of which indicate that borate glass systems have a very real clinical potential in TAE procedures.

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Design and characterization of porous ceramic membranes for passive sampler of water contaminants

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Keywords: passive sampler, ceramic membrane, flow rate, diffusion coefficient

The increasing presence of "emerging contaminants" in wastewaters represents a potential environmental risk. However, very little is known about the incidence and real dangers involved due in part to analytical complications. In order to properly formulate preservation regulation more information about the impact of presence of these contaminants in environment is necessary. Environmental monitoring tools require the use of efficient and reliable sampling and analytical techniques. Currently, grab sampling is the most common way to monitor surface waters although it might not be completely representative if contamination fluctuates with time. Alternatively to active sampling, passive or diffusive samplers (PS) offer information on average pollution levels over several hours or days. PS devices allow the free flow of contaminants from the media to the receiving phase due to the difference in chemical potentials between the external and internal area of the sampler. Organic compounds are retained inside the sampler and its efficiency and performance depends on the design of the membrane as well as the polarity and solubility of the contaminants, the nature of the sampled water and properties of the receiving phase. The aim of this study was to develop and characterize macroporous ceramic membranes for passive samplers (MCPS) for the analysis of water contaminants. The MCPS's designed consist in an alumina porous ceramic tube in which the pore morphology and membrane thickness were varied to achieve for different sampling rates of organic compounds. In this study we used methylene blue as test compound, which can be measured by spectrophotometry to evaluate the diffusion dynamics of the ceramic membranes. This study also compiles the evaluation of the diffusion coefficients, membrane geometrical factor, tortuosity factor and sampling rate of the ceramic membranes. Three different membrane configurations were prepared by slip casting using different pore former, cornstarch and graphite, and membrane thickness. Membranes with 34.5% and 36.9% connected porosity and 1.5 mm thick and with 39.6% open porosity and 1.1 mm thickness were prepared. The pore configuration is bimodal with pores of 80–200 nm diameter. The systems herein proposed represent a new, robust and effective sampling devices to determine water contaminants as allow a high flux of contaminants through the ceramic membrane and a high accumulation potential in the receiving phase.

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Influence of carbonate groups on the low-temperature consolidation by spark plasma sintering of phosphocalcic bioceramics

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Keywords: bioceramics, carbonated apatites, Spark Plasma Sintering, low-temperature sintering

Carbonated hydroxyapatites (CHA) have crystal structure and chemical composition ($Ca_{10x}(PO_4)_{6-x}(HPO_4,CO_3)_x(OH)_{2-x-2y}(CO_3)_y$) close to the mineral part of bone. In contrast to the stoichiometric calcium phosphate hydroxyapatite conventionally used to manufacture implants for bone replacement, they are expected to exhibit better biological properties in terms of dissolution and resorbability. However the main drawback of CHA is to get decarbonated at low temperature, which makes the consolidation of ceramic parts difficult by conventional sintering.[1] Previous studies have shown that it was possible to consolidate at low temperature biomimetic nanocrystalline apatite at low temperature (T<300 °C) using Spark Plasma Sintering (SPS).[2] The challenge of our study was to consolidate CHA ceramics at low temperature by SPS in order to retain the carbonates in the apatite structure as well as a low crystallinity: the objective being to produce a sintered ceramic material with chemical characteristics approaching those of the bone mineral.

The study showed that consolidation at very low temperature (150 °C) by SPS to produce carbonated apatite ceramics was possible provided that the initial powder, synthesized by aqueous precipitation, was amorphous. Conversely, crystallized powders did not consolidate in the experimental SPS conditions tested. This consolidation occurred in the same time as the crystallization of the amorphous compound into apatite. The ceramics obtained were low-crystalline, microporous, non-stoichiometric carbonated apatites having grains of nanometric size and presented advantageous mechanical properties (biaxial flexural strength of 18 MPa).

A thorough investigation of this material was carried out by Fourier Transform Infrared Spectroscopy (FTIR). The distribution of labile (surface) and bulk carbonate species in the A or B sites of the apatite was evaluated, using spectral decomposition and analysis of the vibration bands of the PO_4^{3-} and CO_3^{2-} groups, in order to refine the composition of the sintered material.

For more investigation of the phenomena observed during SPS, calcium phosphate powders of variable chemical composition and crystallinity were also carbonated by surface ion exchange. Then, they were heat-treated by SPS. This method of powder carbonation was set up in order to determine if only the carbonation of calcium phosphate particles surface could be sufficient to obtain consolidated carbonated apatite ceramics after SPS. The characterization of these powders and ceramics using complementary techniques (X-Ray Diffraction, FTIR spectroscopy) helped to specify the evolution of the chemical composition, stoichiometry and crystal structure of materials during the elaboration process.

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Sol-gel derived mesoporous glasses with high surface area and good bioactivity

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Keywords: sol-gel synthesis, bioactive glasses, high surface area, biomaterials

Sol-gel derived mesoporous materials are of big interest in the biomedical field. Mesoporous and ordered mesoporous silica has been investigated as a drug delivery material, due to its high specific surface area, high pore volume and high amount of silanol groups on the surface. Based on this approach mesoporous glasses have been developed with different ions incorporated into the silica network. By incorporating CaO and P_2O_5 bioactive properties can be achieved, that are similar to the well-known bioactive glasses such as 45S5 Bioglass®. Sol-gel is a low temperature approach that allows for a variety in compositions and shapes.

We have produced bioactive glasses in the SiO_2-P_2O_5-CaO system by sol-gel synthesis with high specific surface area of up to 300 m²/g, pore radius of 4 nm. We were able to influence the particle properties through varying synthesis parameters to achieve microscale powders with spherical morphology. The resulting microspheres are promising materials for a variety of life sciences applications, as further processing e.g. granulation, is unnecessary. Microspheres can be applied as materials for powder based additive manufacturing, or in stable suspensions for drug release, in bone cements or fillers.

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Phosphate based glass/ceramic coatings for therapeutic ion leaching in orthopaedic applications

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Keywords: phosphate glass ceramics, heat treatment, therapeutic ions, PVD

Phosphate based glasses (PBG) are fulfilling biomaterials applications from the fibre reinforcement of resorbable polymeric matrices to carriers for therapeutic drug delivery. Vapour deposition has shown its ability to condense tailorable compositions of glasses, maintaining their amorphous tetrahedral structures.[1,2] Post deposition heat treatment has been used to relieve internal stresses in glasses, or to nucleate and grow crystals to initiate the formation of ceramic phases, therefore stabilising their dissolution properties.[3] Coatings of up to 2.7 µm thick have demonstrated linear ion release capabilities and the ability to accommodate a vast array of potentially therapeutic ions to promote osteogenic or antimicrobial capabilities.[4]

Quinternary, P, Na, Mg, Ca and Fe containing coatings were deposited amorphous onto Ti6Al4V substrates and were subsequently heat treated at 500610 °C to observe the effects on structure and dissolution properties. Similar structural changes were observed for two treatments at 500 °C, associated with the formation of Fe_2O_3 hematite crystals whilst XPS showed a reduction of phosphorous from (21.6–1.3) at%, coupled with an increase in iron from (1.4–22.8) at% within the surface layers. Heat treatment at 550 and 610 °C led to the formation of multiple crystalline phases.

As deposited and heat treated coatings at 500 °C were degraded in water for up to 96 h and assessed for ion release in ultrapure water up to 48 h whilst coatings treated at 550 °C and 610 °C were continued up to 28 d. Heat treatment improved the durability of coatings by diminishing the initial exponential solubility profile in the first 2 h of submersion and reduced linear degradation rates by factors of 2.44–4.55 ± 0.35 from 500 °C–610 °C. Similarly this was coupled with a reduction in ion release rates by maximum factors of 3.9, 4.0, 4.3, 3.4 and 7.7 for P, Na, Mg, Ca and Fe respectively. Release rates ranged from 0.39–0.05 ppm h^{-1}, 0.01–0.02 ppm h^{-1} and 0.01–0.02 ppm h^{-1} for the as deposited, HT 500 °C, 30 min and HT 500 °C, 120 min coatings respectively.

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Study of effective parameters on crystallization behaviour in the erbium-doped SiO_2-Al_2O_3-PbF_2 glass ceramic system for Ir-Vis up-conversion applications

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Keywords: oxy-fluoride glass ceramic, PbF_2 nanocrystal, up-conversion, luminescence, rare earth ions

Recently, up-conversion materials are presented as a new candidate for specific Biomedical, photovoltaic and optical applications[1]. Oxy-fluoride glass ceramics can be considered as an appropriate host for rare earth ions in optical applications rather than expensive fluoride single-crystals[2]. To the best of our knowledge, glass technological topics have been neglected in favour of optical properties in previous studies.

In this research, optimal procedures were utilized to develop SiO_2-PbF_2-Al_2O_3-ErF_3 glass and glass-ceramic samples by conventional melting method with appropriate microstructure and optical properties. Many techniques were used to adjust melting and forming methods such as changing mold design, controlling heat tolerance during glass melting and decreasing fluorine loss. The thermal parameters of non-heat treated glasses with various compounds were investigated by DTA /TG. Also, innovative thermal setup was designed to find out glass thermal behaviour visually. According to thermal analysis results, precursor glass samples were heat treated. The heat treated samples phase transition, microstructure and absorption-transmission spectra were identified by XRD, SEM/FESEM and UV-VIS double beam Spectrophotometer, respectively. Moreover, the effects of Er^{3+} doping and increasing Al_2O_3 content on Glass-making capabilities, fluorine loss, phase separation mechanism, crystallization behaviour and optical properties were studied.

Increasing 10mol% Al_2O_3 content in glass compound played key role in decreasing evaporation rate during melting (near 8wt%), increasing Ir-Vis transparency (about 20%), improving the crystallization stability more than 100 °C, preventing uncontrollable and extensive phase separation in glasses; Although Al_2O_3 addition disturbed single phase crystallization of PbF_2. Results distinctly showed that the presence of Er^{3+} ions in composition had significant effect on phase separation, β-PbF_2 single phase crystallization and crystallite size and distribution. In addition, Er^{3+} ions created specific absorption peaks in transmission spectra (400–1100 nm) which are appropriate for up-conversion process. Green and red up-conversion luminescence emissions were observed after 980nm laser excitation. This phenomenon demonstrated β-PbF_2:Er^{3+} formation. Furthermore, β-PbF_2:Er^{3+} lattice parameter shrinkage was observed with increasing Al_2O_3 content, which represented increasing Er^{3+} ions dissolution in β-PbF_2 crystalline structure.

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Cancer diagnosis & therapy using functionalized inkjet-printed mesoporous silica microdots

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Keywords: mesoporous silica, Inkjet Printing (IJP), Evaporation-Induced Self-Assembly (EISA), click chemistry, FRET

Early detection of tumors is advantageous for treatments efficiency. Studies carried out by SPCTS and HCP laboratories have led to a patent in 2013 related to the development of an endoscopic probe suitable for *in situ* early detection and local treatment of tumors[1]. The main advantages of this device are to be local and non-invasive in terms of diagnosis and therapy of cancers compared to current techniques. At first, this device is to be used for head and neck tumors, and for breast and prostate cancers with time.

The Inkjet Printing (IJP) process allows to build 3D structures of various materials (metal, ceramic or polymer) with a high definition, accuracy, flexibility and on industrial scale. Combined with Evaporation-Induced Self-Assembly (EISA) mechanism, 3D IJP allows the deposition on the probe surface, of mesoporous silica multilayer microdots arrays[2] that can be further specifically functionalized by click chemistry[3].

For the diagnosis, bioreceptors are labeled with appropriate fluorophores and anchored to the microdots surface. When interacting with the specific cancerous biomarkers on tumor cells, a conformation change of the bioreceptors occurs, and the fluorophores get closer. Consequently, a Fluorescence Resonance Energy Transfer (FRET) occurs and is spectrally detected by confocal laser microscopy or using the endoscopic device.

Once the diagnosis is effective, this device can be upgraded with therapy function. On that purpose, Photodynamic Therapy (PDT) is used to produce singlet oxygen that leads to cells apoptosis.

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Progress in calcium-magnesium phospho-silicate hydraulic bio-cements for dentistry and orthopedics

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The novel Calcium Phosphate Silicate Cement (CPSC) combines the best biological and structural properties of Calcium Phosphate Cement (CPC) and of Calcium Silicate Cement (CSC). The resulting CPSC is relatively stronger than CPC and has extended and controlled degradability time range, as compared with CPC. The current FDA-approved applications of CPSC include dental root sealers and root repair materials. The materials are distributed worldwide by Vancouver BC Canada company Innovative BioCeramix Inc (IBC), and through the associated network of distributors including Brasseler USA Inc. and Henry Schein Inc.

One area of active CPSC research for orthopedics concerns its setting time, as the currently known CPSC variants set within ~1 hr after water contact. There is a desire to shorten this time to < 10 min for certain dental and orthopaedic applications. One approach includes admixture of biocompatible/biodegradable and fast-setting Mg compounds to CPSC, rendering it now Calcium-Magnesium Phosphate Silicate Cement (CMPSC).

This work reviews our research progress on these novel, faster-setting bio-cements, including both CPSC, and the effects of Ca/Mg on the properties of CMPSC after hydration (setting) at 37 ºC for various length of time, and its final properties (variation of pH, compressive and 3-point bending strength, *in vitro* bioactivity). The phase transformations in CMPSC during setting show that calcium hydroxide, produced during the hydration of calcium silicates, reacts with the phosphate additives to form hydroxyapatite. The *in-situ* formation of a nanocomposite from the hydroxyapatite and calcium silicate hydrates appears responsible for the significant enhancement in CMPSC strength, bioactivity, and biocompatibility, as compared to pure CSC.

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Diopside-tricalcium phosphate bioactive ceramics

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Keywords: diopside, tricalcium phosphate, composites, microstructure, mechanical behaviour, bioactivity

Bioactive ceramics of nominal compositions x $Ca_3(PO_4)_2$ – (1-x) $CaMg(SiO_3)_2$ x = 100, 40 and 20 wt.%), were obtained by solid state sintering of mixtures of a fine synthetic precursor of $Ca_3(PO_4)_2$ and synthetic $CaMg(SiO_3)_2$ powders. Mixing was done by attrition milling using ZrO_2 balls and the dried and sieved powders were shaped into discs by uniaxial pressing. Sintering was performed at 1225 ºC during 2 h using 10 ºC/min as heating and cooling rates. Final specimens were discs of about 7.7 and 3.3 mm of diameter and thickness, respectively. Complete microstructural analysis of the sintered materials, including X-ray diffraction and field emission scanning electron microscopy with microanalysis (FE-SEM-EDS), was performed. The single phase material (TCP) was β-$Ca_3(PO_4)_2$ and the composites (60D-40TCP and 80D-20TCP) were mainly constituted of $CaMg(SiO_3)_2$ and β-$Ca_3(PO_4)_2$; a small amount of $CaSiO_3$ ($\approx$ 3 wt.%) was also homogeneously distributed in the microstructure. Mechanical characterisation was performed in terms of the Weibull distribution of tensile strength determined by the Diametrical Compression of Discs Test (DCDT). Alkaline phosphatase activity (ALP) assay of mesenchymal stem cells was performed in order to evaluate bioactivity.

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Dental restorative ceramics: balance between aesthetics, mechanical properties and long-term stability

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Keywords: dental ceramics, translucency, mechanical properties, stability

The continuous quest for dental materials that offer adequate translucency (aesthetics) combined with superior mechanical properties is driving materials science towards development of innovative tooth-restoration concepts. Today, dentists favour all-ceramic restorations, as they are more biocompatible (metal-free) and can provide more natural appearance.[1]

In this work, yttria-stabilized zirconia ceramics with various levels of translucency were studied. Classical 3 mol% yttria-stabilized zirconia with 0.25 wt.% alumina addition had limited translucency. Reducing the alumina content increased the translucency but slightly compromised the hydrothermal-aging stability. Here we show that engineering the grain boundary of zirconia ceramics allows obtaining a better balance between the translucency, aging-stability and mechanical properties including crack resistance and flexural strength.[2,3] On the other hand, increasing the yttria content to 5 mol% resulted in high-translucent zirconia even for the use in front region with high aesthetic demands, but this material could no more benefit from the transformation toughening effect of tetragonal zirconia. 5 mol% yttria-stabilized zirconia had at the end rather similar crack resistance as lithium-disilicate glass-ceramic for which excellent aesthetic results have been documented.[4,5]

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Poster presentations

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Morphology of hydroxyapatite crystals obtained through the hydrothermal method

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Keywords: biomaterial, hydroxyapatite, hydrothermal

Hydroxyapatite (HA) has been used in many areas of medicine and dentistry due to its biocompatible character. Crystallographic and chemical studies evidence the similarity of the synthetic material to the natural HA. This work focuses on the hydrothermal synthesis method, which enables the control of the parameters associated to the synthesis.[1,2] The products obtained with this method present different morphologies and sizes. The samples were obtained using calcium and phosphorus ion precursors respecting the 1.67 Ca/P relation with the addition of organic additives (glycol ethylene and glycerin) to the reaction medium. Among the characterization analyses performed, the scanning electronic microscopy allowed the observation of the influence of the additives in the formation of crystals. The crystals kept a hexagonal rod with different sizes and thickness. The increase in the additive concentration favored the increase in the crystal size in the direction [00l]. The crystals obtained using ethylene glycol or glycerin presented the same change patterns. The samples Ca/P ratio was determined using energy dispersive spectroscopy which, for the synthesized samples, remained 1.67. X-ray diffraction identified the majoritarian phase as $Ca_5(PO_4)_3OH$, Space Group P 6_3/m. Small amounts of calcium phosphate phases were observed in some samples. Larger peaks observed when the additive was increased indicated reduction in the samples crystallinity. FTIR results revealed the formation of carbonated HA. The method used in this work resulted in the formation of crystals with different morphologies (from the prism like format with hexagonal base to the plate format).

Acknowledgments

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Hydroxyapatite as a system of amoxicillin controlled release

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Keywords: biomaterial, hydrothermal synthesis, amoxicillin

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ is a biomaterial used in dentistry and medicine for implants, due to its biocompatibility and bioactivity. HA can be associated to different types of materials, for example, antibiotics aiming at releasing the drug directly into the damaged tissue, reducing the risk of infection in the implant. However, the use of HA as drug release system is dependent on its structural and morphological properties.[1] Several synthesis methods are found for the production of HA, such as, precipitation, sol-gel and hydrothermal.[2] In this work a study was carried out to obtain HA through the hydrothermal and microwave assisted hydrothermal methods with morphologic characteristics suitable to be used as a system of drug controlled release. The HA samples were obtained using citric acid as complexing agent. The samples were characterized using vibrational absorption spectroscopy in the infrared region by Fourier transform (FTIR) and scanning electron microscopy effect field (SEM / EGF) with accessory coupling spectroscopy energy dispersive (EDS). SEM results revealed that samples obtained are HA nanoparticles with spherical agglomerates. FTIR results indicated that the method enabled the formation of carbonated HA. After characterization, the powders were associated to amoxicillin and microbiological tests *in vitro* were carried out. HA associated to the antibiotic was seen to inhibit bacterial growth with the maximum release time of 72 hours. Other tests were employed to prove the controlled release profile of HA associated to amoxicillin.

Acknowledgments

Authors are thankful to UEPG/CLABMU, and the financial support of CAPES/PNPD, CNPq and Fundação Araucária.

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Role of calcium aluminate phases on the apatite forming ability

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Keywords: *in situ* foaming, hydroxyapatite-alumina composite, calcium aluminate phases, *in vitro* apatite forming ability

The demands on the properties of materials that are appropriate to bone tissue replacement are steadily growing. The reinforced HA composites belongs to ceramics with desirable osteoconductive and osteointegrating properties and also exhibit relatively matched mechanical stability under the body simulated conditions[1,2].

Hydroxyapatite scaffold reinforced by alumina (1 to 10 wt. %) was prepared by *in situ* foaming process with the final total porosity of sintered product up to 70% t. d. The presence of formed calcium aluminate structures were studied by *in situ* X-Ray diffraction analysis from 25 °C to 1300 °C and verified by Raman spectroscopy. Phase's morphology was observed by scanning electron microscopy. The apatite forming ability was performed on the scaffolds sintered at different temperatures with different alumina content immersed in the simulated body fluid. The newly formed apatites were studied in order to identify their structure by X-Ray photoelectron spectroscopy and Raman microscopy. The time dependence of released or consumed Ca^{2+}, Al^{3+} and PO_4^{3-} cations content in applied simulated body fluid was monitored. The paper deals the formation of intermediate and stable phases during thermal treatment of hydroxyapatite- alumina composite foams and their impact on the surface reactions lead to newly apatite species formation.

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Pressureless spark plasma-sintered Bioglass® 45S5 with enhanced mechanical properties and stress-induced new phase formation

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Commercial Bioglass® 45S5 powder was sintered using spark plasma sintering (SPS) technique without the assistance of mechanical pressure with heating and cooling rate of 100 °C/min, dwell temperature of 1050 °C and dwell time of 30 min. Such route enabled the production of samples exhibiting superior mechanical properties in comparison with Bioglass® sintered in furnace. In particular, flexural strength and fracture toughness reached values close to those of apatite-wollastonite bioceramics, already widely used in clinical applications. The residual stresses implemented by indentation promoted the formation of a new phase in samples sintered by SPS. Complementary use of Raman and energy dispersive spectroscopy (EDS) indicated the phase as sodium carbide and a formation mechanism was proposed.

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Design and 3D printing of novel PCL/Bioactive glass scaffolds for bone tissue regeneration

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Keywords: polycaprolacton, Bioactive glass, 3D printing, Finite Element Analysis

Introduction. In this study we investigated the correlation between the mechanical properties of novel polycaprolactone (PCL)/Bioactive glass constructs and the overall compressive strength of 3D printed PCL/Bioactive glass scaffolds. By Finite Element Analysis (FEA), it

was possible to efficiently optimize the scaffold geometry in terms of compressive performance for bone substitution and regeneration.

Experimental methods. The PCL/Bioactive glass composite material was realized by mixing PCL pellets and bioactive glass powders with innovative formulation (BGMIX_Mg[1], size < 20 μm) containing from 0 to 50 wt.% of bioglass. Thermal analysis was conducted on PCL/bioglass composites by DSC and TGA. The mechanical characteristics of the composites were obtained by nano-indentation and used as input parameters for the FEA optimization of the scaffold architecture, together with fibre and pore size, fibre orientation and layer offset. Scaffold mechanical performance was measured in terms of compressive modulus and maximal internal strain. To validate the FEA analysis, 3D PCL/Bioactive glass scaffolds were printed by Fused Deposition Modeling (FDM) and compression tests were performed on them according to ISO 844.

Results and discussion. The elastic modulus and hardness of the PCL/Bioactive glass constructs were ~ 0.3 GPa and ~ 19 MPa, respectively, for the 10 wt.% composite and ~ 0.6 GPa and ~ 45 MPa, respectively, for the 30 wt.% composite. Using these values as input data, FEA analysis showed that scaffolds with suitable geometry and composition PCL/Bioactive glass 70/30 wt.%, exhibited a compressive modulus falling in the range of interest for trabecular bone[2]. This approach, combining FEA and experimental tests, provided scaffolds with strength suitable to withstand physiological loads when used as bone substituted in the trabecular bone.

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Injectable bone cement based on α-tricalcium phosphate

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Keywords: injectable bone cements, apatite, β↔α-TCP transformation, injectability

The main objective of this work was the development of injectable apatitic calcium phosphate cements with mechanical properties suitable for orthopaedic applications. The initial tricalcium phosphate powders used in this study were produced by the wet chemical precipitation process, followed by heat treatment in order to obtain the desired phases (β-TCP and/or α-TCP). The results demonstrated that the allotropic β↔α-TCP phase transformations are noticeably affected by other experimental factors such as the cooling rate and the presence of secondary phases of calcium pyrophosphate or hydroxyapatite.

The calcium phosphate (CPC) bone cement pastes were prepared by mixing the pure α-TCP powders with reactive aqueous solutions of different concentrations of sodium hydrogen phosphate as a setting accelerator. To some aqueous solutions, additives (Aristoflex®TAC, polyethylene glycol 600) were further added with the deliberate intention of improving the rheological behaviour of the cementitious pastes during extrusion. However, during the injectability tests, these additives were found to lower the percentage of extruded paste. It has also been found that the particle size distribution is a crucial factor in determining the rheological behaviour of cementitious pastes.

The combination of α-TCP powder with 2.5 wt% sodium hydrogen phosphate as setting liquid resulted in apatite cements with interesting properties from the point of view of the injectability, microstructure, porosity, mechanical strength and crystalline phases formed.

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Effect of hydrogen dioxide treatment on the osteogenic potential of duck-beak bone derived natural bioceramic microparticles

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Keywords: duck-beak, bone, osteogenic, potential, hydrogen dioxide

As an alternative material to the autogenous bone, duck-beak bone particles for bone substitute has been attracting great attention due to its biological properties. To deliver the most favorable outcome of the medical treatment, it is essential to study the effect of various processing methods of the duck-beak bone. In this study, we compared the two deproteinizing agents for manufacturing duck-beak bone. Group 1 was treated by conventional chemical agent (ethylenediamine), and Group 2 was treated by hydrogen dioxide (H_2O_2). *In vitro* and *in vivo* experiments were conducted parallel to compare the cytocompatibility and osteogenic capability between two processing methods. For *in vitro* tests, human adipose-derived mesenchymal stem cells were planted onto each sample, and their attachment and growing were evaluated. For *in vivo* biocompatibility and osteogenic properties, the samples were applied on the critical sized calvarial bone defect of the rats. Group 2 showed significantly higher cell attachment, but Group1 showed slightly higher cell proliferation. In *in vivo* test, all groups have shown biocompatibility and increased level of osteogenic potential. However, Group 2 had significantly higher bone regeneration ($p < 0.05$). This experiment confirmed that H_2O_2 can be an optimal processing method for duck-beak bone particle.

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Microstructure and properties of bioactive glass-ceramics

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Keywords: apatite, glass ceramics, implants, bioactive

Meat processing facilities produce significant amount of raw animal bone waste representing a serious biohazard. For this reason the safe deposition of these bones is of utmost importance. The main mineral constituent of these bones is calcium phosphate, therefore they can be used as a precursor for production of bioactive glass-ceramics. A process was developed to convert animal bones into a valuable secondary raw material of calcium phosphate based glass-ceramics for bone replacement, tissue repair, and augmentation. Bioactive glass-ceramics containing β-whitlockite/α-whitlockite and wollastonite were manufactured from chemically and heat treated, protein-free bovine bone as well as a base glass prepared by melt quenching. Body fluids (similar to the blood plasma) enhance apatite formation on the surface of calcium phosphate based bioceramic implants, which in turn improve the bone-binding strength of such devices. A systematic investigation of hydroxyapatite formation on the surface of bioactive glass ceramics immersed into simulated body fluids (SBF) was therefore conducted on glass ceramic samples produced from high temperature sintered animal bones. Significant changes of phase composition, microstructure, as well as microhardness of surface prior to and after SBF-treatment were observed. Open porosity correlates with other results. Dissolved constituents (Ca and P) of bioactive glass ceramics were quantified by X-ray fluorescence analysis of SBF. Optimum conditions were determined by using microhardness, porosity, and dissolved Ca as independent variables.[1]

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Simple and reinforced biological-derived hydroxyapatite coatings for metallic implants

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Keywords: reinforced biological-derived hydroxyapatite, high adherence, *in vitro* tests, pulsed laser deposition

We report on simple and reinforced hydroxyapatite (HA) thin films synthesized by Pulsed Laser Deposition from sustainable resources (bovine and ovine bones) onto medical grade Ti discs. The role of reinforcement agents (e.g., Li_2O, Li_2CO_3, Li_3PO_4) on the morphology, structure, bonding strength and cytocompatibility of the films was investigated by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS), X-Ray Diffraction (XRD), Fourier Transformed Infrared (FT-IR) Spectroscopy, surface energy measurements, pull-out and *in vitro* tests (bioactivity in simulated body fluid, SBF, and cytocompatibility in human mesenchymal stem cells, hMSC).

SEM investigations evidenced that the morphology of the surfaces consisted of particulates with mean diameters in the range of (2–3) µm. FT-IR and XRD analyses demonstrated that the synthesized structures consisted of a pure HA phase, with different degrees of crystallinity mainly influenced by the reinforcement agents. A quasi-stoichiometric target-to-substrate transfer was inferred from EDS analyses, with a Ca/P ratio corresponding to a biological apatite. For all synthesized structures, a hydrophilic behaviour was evidenced, which is known in the literature to be related to an improved surface attachment of osteoblast cells. The pull-out measurements have indicated adherence values superior to the threshold imposed by International Standards, the highest values being determined in the case of reinforced structures. After only three days of immersion in SBF, FT-IR spectra corresponding to all synthesized structures showed a remarkable growth of a biomimetic HA layer which demonstrated the excellent bioactivity of the films. *In vitro* viability tests revealed that high concentrations of Li_2O within HA thin films were cytotoxic for hMSC, whilst incorporation if Li_2CO_3 and Li_3PO_4 in HA promoted cells harmonious growth on film surfaces.

Due to proven physical-chemical characteristics and superior cytocompatibility, along with the low fabrication cost from sustainable resources, these reinforced biological-derived materials should be considered as a prospective solution for future progress of metallic implants field.

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Open-celled glass-ceramic foams from alkali activation and sinter-crystallization of bioglasses

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Keywords: alkali activation, gel casting, bioactivity, wollastonite, diopside, glass-ceramics

Highly porous wollastonite ($CaSiO_3$)-diopside ($CaMgSi_2O_6$) glass-ceramics have been successfully obtained by a new gel-casting technique. The gelation of an aqueous slurry of glass powders was not achieved according to the polymerisation of an organic monomer, but as the result of alkali activation. The alkali activation of a Ca-Mg silicate glass (with a composition close to 50 mol% wollastonite – 50 mol% diopside, with minor amounts of Na_2O and P_2O_5) allowed for the obtainment of well-dispersed concentrated suspensions, undergoing progressive hardening by treatment at low temperature (80 °C), owing to the formation of C-S-H (calcium silicate hydrate) gel. An extensive direct foaming was achieved by vigorous mechanical stirring of partially gelified suspensions, comprising also a surfactant. The open-celled structure resulting from mechanical foaming could be 'freezed' by the subsequent sintering treatment, at 800–900 °C, causing a substantial crystallization. A total porosity exceeding 85%, comprising both well-interconnected macro-pores and micro-pores on cell walls, was accompanied by an excellent compressive strength, above 3 MPa. An extension of the approach to another Ca-Mg bioglass (CEL2, richer in Na_2O and P_2O_5), will be presented as well.

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Influence of plasma treatments on the surface of Al_2O_3-5vol%ZrO_2 nanocomposites in the formation of calcium phosphate phases

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Keywords: nanocomposites, calcium phosphate, plasma surface treatments, biomimetic coating, alumina-zirconia

The bioinert nature of the Al_2O_3-ZrO_2 nanocomposites has stimulated the development of techniques to make the biological performance of these ceramics more suitable.[1] For this purpose, the biomimetic coating has been used to promote the deposition of different calcium phosphate phases[2] onto theirs surfaces, improving the bioactivity of the Al_2O_3-ZrO_2. Besides, the surface treatment prior to the biomimetic coating could favor the formation of a particular calcium phosphate phase, determining the successful implementation of an implant as well as the influence host tissue response. Therefore, the objective of this study is to evaluate the influence of different plasma surface treatments in the formation of calcium phosphate phases on the surface of Al_2O_3-5vol%ZrO_2 nanocomposites. To do so, Al_2O_3-5vol%ZrO_2 samples were shaped, calcined at 400 °C, sintered at 1500 °C, subjected to different plasma surface treatments (20%N_2-80%H_2, 40%N_2-60%H_2, 40%N_2-40%H_2-20%O_2, 30%N_2-50%H_2-20%O_2, 100%N_2 and 100%O_2) and biomimetically coated. The surface characterization was performed by atomic force microscopy, confocal microscopy, X-ray diffraction, and infrared spectroscopy. The plasma treatments influenced the chemical and physical characteristics of the surfaces of the nanocomposites, especially for the follow plasma compositions of N_2-H_2-O_2. For these conditions, the content of calcium phosphates formed was significantly higher than for the nanocomposites treated by others plasma compositions as well as for untreated nanocomposites. It was also observed that the preliminary plasma surface treatment favored much more the formation of hydroxyapatite phase than the formation of alpha-tricalcium phosphate and beta-tricalcium phosphate phases. These differences among the content formed phases affected the homogeneity of calcium phosphate distribution on the treated surface of the nanocomposites. Thus, the plasma surface treatments that the Al_2O_3-5vol%ZrO_2 nanocomposites undergo prior to the biomimetic coating are believed to effectively contribute to the adhesion, proliferation and biofixation of the desired cell type on bone implants.

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Characterization and SBF evaluation of neat and heat treated SiC fibers-containing polycaprolactone composites

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Keywords: polycaprolactone, silicone carbide, thermal treatment, bioactivity, SBF media

Polycaprolactone (PCL) has been in use as a biodegradable polymer for tissue engineering and drug delivery applications. Its application in the treatment of defective bone is based on its integration with ceramic reinforcements to improve their mechanical properties. Among these reinforcements, ceramic fibers provide, not only mechanical support, but may also enhance the bioactivity of the polymer if it has its built-in bioactivity characteristics. Silicon carbide (SiC) is classified as a structural ceramic with superior mechanical properties. SiC is also classified as a bioinert material. In the current study, SiC ceramic fibers, both as received (SiC) and after heat treatment at 950 °C (TSiC), were mixed with PCL solutions in $CHCl_3$ in percentages up to 6 wt%. Suspensions were casted and dried at room temperature. Composites prepared thereafter, were characterized for their composition by XRD, FTIR and TGA techniques and for their microstructure using SEM technique. Composites were also subjected to measurement of their tensile strength using a Schimadzu mechanical testing machine and were evaluated for their preliminary *in vitro* characteristics by soaking in SBF media for up to 14 days at 37 °C. Results showed formation of a thin layer of SiO_2 onto the surfaces of the SiC fibers. SiC and TSiC were homogeneously distributed within the PCL polymeric matrix, as revealed by SEM investigation. Mechanical properties and SBF characteristics were both shown to depend on the type and concentration of the reinforcing fibers in the polymer matrix.

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Preparation and characterization of HAp-wollastonite composites and their performance in SBF media at 37 °C

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Keywords: hydroxyapatite, wollastonite, chemical synthesis, bioactivity, SBF media

Hard tissues, such as bone and teeth, are natural composites of hydroxyapatite (HAp) nanocrystallites and collagen nanofibrils.[1] The unique properties of natural bone stems from the mechanical interlocking between these ingredients. Bone-like implants of various compositions have been prepared for total or partial fixation of defective bone. In the current study, bone-like HAp was prepared in the presence of various percentages of bioactive highly crystalline calcium silicate (wollastonite) fibers at 70 °C and pH 10–11. Prepared composite powders were heat treated at 800 °C. As-prepared and heat treated powder composites were characterized for their composition by XRD, FTIR, TGA and for their morphology using SEM techniques. Powders were further aged in SBF media and maintained at 37 °C for up to 14 days. Results showed the dependence of the HAp structure and crystallinity on the type and concentration of wollastonite fibers. Moreover, and after evaluation in SBF media, wollastonite fibers were shown to provide sites for the precipitation of bone-like HAp crystallites, indicating the preliminary bioactivity of the prepared composites powders.

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Preparation and application of silica-coated maghemite in the isolation of plasmid DNA

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Keywords: surface treatment, superparamagnetic nanoparticle, maghemite, plasmid DNA

The aim of this study was to prepare the magnetic bead for purification plasmid DNA using low cost γ-Fe_2O_3 phase nanoparticle on behalf of Fe_3O_4 phase nanoparticle with limited productivity. As the technology of separation and purification biomolecule using magnetic bead is based on the superparamagnetic property, the magnetic property of γ-Fe_2O_3 phase could replace the intrinsic property of Fe_3O_4 phase. However, it has relatively low surface charge for bonding SiO_2 layers for selective bonding with plasmid DNA. In this study, for that rea-

son, surface of the γ-Fe_2O_3 nanoparticles were modified with hydrogen chloride or ammonia, which are acid and base, to secure a surface state for forming the SiO_2 layer on its surface. In addition, the dispersibility in the aqueous solution was improved by the modified surface characteristic, and it could be provided an environment in which a single layer can coated on its single particle. Surface modified the γ-Fe_2O_3 nanoparticles were successfully coated SiO_2 layer through Stöber process. Morphology of prepared γ-Fe_2O_3@SiO_2 nanoparticle were observed by FE-SEM, and TEM. Moreover, the behavior of changes of surface properties were measured by FT-IR, and Zeta-potential. Particle size distribution data as well as Zeta-potential value was understood tendency of dispersion force in the suspension. Magnetization of the specimens were estimated by VSM. The performance evaluation of magnetic purification of plasmid DNA analyzed directly by agarose gel electrophoresis and UV spectroscopy.

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Customized ceramic implants made by additive manufacturing

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Keywords: additive manufacturing, implants, bioceramics, tricalcium phosphate, alumina, zirconia

Lithography-based additive manufacturing (AM) technologies based on photopolymerization have gained increasing interest for biomedical applications because of their high precision and resolution. This contribution focuses on ceramics made by lithography-based ceramic manufacturing (LCM) for two main application areas: permanent implants on the basis of zirconia and alumina ceramics as possible substitutes for titanium implants in cranio-maxillofacial surgery or for blood pumps, and resorbable ceramics such as tricalcium phosphate (TCP) or hydroxyapatite as scaffolds in regenerative medicine.

For permanent implants the main advantage of printed ceramics is the possibility of easily making tailor-made designs based on patient-specific CT data. Showcases include plates and screws for fixation devices but also implantable blood pumps.

On the other hand, printed compounds based on bioresorbable ceramic materials such as TCP would be ideal candidates for temporary bone substitute materials in tissue engineering due to the similarity to native bone tissue.

This work presents the results regarding the shaping of TCP by means of LCM. The layer-by-layer principle of this method enables the fabrication of highly intricate structures with virtually no limitations regarding geometrical complexity. Scaffolds, cellular structures or parts with defined macroporosity can be shaped using LCM to provide environments for cells to adhere, migrate and proliferate throughout the structure.

For *in vivo* experiments printed TCP scaffolds were implanted into New Zealand white rabbits. The results based on histological sections showed excellent results in terms of defect bridging and the area of regrown bone compared to titanium. Especially in presence of bone morphogenetic protein-2 significant improvements could be measured indicating the suitability of these printed scaffolds as bone substitute material.

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Colored powders for bioceramics based on calcium phosphates

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Keywords: bioceramics, calcium phosphate, 3D-printing, stereolithography, osteoconductivity

Composite materials containing phases of tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) and/or hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) have been approved and authorized for clinical use in the most countries of the world. The main advantages of these materials include good biocompatibility and osteoconductivity *in vivo*. Chemical composition of ceramic materials based on HA and TCP are very similar to those of bones of animals and humans. These materials are not toxic and they do not cause allergic reactions. However, they have the following disadvantages: low speed of bioresorption, weak stimulatory effect on the growth of new bone tissue (osteoinduction), low fracture toughness and low fatigue strength under physiological conditions.

The selection of various calcium salts as initial ingredients allowed us to control a predetermined pH level in the reaction zone. Nanosized calcium phosphate powder synthesized from 0.5 M solutions of calcium acetates/saccarate and ammonium hydrophosphate contained a significant amount (64%) of sucrose as the reaction by-product. A microporous ceramic with a pore size from 1 to 6 μm and a relative density of 56% was obtained on the basis of calcium phosphate powder synthesized from aqueous solutions of monocalcium saccharate and ammonium hydrophosphate. A significant linear shrinkage of powder workpieces after calcination (up to 40% after calcination at 1200 °C) indicates a high activity of the synthesized powder with respect to sintering. The phase composition of the ceramic represented by β-TCP and HAP allows one to consider the synthesized powder to be acceptable for the manufacture of bone implants. Ceramic composites containing these phases are widely used as materials for bone implants.

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Al_2O_3–ZrO_2–TiO_2 nanocomposites for dental applications

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Keywords: dental bioceramics, alumina, zirconia, titania, mechanical properties, microstructure

Alumina and Zirconia based ceramics are preferred over metallic biomaterials in orthopaedic and dental applications. Their widespread use is due to their good biocompatibility, aesthetics (dental restoration), good mechanical properties (high hardness, low rates of friction) and chemical resistance.[1] However individual Al_2O_3 applications suffered for failure problems due to alumina intrinsic low toughness,[2] while a major drawback of zirconia ceramics are the *in vivo* ageing related defects due to the martensitic phase transformation, from tetragonal to monoclinic structure, when in contact with physiological fluids.[3] Alumina-zirconia composites which combine the high alumina hardness with the fracture resistance of zirconia is an alternative choice. Several studies on Al_2O_3/ZrO_2 composites are indeed reported in literature.

Moreover, the addition of small amount of different metal oxide such as TiO_2 have been proposed to promote the sintering behaviour, customize the microstructure and improve the mechanical properties.[4] There are some publications in literature about the effect of titania on Zirconia Toughened Alumina (ZTA) but no study on sintered ternary ceramic composites of Al_2O_3–ZrO_2–TiO_2 has been carried out yet specifically related to dental applications.

The main purpose of the present study is the development of Al_2O_3–ZrO_2–TiO_2 nanocomposite ceramics targeted to dental applications. Al_2O_3, ZrO_2 and TiO_2 powders were mixed, uniaxially pressed and sintered at 1400 °C to obtain the desired composites. Microstructure and phase composition of the sintered ceramic composites were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). The mechanical properties: Vickers hardness, Young's Modulus and strength were also examined. The results revealed that the Al_2O_3–ZrO_2–TiO_2 system could offer different promising composite materials for a wide range of dental applications.

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Functionally graded porous Si_3N_4 ceramics produced by tape casting and sintered in nitrogen

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Keywords: tape casting, silicon nitride, porous, functionally graded materials

Porous Si_3N_4 ceramics have recently acquired great interest and been studied intensively due to their superior mechanical, physical and chemical performances. They have been widely applied in the fields of environmental protection, chemical industry, aviation, biomaterials, etc.[1–4]

Thin layers of ceramics can be produced by tape casting to be used as single layers or to be stacked and laminated into multi-layered structures. Various types of pore formers are being used for the fabrication of ceramics with controlled porosity. Porous silicon nitride ceramics having properties similar to the human bone are sintered and characterized in order to develop a material applicable as bone substitute.

In this study a process for the tape casting of silicon nitride ceramics has been developed and comparison is made between different sintering temperatures. For this purpose, silicon nitride functionally graded ceramic layers were sintered at different temperatures via nitrogen gas sintering. A slurry, consisting of the silicon nitride powder in a solvent with additives like dispersants, binders and plasticizers was cast on a stationary surface. In the study, non-aqueous-based tape casting of Si_3N_4 was carried out in a non-continuous single blade tape casting machine. The green tapes were then dried, laminated and mechanical pressing by cold isostatic pressing (CIP) was carried out. After pressing they were sintered to obtain a functionally graded ceramic. Porous silicon nitride (Si_3N_4) ceramics were sintered in nitrogen atmosphere graphite element furnace between 1650 °C–1750 °C and 1850 °C with sintering additives like Al_2O_3 and Y_2O_3. The sintered layered material was characterized using SEM and XRD.

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Apparatus for treatment of skin and subcutaneous cancer diseases by hyperthermic methods

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Keywords: controlled local hyperthermia, necrosis, ulceration, metastasis

To develop mono-therapeutic effect of hyperthermia against cancer diseases, on the basis of experimental material, a laboratory device "Lezi", was used which was created in Georgia at the Bionanoceramic and Nanocomposite Materials Science Center of Georgian Technical University (National Center of Intellectual property of Georgia "Georgian Patent", Certificate of Deposition # 5054. "Controlled local hyperthermia for treatment of cancer diseases"). In all animals (albino rat, 3 month age mice) inhibition of cancer disease and development of intra-tumor necrosis were fixed. After 7–10 sessions tumor was ulcerated, that refers to irreversibility of the process and the efficiency of the applied method of hyperthermia (Conclusion of Laboratory of Morbid Anatomy "PathGeo". Examination # 3119012, Tbilisi, Georgia).

On the basis of results of morphological study it was proved that liver and lungs (main target bodies) are intact; secondary tumor injuries are not fixed.

Thus, we can conclude, that during cancer mass lysis that is conditioned by local hyperthermia, matastasis in bodies does not take place. Clinical device was created for controlled local hyperthermia to treat surface diseases.

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Cerium-doped bioactive 45S5 glasses: spectroscopic, redox, bioactivity and biocatalitic properties

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Keywords: cerium, bioactive glasses, catalase mimetic activity, superoxide dismutase mimetic activity, FTIR, XRD, XPS

The ability of Ce-containing bioactive glasses, based on 45S5 Bioglass®, to inhibit oxidative stress in terms of reduction of hydrogen peroxide and superoxide, by mimicking the catalase and superoxide dismutase activity is reported in this work. The best catalyst activities were obtained for the glass with the higher content of cerium (H_5.3 = 5.3% mol of CeO_2 in the nominal glass composition). Moreover, the detailed study of the surface during the mimic enzymatic activity tests shows the formation on the glass surface of a Ca-P rich layer where the presence of Ce ions favours the formation of $CePO_4$. The formation of $CePO_4$ inhibits the formation of hydroxyapatite decreasing the bioactivity of the glass with higher % of CeO_2 in the glass composition. This study allows also to find the best Ce^{3+}/Ce^{4+} ratio in order to optimize the catalytic activity toward the decomposition of hydrogen peroxide

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Synthesis, characterization, redox properties and *in-vitro* bioactivity of glasses coated by alginate

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Keywords: Ce-containing bioactive glasses, alginate coating, catalase mimetic activity

Alginate is a polymer widely applied in the pharmaceutical industry (e.g. excipient for drugs, dental impression material, and a wound dressing). As a biomaterial, alginate has a number of advantageous features including biocompatibility and nonimmunogenicity and they are likely related to its hydrophilicity. The gentle gelling behavior of alginate allows encapsulation of various substances with minimal trauma. A chemically modified alginate is currently used clinically as a drug delivery vehicle for proteins that promote regeneration of mineralized tissue and as a carrier for transplanted cells.[1] The addition of Ca ions into a solution of Na-alginate causes a cross linkage forming Ca-alginate system. The Ca-alginate is insoluble in aqueous solution and culture medium. This enables it to remain as supporting structure for the seeded cells when it is used as a scaffold both *in vitro* and *in vivo*.

Bioglasses are the most preferred bioactive fillers that form a bond to both hard and soft; this is due to formation of hydroxyl-carbonated apatite (HCA) layer on their surface in physiological fluid. The addition of bioactive glass particles into scaffold material not only improves the biomineralization capability of the composite scaffolds but also increases the stiffness of the scaffold material and the surface adsorption of proteins.

In this paper we report the preparation of scaffold (beads) formed by bioactive glasses and calcium alginate, their solid state characterization and the effect of alginate coating on the bioactivity and the catalase mimetic activity of Cerium-containing glasses.[2] The investigated glasses are obtained by melting method: 45S5 Bioglass® (H) and 50S25N25C (K) glasses and sol-gel coupled EISA method: mesoporous bioactive glasses (MBG) and the same glasses doped with CeO_2 up to 5.3%mol: H 5.3Ce_alg, K 3.6Ce_alg, MBG 5.3Ce_alg; the mean experimental wt % composition of beads is 60% glass, 40% alginate. The results indicate that i) all Ce-containing beads maintain catalase mimetic activity that varies in the order: MBG 5.3Ce_alg >> H 5.3Ce_alg > K 3.6Ce_alg; ii) catalase mimetic activity is observed also for the beads of undoped glasses, iii) the amount of H_2O_2 decomposed varies with the glass composition, iv) the absence of a mutual influence of alginate and cerium on samples behavior. The hydroxyapatite formation is observed only for MBG 5.3_alg in view of its high surface area.

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Calcium phosphate ceramics from hydroxyapatite suspensions containing sucrose and diammonium phosphate aqueous solutions

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Keywords: calcium phosphates, calcium polyphosphate, calcium pyrophosphate, calcium orthophosphate

One of the most important development directions of modern medical materials science is the creation of inorganic materials for artificial bone implants. The regenerative medicine development requires the creation of resorbable materials based on calcium phosphates in which the Ca/P ratio is smaller than in the main inorganic component of the bone – hydroxyapatite (HA, Ca/P = 1.67). Creation of such materials requires the development in methods for synthesis of calcium phosphates with Ca/P ratio = 1.5; 1.0; 0.5. The composite materials containing phase of calcium polyphosphate (Ca/P = 0.5) have the highest solubility. The purpose of the present work is to obtain ceramic materials containing calcium polyphosphate, calcium pyrophosphate and calcium orthophosphate phases.

We assume that depending on the components ratio, various bioresorbable phases are formed via following reactions during the heat treatment.

$$3Ca_{10}(PO_4)_6(OH)_2 + 2(NH_4)_2HPO_4 = 10Ca_3(PO_4)_2 + 4NH_3 + 6H_2O$$
$$Ca_{10}(PO_4)_6(OH)_2 + 4(NH_4)_2HPO_4 = 5Ca_2P_2O_7 + 8NH_3 + 7H_2O$$
$$Ca_{10}(PO_4)_6(OH)_2 + 14(NH_4)_2HPO_4 = 10Ca(PO_3)_2 + 28NH_3 + 22H_2O$$

The ceramic materials were obtained from highly concentrated hydroxyapatite suspensions in an environment of sucrose and diammonium phosphate aqueous solutions. Cord-shaped samples were formed via 2 mm diameter plastic injectors. The ability to form homogeneous paste layers and stable multi-layer constructions was studied. The most reassuring results were given by suspensions with HA/sucrose solution ratio of 0.8 g/ml and sucrose aqueous solution concentration of 0.5M.

After molding the samples were sintered in the range of temperatures from 900 °C to 1100 °C depending on the target phase. Phase composition of the sintered samples is presented below. The properties of ceramic materials obtained were also studied with thermal analysis (TA), mass spectrometry (MS) and scanning electron microscopy (SEM).

Target phase	Ca/P ratio	Sintering temperature	Phase composition
β-$Ca_3(PO_4)_2$	1.5	1100 °C	β-$Ca_3(PO_4)_2$
β-$Ca_2P_2O_7$	1.0	1100 °C	β-$Ca_2P_2O_7$, β-$Ca_3(PO_4)_2$
β-$Ca(PO_3)_2$	0.5	900 °C	β-$Ca(PO_3)_2$

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One-pot sol-gel synthesis of scaffolds for biomedical applications

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The development of three-dimensional porous structures (scaffolds) with ability to interact with the body leading to the formation of new bone at a rate equal to its own degradation rate has become a major challenge in tissue engineering.

In the present study the scaffolds for bone regeneration applications were developed, within the glass systems SiO_2-CaO-TiO_2 and SiO_2-CaO-ZrO_2 produced by one-pot sol-gel method using two types of surfactants (sodium lauryl sulphate, SLS, and polyethylene oxide, PEO) as porogenic agent. The study was focused on the influence of the type and amount of surfactant used, the introduction of alkoxides of zirconium and titanium, and the potential bioactivity of the scaffolds.

The use of a nonionic surfactant (PEO) as a porogenic agent, allowed the production of monolithic scaffolds with morphological characteristics more interesting that the ones produced by the introduction of an anionic surfactant (SLS). The former showed a homogeneous network of macropores interconnected and with larger macropores (> 50µm) as well as higher values of surface area ($262m^2$ / g). In addition, it was also found that the scaffolds of the system SiO_2-CaO-ZrO_2 showed significantly greater surface areas than the scaffolds produced from the system SiO_2-CaO-TiO_2, showing therefore a greater ability to interact with the surrounding medium and form an apatitic surface layer.

The bioactivity tests showed that all scaffolds exhibited the formation of a layer of calcium phosphate on their surface, and a constant degradation rate, thus showing the high potential of applying these materials in the field of bone regeneration.

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Mechanical characterization and corrosion behavior of protective TiC/amorphous C nanocomposite coating as surface thin film

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Keywords: TiC/a:C protective coating, potentiodynamic polarization method, mechanical properties, SBF, ICP-OES

The long-term performance of surgical implants is often limited by their surface properties (such as poor tribological property). There are a colorful range of the various developments, so, using different nanocomposite coatings in order to improve the mechanical properties are widespread. Ceramic titanium carbide/amorphous carbon (TiC/a:C) protective nanocomposite thin film may be a potential candidate for such a surface protection coating to the different implant materials which serves as barrier layer. The main goal of my research work is to study the influence of TiC/a:C protective thin film on the corrosion, mechanical and tribological properties of sandblasted/polished Ti and TiAl6V4 substrates. For these purpose, the coatings were developed by simultaneously depositing Ti and C on the mentioned wafers using DC magnetron sputtering system in argon (0.25 Pa) at room temperature. The X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were used to study and compare the chemical compositions and morphologies of the deposited TiC/a:C protective thin films. The mechanical characteristics of the films were investigated by nanoindentation technique while the tribological behavior of them was examined by a ball-on-disk tester (CSM tribometer). The electrochemical corrosion behaviors of the samples were investigated in simulated body fluid (SBF) by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques at 7.4 pH and 37 °C. Besides the electrochemical techniques, metal ion release has been quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES). The experimental results obtained from different electrochemical methods, ICP-OES and SEM showed that the TiC/a:C protective coating on sandblasted implant device improve the corrosion properties of the implant material and it is able to control the metal ion release. So, it is also proved that the roughening the surface by sandblasting can enhance the corrosion resistance. However, the presence of V was detectable in each case, the Al and Ti ions have been detained by the TiC/a:C thin film coated s.b. TiAl6V4. It was also shown, that the hardness and tribological property of the bare implant materials are improving by four orders of magnitude with the TiC/a:C nanocomposite coating beside a moderate elastic modulus value. The highest hardness (H) of ~ 28 GPa ± 3 with friction coefficient of ~ 0.20 ± 0.07 was observed in case of the film prepared at ~ 40 at% Ti content. The main conclusion of my research is that a ceramic TiC/a:C thin film with ~ 20 at% a:C and ~40 at% Ti contents would be a suitable choice for a protective nanocomposite coating.

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Bioceramics based on $CaK_xNa_{1-x}PO_4$ (x = 0÷1)

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Keywords: bioceramics, phase diagram, rhenanite, bone implants

Nowadays, calcium phosphate bone implants are of great interest bearing in mind their principal biocompatibility and well-elaborated processing routes. Such materials should be, at least, rather resorbable and facilitate newly bone ingrowth (osteoconductivity). At present, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and tricalcium phosphate ($Ca_3(PO_4)_2$), the former is less resorbable, are used to treat the damaged bones. Low resorption rate of hydroxyapatite means that an implant cannot dissolve in time and a bone de-novo grows up on implant surface leading to increase of probability of fracture. One of the way to increase resorption rate (that means to increase solubility) of the implant is to enlarge its molar volume (in fact, cell volume of materials lattice). From this viewpoint, a replacement of a part of calcium ions in tricalcium phosphate lattice to sodium or/and potassium one follows such a strategy very well. In this case, $Ca_{3-x}(K_yNa_{1-y})_{2x}(PO_4)_2$ can be regarded as almost ideal composition for such an intent.

In this study we determined phase relationships in the system of $CaKPO_4$ - $CaNaPO_4$ and described an intermediate phase noted us as X, having a range of its homogeneity and the temperature of its phase transition about 657 °C. As revealed by SEM, ceramics based on these compositions demonstrated domain-like microstructure resulted from phase transformation of complex nature.

Strength properties of the ceramics under study was measured by B3B method. Decrease of strength value for x = 0.5-0.7 was attributed to phase transformation accompanied by volume changes.

Dissolution behavior of the $CaK_xNa_{1-x}PO_4$ ceramics in model solutions at constant pH was studied and compared with other calcium phosphates as well as thermodynamic predictions.

Acknowledgment

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Mechanical properties of aging resistant coated 3Y-TZP

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Keywords: zirconia, dip coating, aging, B3B, LTD

Since Garvie[1] first publication on zirconia phase transformation, which occurs in the presence of mechanical stresses, a lot of studies lead to improvement of this material properties. Bending strength, for example, was reported for him to be in the order of 650 MPa, while nowadays this number is easily found above 1 GPa.[2,3] Despite great advances, when stabilized by yttria (Y-TZP), water molecules diffusion can promote phase transformation without mechanical stress, reducing material strength in a phenomenon called Low Thermal Degradation (LTD) or aging.[4] Because yttrium is a trivalent metal, when bonded with oxygen, and zirconium is tetravalent, when the former is used to stabilize zirconia tetragonal phase an oxygen unbalancing is promoted and vacancies are generated. These vacancies are reported as the reason for tetragonal phase stabilization, even for low yttria content added, but they also make, allied to the metastability of the phase, Y-TZP susceptible to aging.[5,6] However, other oxides as magnesium, calcium and cerium, can be also used to stabilize tetragonal phases with the advantage to not generate a significant amount of oxygen vacancies, and, therefore, showing almost no aging.[5,7] Ceria, for instance, stabilizes the tetragonal phase of zirconia with really appreciated fracture toughness and having a strong aging resistance.[5–7] The disadvantage is that mechanical strength achieved by using different yttrium oxide contents, to stabilize cubic phase, or other stabilizers is substantially lower. In this work, mechanical properties of 3Y-TZP and aging resistance of 12Ce-TZP and Y-PSZ were combined. To reach this objective, 3Y-TZP disks were pressed and subsequently dip coated, as green bodies, in suspension containing 12Ce-TZP or Y-PSZ. Co-sinterization was performed in air for 2 hours at 1400 and 1500 ºC, depending of coating. Suspensions and process were optimized to obtain the thinner and denser layer as possible. Aging was evaluated for coatings and bulk showing that produced layers are able to protect the bulk. B3B and micro indentation tests were performed to evaluate the influence of layers in flexural and Young modulus of coated samples.

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Acceleration of the conversion of HA to TCP by the densification process

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Keywords: HA, TCP, HA decomposition, densification and grain growth grain growth

Hydroxyapatyite (HA) powder samples and disc samples, pressed from the same powder type, have been heated to temperatures in the range 1200 to 1300 °C. Subsequent X-ray diffraction analysis showed that the powder samples underwent far less transformation to tri-calcium phosphate (TCP) than the pressed discs, which also underwent densification and grain growth. Further analysis of sintered disc materials showed a definite correlation between HA to TCP conversion and grain size with the volume fraction of TCP increasing with grain size. The data is discussed in terms of material degradation mechanisms and material transport mechanisms during sintering and it is concluded that the enhanced degradation rates during densification are due to grain boundary material transport, which involves decomposition of hydroxyapatite to constituent ions or sub-assemblies. In contrast the decomposition of the powdered material is solely dependant on dehydroxylation of surface layers and subsequent equilibration of the resultant reaction products with the underlying hydroxyapatite.

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Antibacterial efficiency of alkali-free biocompatible glasses additivated with ZnO and/or SrO active agents

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Keywords: biocompatible glass, alkali-free, antimicrobial, implant coatings, magnetron sputtering

Bioactive glasses (BG) are a remarkable class of materials based on oxides, which possess the highest index of bioactivity, reflected in their ability to form a strong bond with the living tissues (both hard and soft) in a very short period.[1,2] Such properties make them ideal candidates for the biofunctionalization of titanium (Ti) implants in view of boosting their osseointegration. However, the significant mismatch in the thermal expansion coefficients (CTE) of the classical BG systems ($\sim 15–17\times10^{-6}/°C$) and Ti ($\sim 9.2\times10^{-6}/°C$), impeded the successful use of BGs as implant coatings, thus limiting for the moment the applicability of these osteoproductive materials only to applications bearing low biomechanical loads.

On the other hand, the microbial contamination with extremely resistant and adaptive strains is one of the major issues in osseous surgery. Furthermore, in dental surgery one cannot obtain the aseptic conditions achieved in the current general or orthopaedics surgery. The impossibility to attain aseptic conditions, but only to limit contamination, demand implant surfaces that do not permit colonization with commensal bacteria, or even enable bacteriostatic or bactericidal effect.

Thereby, in this study series of innovative alkali-free BG formulations (SiO_2-CaO-MgO-P_2O_5) with ZnO and/or SrO antimicrobial agents are introduced and thoroughly studied, from physical-chemical and biological points of view, in both bulk and thin film form. The concurring action of combined antimicrobial agents are surveyed in the search of the most effective ratios, capable to simultaneously enable reduced CTEs and prevent the adaptability/resistance of microorganisms, with the aim of delineating the best dental implant coating design.

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Macroporous composite scaffold (HA/TiO_2) with enhanced mechanical properties

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Keywords: scaffold, bone, hydroxyapatite, titanium dioxide, macroporous, ceramic, foam

In the field of bone surgery, the development of bone substitutes for load-bearing bone parts represents one of the most challenging applications, especially due to the difficulty of expressing high bioactivity and bone-like mechanical properties simultaneously[1]. The present work proposes a modified foaming process[2] to produce porous HA and composite TCP/TiO_2 scaffolds in relatively short time, where the pore extent and organization can be tailored in a reliable and repeatable manner to offer wide, pervious pathways to cells and fluids, in association with high mechanical strength, to meet specific demands in bone surgery.

HA powder was calcined and sieved under 150 µm, and used to prepare HA scaffolds or to be mixed with TiO_2 nanoparticles to obtain, after sintering, TCP/TiO_2 scaffolds. A high-energy ball milling process was used to prepare ceramic suspensions for the foaming process. Then, the foamed suspensions were poured in paper moulds and dried at room temperature to obtain stable ceramic foams. HA and TCP/TiO_2 scaffolds with different porosity were prepared by varying the air volume into the jar before the last stirring. Finally, a high-temperature thermal treatment was used to consolidate the green bodies.

The XRD patterns revealed that, whereas HA scaffolds maintained phase purity after sintering, the composite scaffolds were made of TCP, TiO_2 and small amount of calcium titanate ($CaTiO_3$). The reduction in the porosity extent led to a remarkable and significant increase of both compressive strength and Young's modulus. Cell tests carried out by using MG-63 human osteoblast-like cells, reported very good cytocompatibility and cell viability, with very good cell morphology in contact with the porous scaffolds. The obtained results suggested that the use of a direct foaming method and planetary ball milling, can result in a simple and quick approach to generate porous bioactive scaffolds with improved mechanical performance.

The statistical evaluation of the mechanical properties enabled to validate the proposed synthesis method in respect to repeatable and reliable production of highly porous bone scaffolds. A simple model of the process parameters also pointed out the feasibility of flexible design of porous scaffolds even for load-bearing applications, thus opening to new personalized therapies.

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3D cellular silicon nitride structures and their *in vitro* viability for bone regeneration

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Keywords: silicon nitride, cellular, robocasting, bioactivity

Highly porous cellular ceramics are commonly employed in applications where conditions of high temperatures, extensive wear and corrosion media exist (like filters, catalyst supports, heat sinks...)[1]. However, one of the most challenging uses is as biomaterial for bone replacement or regeneration. On the other hand, Robocasting[2], a filament-based printing method that requires concentrated shear thinning colloidal inks to extrude continuous filaments, arises as a promising additive manufacturing technique to produce cellular ceramic scaffolds. In fact, biomaterials such as hydroxyapatite (HA) and β-tricalcium phosphate (β-TCP), have been printed by this method[3], although the main problem for application of these macroporous scaffolds still lies in the poor mechanical resistance associated with their composition and porosity. Silicon nitride (Si_3N_4) has shown to be a biocompatible material[4]. Additionally, due to its high strength and toughness, it could be a great candidate to fabricate scaffolds for custom orthopedic applications.

In the present work, Si_3N_4 structures with sintering aids were 3D printed by Robocasting with a pattern of macroporous cavities of 400–600 µm. The optimization of the ceramic inks favoured the controlled extrusion through the fine nozzle (330 µm) while avoided sagging. The inks had a total solids volume fraction of 0.40 and a content of organic additives ≈10–12 wt.% that imparted a pseudoplastic behaviour with yield stress rheology. After printing, drying and calcining processes, the 3D-structures were sintered either in a conventional graphite furnace or by spark plasma sintering technique, under controlled N_2 atmosphere and low-pressure in both cases. These sintered cellular 3D-structures displayed densities above ≥ 96–99% of the theoretical value and ~18–22% of linear shrinkage. Results on the densification, weight loss, linear shrinkage, semi-quantitative analysis of crystalline phases, microstructure analysis and the mechanical properties of these structures are comparatively discussed. In addition, the bioactivity and ion release rate in simulated body fluid (SBF) of these 3D-structures as well as their influence on protein adsorption (Bovine Serum Albumin) were evaluated for its potential application in bone regeneration.

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Functionally graded porous Si_3N_4 ceramics produced by tape casting and sintered in air

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Keywords: tape casting, silicon nitride, porous, functionally graded materials

Silicon nitride (Si_3N_4) is a synthetic non-oxide ceramic that is used in many industrial applications, and has been investigated or adapted as a biomedical material since 1989. Porous silicon nitride ceramics having properties similar to human bone have been sintered and characterized with a primary purpose to develop a material to be used as bone substitute. Functional grade materials are preferred to represent the human bone. Tape casting provides a good grading of this type of material.

The aim of this work was to evaluate the effect of sintering temperature on silicon nitride functionally graded ceramic layers sintered at different temperatures via air sintering. A slurry, consisting of silicon nitride powder in a solvent with additives like dispersants, binders and plasticizers was cast on a stationary surface. The green tapes were then dried laminated (including different amount of porosifier) and mechanically pressed at 3 different pressures (100 MPa, 200 MPa and 300 MPa) by cold isostatic pressing (CIP), then finally sintered to obtain a functionally graded porous ceramic.

Porous silicon nitride (Si_3N_4) ceramics were sintered in air atmosphere tube furnace at temperatures between 1300 °C to 1600 °C with sintering additives Al_2O_3 and Y_2O_3. In the study, non-aqueous-based tape casting of Si_3N_4 was carried out in a non-continuous single blade tape casting machine. The sintered layered material was characterized using stereo microscope, SEM and XRD.

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Surface functionalization of novel silicate bioactive glass by bioinspired coating

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Keywords: bioactive glass, polydopamine, silver nanoparticles, surface functionalization

Bioactive glasses are widely considered in bone tissue engineering applications[1]. These applications involve dental and orthopaedic implants fields. Surface functionalization offers the possibility of modifying the properties of the surface of the substrate without changing the bulk properties. Polydopamine is a bioinspired polymer whose extraordinary properties were discovered in 2007. Among the outstanding properties of polydopamine, it offers a platform for post-modification (i.e.: electroless deposition of metal particles)[2]. In this work, we have synthesized a new silicate bioactive glass. The novel bioactive glass (so-called BG1) was fully characterized by DSC/TGA, hot stage microscopy, XRD, XRF and SEM techniques. The sintering behaviour of the substrate was studied and BG1 powder was sintered into 1 cm disks of 3 mm thickness. In a second step, surface of BG1 was modified by coating with polydopamine. Afterwards, we deposited silver nanoparticles onto the surface of the bioactive glass in order to confer an antimicrobial behaviour to the samples. The biomineralization ability of the samples was tested by soaking them in simulated body fluid (SBF). Formation of an hydroxyapatite layer on the surface was assessed by SEM, ICP-OES and XRD. Results show the successful achievement of both polydopamine and silver nanoparticles deposition on the bioactive glass surface. In addition, the formation of an hydroxycarbonate apatite layer on the surface of the samples after soaking them in SBF was confirmed. These results will be compared with standard Bioglass 45S5®.

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Sintering, mechanical and *in vitro* behaviour of wollastonite-diopside and wollastonite-tricalcium phosphate ceramic foams for bone regeneration

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Keywords: wollastonite, diopside, TCP, scaffolds

Ceramic foams are a class of high porosity materials that are used for a wide range of technological applications[1]. In the present work highly porous ceramics foams for bone regeneration or replacement were prepared.

The study was focused on the design, obtention and characterization of highly porous scaffolds of $CaSiO_3$-$CaMgSi_2O_6$ (W-D) and $CaSiO_3$-$Ca_3(PO_4)_2$ (W-TCP) bioceramics. Polymeric sponge replication method[2] by impregnating with concentrated ceramic slurries was employed to synthesize the ceramics foams.

In this process, commercial polymeric sponges were impregnated employing well-dispersed concentrated slurries with a low content of organic additives. For the replication technique polyurethane sponges with dimensions $40\times20\times10$ mm^3 were used as templates. The coated polymers were dried and carefully heating for burning-out the polymer. Later the optimized porous scaffolds were sintered in air at high temperature (1300–1450 °C). A comparative study of the different compositions scaffolds was made. Size, morphology, microstructure, crystalline and glassy phases, micro and macro-porosity, compressive strengths and elastic modulus were determined and discussed. In addition, bioactivity and ion release rate were assessed in simulated body fluid (SBF).

It was found that the physico-chemical parameters of slurries (concentration, viscosity, pH, etc.) are relevant for generating a stable and self-supporting ceramics scaffold and achieve appropriate green bodies. The apparent density of all cellular structures obtained correspond to 98–99% of the theoretical density, with a total macroporosity between 60–85%. To point out, scaffolds become denser as the slurries density increases. The SEM studies showed that highly porous structures with completely interconnected macropores (200–600 µm) and different size of micropores were obtained. The interconnect porosity, mechanical strength and bioactivity of the scaffold make them suitable for bone regeneration in non-load bearing sites.

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A critical analysis of the strength evaluation of Ce-TZP composites for dental applications

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Keywords: biaxial flexural strength, zirconia composites, phase transformation

Zirconia based ceramics have proven to be successfully and widely used for biomedical applications due to their excellent mechanical properties, resulting from the stress induced tetragonal to monoclinic phase transformation occurring in this materials. Besides the comprehension of this transformation toughening mechanism, there have been a significant advances in the design and control of the microstructure of zirconia based ceramics and composites. Recent studies have shown that CeO_2-stabilized tetragonal zirconia (Ce-TZP) based composites are promising for dental applications due to their high toughness and resistance to aging.

Biaxial flexural tests are increasingly used to evaluate the fracture strength of bioceramics, due to the simple preparation of required samples. In particular, the piston-on-3-balls (P3B) test is used to the certification of ceramic materials in dentistry (ISO 6872-2008). In this study, the validity of this test to evaluate the fracture strength of Ce-TZP composites is discussed. Its results are compared to those of the common 4-point bending test for Ce-TZP/Al_2O_3 composites with *in-situ* formed platelets of strontium and lanthanum hexa-aluminates. The results show that the P3B test drastically overestimates the strength values of these materials. This can be related to the extensive transformation zones and the resulting substantial compressive residual stresses in the biaxial configuration, compared to the uniaxial one. This aspect should therefore be integrated when designing a component from such transformable ceramics.

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Hydrothermal deposition of biocompatible ferroelectric $BaTiO_3$ coatings for bone implants

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Keywords: ferroelectrics, hydrothermal synthesis, biocompatibility, bone implants

Our paper[1] showed that surface charge due to ferroelectric polarization influences the electric double layer and diffusion layer in a liquid at the surface. We also proved that surface charge of ferroelectrics promotes bone cell growth and proliferation, but the sign of the charge does not play important role.[1,2] Therefore coating of bone implants by electrically active ferroelectric materials could be advantageous for healing.

We tested various techniques for coating of Ti39%Nb substrates (the alloy suitable for bone implants construction) by ferroelectric $BaTiO_3$. Pure Ti was also used for comparison. Hydrothermal synthesis was found as a suitable one, it can be used for curved surfaces, it is relatively cheap and can be extended from laboratory preparation to a larger-scale production. At first, the substrates were cleaned and annealed in oxygen at 500 °C for 24 hr to form TiO_2 layer. $BaCl_2$ and NaOH were dissolved in reboiled deionized water under argon atmosphere to prevent $BaCO_3$ formation, potential $BaCO_3$ precipitates were removed by a single-use syringe filter. Formed $Ba(OH)_2$ reacted with TiO_2 to $BaTiO_3$, the hydrothermal synthesis was performed in an autoclave with a 50 ml Teflon insert at 250 °C for 6 weeks. XRD detected nanocrystalline $BaTiO_3$ (crystallite size ~40 nm from Rietveld refinement) together with about 35% of TiO_2 and TiNb substrate. SEM also showed nano-size grains. Micro Raman spectra detected $BaTiO_3$ and TiO_2 (rutile), the small Raman peak near 300 cm^{-1} of B_1 symmetry indicated the presence of tetragonal ferroelectric phase of $BaTiO_3$. PFM indicated random orientation of grains and electric dipoles. XPS detected nearly stoichiometric Ba:Ti ratio in the surface layer. Bone cell growth was enhanced on $BaTiO_3$/Ti39%Nb surfaces. Detailed biologic experiments are in progress.

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Wet chemically precipitated porous hydroxyapatite powders

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Keywords: hydroxyapatite, wet chemical precipitation technique, apparent porosity

Bioactive ceramics are important for forming biochemical bonds with the body tissues. They are widely used in several orthopaedic and dentistry applications. Hydroxyapatite (HA) is a member of this class and already found in human hard tissues such as bone and dentin as the mineral component.[1] Wet chemical precipitation technique is a feasible way to produce HA powders in large quantities economically and practically. In this study, porous HA powders were obtained by using calcium hydroxide ($Ca(OH)_2$, ACS Reagent ≥95%, Sigma-Aldrich) and phosphoric acid (H_3PO_4, ACS Reagent, ≥85% wt. in H_2O, Sigma-Aldrich) as the calcium and phosphorus precursors.[2] Wet synthesis methods can be influenced by various parameters such as the reaction temperature of the starting materials, pH of the reaction system, reactant addition rate, etc. This research concentrates on the HA powders obtained by considering the reaction temperature (50 °C and 85 °C) and acid addition rate (slow-5.5 ml/min and rapid-1.5 ml/min) as the process parameters. Cconcentrations of the $Ca(OH)_2$ suspension and the H_3PO_4 solution were arranged according to the (Ca/P) molar ratio which is 1.67 for stoichiometric HA. After the acid-alkaline reaction, the suspension was ripened for 7 days. At the end of the aging period, decantation was carried out to separate the precipitate and the supernatant. The wet precipitate was dried for 7 h at 110 °C and then the dried precipitate was heat-treated at 1250 °C for 2 h. The hard structures obtained as the result of heat treatment were ground by employing a mortar grinder. The ground powders were formed into cylindrical pellets with the (h/d) ratio set as 1.5 utilizing a uni-axial hydraulic press and stainless steel molds. These prepared green pellets were sintered at 1250 °C for 1 h.[3] Bulk density and % apparent porosity measurements of the sintered HA pellets were realized depending on the well-known Archimede's Principle. X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) analyses were performed to characterize the chemical, molecular bonding, microstructural and elemental properties of the synthesized HA powders.

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T07: Challenges and opportunities in industrial ceramics

Invited lectures

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A personal perspective of ceramic research collaborations with industry

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This talk will describe personal experience over the last 35 years of working with industry on ceramic research in the refractories, glass, electroceramics, nuclear, whitewares and engineering ceramics areas. Key benefits and drawbacks of such collaborations will be discussed.

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New challenges in occupational health in the European ceramic industry

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Keywords: nanoparticles (NPs), respirable crystalline silica (RCS), indoor air, occupational exposure, ceramic industry

It is well known that one of the most important health risk in the ceramics industries is the respiratory exposure to chemical agents, usually in particulate form. In this regard, a lot of attention has traditionally been paid to the exposure, effects and control measures to micro-sized fractions of dust, especially those containing respirable crystalline silica (RCS) and lead, since a significant number of workplaces in the ceramic industry have been and are potentially affected by these pollutants. Even though, the epidemiological data suggests that the European ceramic industry has suffered a relatively limited number of workplace diseases linked to these pollutants, the new development in ceramic materials (e.g.: nano-sized materials) and processing (e.g.: ink-jet printing) as well as the new findings in toxicology (e.g.: nano-particle health effects) and new legal requirements (e.g.: classification of RCS as carcinogen) are opening new challenges, and opportunities, in occupational health.

This talk is focused on the recent advances of the author's research group in two of these new challenges: i) exposure to airborne nano-sized particles in the ceramic industry, and. ii) development of processes for detoxifying raw materials containing RCS.

Nanoparticles (NPS) may be generated in industrial processes either when engineered nanoparticles are handled or when processes involving high-energy (mainly thermal or mechanical) are developed. Therefore, industrial ceramic processes which usually include high-energy stages, have a significant potential for producing unintentional NPs release. In this work, the developed methodology for adequately monitoring the NPs in industrial settings, and, the monitoring NPs release results obtained in several industrial ceramic processes are presented. The research line includes the study of thermal (such as thermal plasma spraying or conventional firing) and mechanical processes (such as milling or mechanical treatments). The results obtained so far evidenced the significant emissions and impact on workplaces exposure of several of the studied processes, especially thermal processes. The developed methodology has also allowed the efficiency of some of the proposed control measures to be quantified.

In a previous project an effective RCS detoxification process was carried out and implemented at industrial scale in traditional ceramic manufacturing, but the developed process implies a chemical reaction in an aqueous media (wet process). Based on the promising results obtained in that project, a new detoxification treatment without the need of an aqueous step (dry process) is currently being developed (SILIFE project). The applicability is also foreseen to be tested at industrial scale in different processes and products and not limited to ceramic material. In this talk the preliminary results of the dry RCS treatment at lab scale will be presented, as well as, the new legal requirements established by the European Union for industries potentially exposed to RCS.

In summary, this communication tackles two of the most important challenges in occupational health in the coming years for the European ceramic industry: nanoparticles and RCS exposure. These examples show the need to perform research studies at industrial scale, in order to establish adequate protocols to minimise occupational exposure in real conditions and at affordable costs.

Acknowledgement
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Industrial materials: the challenges for smart coatings

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Keywords: smart surfaces, wettability, amphiphobicity, durability

Today, many different industries need of innovative solutions allowing to make of the same bulk material a new multifunctional one with improved added value, to be easily integrated at a larger scale. Wettability is a fundamental property of a solid surface, whose control plays a key role in industrial sectors such as ceramic and glass ones, aerospace, naval or maritime, electronic and mechanical, and so on. The assessment of the criteria to modulate wetting –

which depends in a complex way on surface chemistry and microstructure interacting with the working environment and on the contact fluids – is among the biggest challenges of innovation in materials' science.

In the last ten years, a lot of studies tried to mimick the outstanding ability of living organisms to repel water and/or oily substances thanks to their perfectly, mostly hierarchically, organized structures and controlled chemistry, and to replicate it on synthetic materials. Current knowledge highlights that high contact angle (CA>150°), CA hysteresis lower than 5° in dynamic phenomena and an extremely reduced surface energy are required to produce i.e. self-cleaning materials, de-icing, anti-fouling, low friction components as well, etc. This lecture focuses on the design of *amphiphobic* glasses and ceramics, metals and alloys, whose surface behaves simoultaneously as *superhydrophobic* and *oleophobic*. Nano-oxides suspensions with an average particle size of less than 30 nm, eventually coupled with perfluorinated, lubricant compounds, have been used to modify the material surfaces giving rise to solid-liquid-air working interfaces or, alternatively, to solid-liquid-liquid ones. Dip coating, automated spraying or roller printing were selected as deposition techniques thanks to their high industrial feasibility. Optically transparent, homogeneous, nanostructured organic/inorganic hybrid coatings, with a thickness commonly in the 200–300 nm range that, if any, can be implemented up to some microns, have been generated by sol-gel method, followed by thermal processing and introduction of low energy elements. Static contact angles with water as high as 178°±1° were obtained, the same materials presenting excellent de-wetting phenomena, with CA hysteresis lower than 5°±1°. A full characterization of the surface chemistry was undertaken by XPS analyses, while FESEM observations allowed to estimate the coating's thickness (300–400 nm) and the different structural features (flower-like lamellas, agglomeration of spherical nanoparticles, etc). The potential applications of *amphiphobic* materials still clamp on durability under different conditions (i.e. chemically aggressive environments, presence of mechanical stresses, friction effects, etc), so that materials' scientists are even more asked to design lasting products able to keep unchanged their performances over the time. Good mechanical resistance and durability to wearing phenomena, anti-frost performances and resistance to chemical attacks of properly designed functional surfaces will be presented, according to different scenarios. The obtained results encourage to think that durable *smart* materials can be planned, bringing great convenience in many strategic industrial processes.

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Pathway towards high recycled content traditional ceramics

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Keywords: ceramic tiles, secondary raw materials, circular economy, sustainability

Nowadays plenty is already known about traditional ceramic tiles. More than one hundred scientific works dealing with waste recycling in porcelain stoneware mixes are available in literature and over twenty research results have been patented. Until about 2005, the research demonstrated just a limited substitution of waste, such as scrap glass, in traditional tile mixes (up to 10% of packaging glass and up to 5% of cathode ray tube glass). The main technological risk inhibiting a significant industrial production was the low stability during firing (high pyroplastic deformation) of tiles.

Recently, the European Commission published several communications focusing on energy recovery from waste[1] and greater recycling and reuse[2] able to bring benefits for both the environment and the economy. The revised legislative proposals on waste set clear targets for reduction on waste (i.e. recycling of 75% of packaging waste by 2030) and establish ambitious and credible long-term path for waste management and recycling. In this frame, Ceram-Unie stressed that resource efficiency requires an LCA approach, highlighting that social and economic aspects of sustainability should always be considered in the EU legislation.

With the target to demonstrate a reduction of the environmental impact and a significant reuse of end of waste materials, a new concept of traditional ceramic was developed in the last years. At least 60% of natural raw materials are replaced by (i) new glassy raw materials coming from vitrification of different waste able to crystallize during firing or (ii) different type of waste opportunely balanced allowing a “waste synergy” during firing. In both cases, the innovative ceramic mixes are mainly constitute by secondary raw materials able to crystallize during firing. It allows to obtain products with good stability during firing, overcoming the technological risk linked to the pyroplastic deformation.

Industrial production of these kind of innovative tiles has been already demonstrated within the European founded project WINCER,[3] in which ceramic tiles (25×25 cm and 30×60 cm) containing 85–95%% of secondary raw materials were obtained by sintering about 150–200 °C lower respect traditional tiles. Beyond the social and environmental benefits for the sustainability of waste management, about 25% of industrial costs abatement can be reached due to the lower expenses for raw materials, lower energy and methane consumption.

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Oral presentations

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Mechanical reinforcement of traditional ceramics by incorporating glass-fibres

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Keywords: glass fibres, bricks, compressive strength

Nowadays bricks are manufactured with a very mature process in terms of technology and energy efficiency. But recently, new challenges are appearing with environmental issues defined by European policy and regulation.[1] A key innovation concerns the energy recovery for new efficient building, implying the development of new types of bricks with always higher compressive strength and thinner walls and/or combining isolation materials. It also concerns the refurbishment of existing building: the external walls insulation from the outside requires thinner bricks to maintain building dimensions.

Reinforcement of building materials with glass fibres has been already studied at room temperature into concretes. This works aims at introducing glass fibres into bricks. Glass was chosen because of its chemical composition quite close to bricks. But during processing at quite high temperature, specific glass is required in order not to denature the fibres. That's why E-CR glass from 3B-Fibreglass Company[2] were used.

Several Belgian clays or mixtures were used as hosts of glass fibres. Bricks were processed in different ways and characterized according to standards specifications. It was shown that fibre addition does not change the visual aspect of bricks. The comparison between bricks without and with glass fibres shows no differences on main properties – density, porosity, water absorption after immersion, capillarity – except for compressive strength: the addition of 5 to 10%wt of glass fibres increases hugely the mechanical resistance for molded bricks.

Acknowledgement
The DGO6 of Wallonia is acknowledged for the financial support (project n°1510586).

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Chemical strengthening of industrial glazes suitable for ceramic tile

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Keywords: glaze, strengthening, hardness

Glazed ceramic tiles are used principally for wall and floor covering because of high resistance to chemical attack, even if the mechanical resistance is typical of fragile material. To improve the mechanical resistance of fragile inorganic materials ion exchange processes are industrially applied with good results, since many years[1]. The purpose of this study was to verify the applicability of a well-known glass hardening process to glazed ceramic tiles. Moreover also coloration of glazed ceramic tile through ion exchange was investigated.

Materials and Method. Microstructural and mechanical properties of the glazes were determined before and after different ion exchange processes on three different types of commercial ceramic glazes and on other three new glazes (not commercial available). The microstructure was investigated through scanning electron microscopy (SEM) in conjunction with energy dispersive spectrometry (EDS). In particular, the distribution of ions before and after the ion exchange was determined with these techniques. Also the hardness of the glazes was investigated through micro Vickers Hardness on different loads, in order to correlate the ions distributions with the hardness and to evaluate the glaze most suitable for this process. Finally L* a* b* coordinates and ΔE parameter were measured in order to identify any variation in colour.

Results. Only one of the commercial glazes was suitable to ion exchange process, thanks to its high Na_2O content, with the respect of the majority of the glazes nowadays on the market of ceramic tile production. The other three new glazes, were B_2O_3, Na_2O Li_2O and P_2O_5 contents were modified, give interesting results also in terms of mechanical properties. In fact, under certain conditions of ion exchange, an increment of +25% of hardness was observed. Finally a coloration of the glaze was observed employing $Co(NO_2)_3$ as melted salt, together with KNO_3.

Conclusion. The results suggest that ion-exchange process is positively affected by an appropriate combination of ions in the glaze formulation and a low amount of commercial ceramic glazes are nowadays suitable for ion exchange.

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Performance of lightweight coated oxide ceramic composites for industrial high speed wood cutting tools: a step closer to market

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The introduction of lightweight cutting tips in industrial wood machining could lead to machining at much higher speeds and thus greatly increase efficiency. One possible way to achieve this is through lightweight ceramic composites. An Al_2O_3 ceramic matrix was selected and reinforced with particles resulting in a density of approximately one quarter of the currently used heavy tungsten carbide tools (density of > 15 g/cm^3). Furthermore, a coating was applied to the ceramic cutting tools in order to increase the stability of the cutting edge. A combination of reduced coefficient of friction, frictional forces and a resulting decrease in temperature can lead to a reduction in chipping at the cutting tip. Chipping has always been the major drawback of ceramic cutting tools for industrial wood cutting. A ceramic composite containing 25 vol.% of submicron and nano sized SiC particles shows good mechanical properties with HV_2 = 21.5 GPa and K_{Ic} = 4.5 MPa m$^{1/2}$. This composition performed very well in industrial cutting trials on laminated beech. The cutting performance was increased further by use of an industrially available coating on the tools. The quality of the cut wood surface has always been difficult to characterize when comparing cutting tool materials and is often performed qualitatively by experienced carpenters by touch. The surface quality of the machined laminated beech was for the first time quantitatively characterized using Gelsight 2.5D tactile sensing.

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Influence of oil shale ash addition on thermophysical processes in an illitic clay during heating

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Keywords: illite, oil shale ash, thermal analyses, mass spectrometry

As a base material, illitic clay (containing 80% of illite) originated in Miskolc region, Hungary was used. The clay was crushed, milled and sieved to obtain particles < 100 µm. Estonian oil shale (EOS) ash was prepared by dry milling to obtain a powder with homogenous particle size distribution. Clay and EOS ash mixtures were prepared with 4 different ratios of EOS ashes (from 10 to 40 wt.%). To the as-prepared clay and EOS ash dry mixtures distilled water was added to obtain a plastic mass from which samples of rectangular shape were made. The samples were dried freely on air for 72 h.

Differential thermal analysis (DTA) and thermogravimetry (TG) methods with simultaneous mass spectrometry analysis of evolved gases were used to characterize the processes taken place at thermal treatment of samples. To avoid the temperature shifts of the processes investigated in different measurement equipment, the all thermal analyses were conducted with the heating rate of 5 °C/min up to 1000 °C.

Structural analyses of samples were performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition, the specific surface area (SSA) and porosity of samples were also determined.

Several thermally induced processes take place in illite-EOS mixtures during heating. Firstly, the physically bound water is removed (< 350 °C). Dehydroxylation of illite starts at 450 °C and continues up to 700 °C, between 350-500 °C takes place the decomposition of $Ca(OH)_2$. As the amount of the EOS ash increases, the thermal effect of the dehydroxylation decreases, but considering the content of $Ca(OH)_2$ in the mixtures the total mass loss in this temperature range increases. At temperatures above 600 °C the carbonates, contained in EOS ashes, start to decompose performing completely at 850–900 °C.

The results reveal a possible utilization of oil shale ashes in the manufacturing of industrial ceramics by reducing the amount of the clay needed.

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Differences in mullite crystal growth in triaxial ceramics containing K- and/or Na- feldspar

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Keywords: mullite, cristalization, porcelain, feldspar, X-ray difraction, SEM

The triaxial vitreous ceramics are containing in majority the glassy phase (50–70%), commonly 2 crystal phases can be observed: (1) quartz (and, or cristobalite) and (2) mullite. The second one can be found as primary (flat, disk shape) and secondary mullite (needle shape). Some authors say that secondary mullite is represented by large needles and they also define third type as small needles. Crystals of needle mullite have large influence in mechanical properties of triaxial vitreous ceramics. Those crystals are crystallizing in clay - feldspar environment in temperatures above 1200 °C. Triaxial bodies were prepared employing different feldspars. Mixtures were sintered in different viscosities of melt which were controlled by temperature. Influence of soaking from 30 to 180 min was checked. Received samples were checked with X-rays phase analysis and Scanning electron microscopy. The authors focused mainly on mullite's shape parameters and its content.

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Improvement of enamel coatings used as food contact materials in industrial applications

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Keywords: enamel, migration, food contact materials

Chemical bonding is one of the mechanisms providing the holding ability of enamel on substrate. Diffusion of FeO from the substrate to the enamel, and NiO and CoO from enamel to the substrate is the basis of the chemical bonding.[1–3]

In this study, we used different frits containing different amounts of NiO and CoO to investigate the effects of these metal oxides on the holding ability of enamel coating. Firing temperatures for enamel were kept stable at 810, 830 and 850 °C for the different experimental sets, and firing times were 2 and 6 min for 810 and 850 °C, 4 and 5 for 830 °C, thus we could observe the effect of firing time and temperature for the different compositions of frit.

After the experiments, we performed SEM and EDX analysis to investigate the holding mechanism between enamel and substrate materials. By linear analysis and linear mapping, we could observe the elemental diffusion from substrate to enamel, and from enamel to substrate. In addition to this, we performed migration tests and ICP MS analysis to determine the amount of the Ni and Co which can migrate from the enamel to food. Furthermore, we performed impact tests to determine the holding abilities of enamel in terms of composition of frit, firing time and temperature.

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Ceramic tile surfaces: cleanability and durability performances

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Keywords: durability, cleanability, accelerated aging, ceramic tiles

In recent years, the durability concept of ceramic surfaces has become a key factor during design process. A deep knowledge of product performances is essential to select suitable product for any environment or use. However, standard procedures to evaluate and assess the durability performances still lack. It is due to the fact that it is rather hard to keep under control a wide range of factors causing deterioration (environmental conditions, chemical agents, weathering, mechanical stresses). In any case it is possible setting-up a method by focusing only on few factors related to one aspect of the performance under a well-defined set of conditions, thus simplifying the procedure. The aim of this work is to evaluate the durability of ceramic tile surfaces by focusing on their cleanability. Surface cleanability, i.e. the facility and efficiency of dirt and stain removal, is an essential technological feature for ceramic tiles, even if little is known about the durability of this characteristic.[1] Among ceramic tiles, porcelain stoneware is the most performing product due to high density, surface hardness, abrasion and stain resistance. However, to attain aesthetic characteristics, porcelain stoneware tiles are often lapped to increase their gloss. Removing a fine layer of glaze, the lapping process induces several changes in the surface microstructure (micro-cracks and flaws formation, opening of pores). This may compromise the cleanability performance of tiles[2] and it can be improved by using commercial protective treatments able to fill up pores and holes, thus preventing the penetration of dirt and staining agents. Many of the surface treatments are generally subjected to ageing and weathering, so a stable performance over time cannot be ensured. In this work, commercial lapped porcelain stoneware tiles with and without protective treatment were investigated. Comprehensive sets of both accelerated and natural ageing tests have been carried out and compared. Accelerated ageing was performed by applying optimized soiling mixtures on tile surfaces to reproduce chemical and mechanical actions simulating the working conditions and traditional cleaning operations. Durability test was also performed by fixing tiles on floor after 3 and 6 months of natural ageing. Surface characteristics (microstructure, topography, roughness) were analyzed before and after cleanability and durability tests. Correlation of the results allowed to set-up a protocol for durability performance of lapped tile.

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The significance of Okpella granite in ceramic glaze formulae

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On the northern part of Edo State Nigeria is Auchi, the administrative headquarters of Etsako Local Government Area with Okpella in Etsako East from where huge mountain of mineral Granite abound. It was from a part of these mountains that samples of Granite pieces were collected, milled and analyzed. The Mini pal 4 version with PW 4030 series of the X-ray Spectrometer, which is an energy dispersive microprocessor controlled equipment of the Centre for Energy Research and Training (CERT) Ahmadu Bello University, Zaria was were the Granite sample was analized. It was this analytical instrument designed for the detection and measurement of elements present in soil mineral sample that revealed the ceramic potentials of the Okpella Granite in glaze composition.

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The effect of addition of alkali metals oxide on selected parameters of the ceramic glazes

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Keywords: ceramic glaze, alkali metals oxygen, glaze structure, physicochemical properties

In the scientific literature there are two ideas concerning the behavior of alkali oxides in ceramic glazes. First, that sodium and potassium oxides have almost the same influence on the properties of ceramic glazes. Due to this fact, in the Seger formulas summary molar content of alkali oxides are often found (Na_2O+K_2O or R_2O). In the second case, the prevailing opinion is, that these oxides differ in functionality due to different behavior during thermal treatment and the impact on structure of internal network of glassy phase of glazes. The article presents the results of selected physicochemical parameters of ceramic glazes the glazes from SiO_2-Al_2O_3-CaO-MgO-R_2O in the presence of various alkali metal oxides (R = Na, K, Li). Additionally, the presentation shows some conclusions of the influence of alkali metal oxides on the internal structure of the glazes.

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The structure of raw porcelain glazes modified by the zirconium oxide addition

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Keywords: glazes, zirconium oxide, IR, NMR, Raman spectroscopy

The growing demands for the ceramic glazes creates the necessity for more detailed research on the influence of oxides on the properties of ready-prepared glazes. The complexity of multi oxides systems of glazes causes difficulties in analyzed this system and make some problems to describe the influence of adding oxides on the glazes. The interaction between the single oxides included in the composition of glaze should also be analyzed. The presence of each oxides, even in small amounts, could have a significant impact on properties of obtained glaze.

The objective of this study was determining the effect of addition of zirconium oxide on the structure of ceramic glazes, for firing process at 1230 ^{o}C. The glass-ceramic materials from SiO_2-Al_2O_3-Na_2O-K_2O-CaO-MgO system were examined. The zirconium oxide was added in five different amounts (1,5; 3; 6; 12; 24 wt.%). In addition the sample without zirconium oxide as the reference sample were prepared. The structure of this glazes was described based on the results from Infrared Spectroscopy (IR), Raman spectroscopy and spectroscopy of Nuclear Magnetic Resonance (NMR). This data were linked with the results from X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) with microanalyzer (EDS). All of obtained results create a lot of interesting dependences, which are the consequences of the addition of the zirconium oxide to this glass-crystalline materials.

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Glass-ceramic foams from 'inorganic gel casting' and sinter-crystallization of waste glass mixtures

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Keywords: gel casting, alkali activation, waste-derived glass-ceramic foams

Highly porous open-celled glass-ceramics have been successfully obtained by a new gel-casting technique. The gelation of an aqueous slurry of glass powders was not achieved according to the polymerisation of an organic monomer, but as the result of alkali activation of fine glass powders[1]. The alkali activation of a Ca-rich glasses, consisting of common soda-lime glass and glass from the plasma processing of municipal solid waste ('Plasmastone')[2] allowed for the obtainment of well-dispersed concentrated suspensions, undergoing progressive hardening by treatment at low temperature (75 °C), owing to the formation of C-S-H (calcium silicate hydrate) gels. An extensive direct foaming was achieved by vigorous mechanical stirring of partially gelified suspensions, comprising also a surfactant. The open-celled structure resulting from mechanical foaming could be 'freezed' by the subsequent sintering treatment, causing a substantial crystallization of Ca-Fe silicates. Viscous flow sintering and crystallization could be tuned depending on the firing temperature (from 800 to 1000 °C) and balance between soda-lime glass and waste-derived glass. For optimized foams (20 wt% soda-lime glass – 80 wt% Plasmastone, fired at 1000 °C), a total porosity exceeding 80% was obtained, comprising both well-interconnected macro-pores and micro-pores on cell walls, being accompanied by good compressive strength, above 1 MPa. Owing to the open-celled morphology the obtained glass-ceramic foams could be applied as filters as well as catalytic supports.

Acknowledgement

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Mullite foams from engineered alkali activated suspensions

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Keywords: gel casting, alkali activation, cellular ceramics, mullite

The progressive hardening of suspensions associated with inorganic polymerization has been already shown to offer interesting possibilities for the development of highly porous foams. In fact, air may be easily incorporated by vigorous mechanical stirring, with the help of surfactants. The cellular structure is stabilised by the increase of viscosity caused by the same curing reactions, configuring an 'inorganic gel casting'.[1,2] The present paper is aimed at extending the approach to mullite foams, obtained by the thermal treatment of engineered alkali activated suspensions. 'Green' foams were first obtained by gel casting of a suspension for Na-geopolymer enriched with reactive γ-Al2O3 powders. Sodium was later extracted by ionic exchange with ammonium salts. In particular, both removal of Na+ ions and retention of the cellular structure were achieved by immersion in ammonium nitrate solution (at 60 °C, overnight). Finally, the ion-exchanged foams were successfully converted into pure mullite foams by application of a firing treatment at 1300 °C, for 1 h.

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Powder rheology and compaction behavior of spray dried bodies for porcelain stoneware slabs

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Keywords: compaction, porcelain stoneware, powder rheology, spray dried bodies

The technological behavior of porcelain stoneware bodies strongly depends on the rheological properties and response to compaction of spray-dried powders during the deposition and pressing stages, particularly in the case of large slabs. Even the firing behavior betrays the features of powder compacts, especially in terms of shrinkage and densification kinetics. Although the literature offers some insights into the characteristics of spray dried powders

for ceramic tiles, both red stoneware and porcelain stoneware, no data are available on bodies currently utilized to manufacture large slabs (>4 m^2) by novel technologies.[1,2] In order to fill this gap, a systematic approach to properties and behavior of spray dried powders for porcelain stoneware large slabs was carried out within the IPERCER project.[3] For this purpose, nine industrially-manufactured spray dried bodies were characterized for particle size and agglomerate size distribution; shape, moisture and internal porosity in function of agglomerate size; rheological properties of powders (flowability, static and dynamic angles of repose, poured and tapped densities); compaction behavior (curves of bulk density, intergranular and intragranular porosity in function of applied load); firing behavior (effect of green porosity and density on firing shrinkage, bulk density, open and closed porosity, phase composition). The aim is to gather the information necessary to model the behavior during deposition (in mould or on tape) and pressing. Results reveal the occurrence of two types of spray dried powders in terms of agglomerate size distribution, even though most physical properties are similar. This has a significant effect on some rheological properties (flowability and tapped density, but not angles of repose), leading to some differences in the features of compacted bodies. The features of green compacts are somehow inherited by the fired bodies, even though the starting differences are damped in the fired bodies. In conclusion, there is room to improve the performance of spray dried bodies by pointing out a compromise between powders flowability, compaction and densification during firing. The challenge is to transfer this progress to the management of industrial spray driers, at present focused on energy efficiency and constancy in the moisture content.

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Comparative analysis of surface properties for assessing slip resistance of glazed ceramic tiles

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Keywords: ceramic tile, slip resistance, slipperiness, Pendulum Test Value, surface roughness

Ceramic tiles, playing a major role in the performance of flooring, have to meet many requirements at the same time according to EN 14411. As far as application of these materials is concerned there is a great importance of defining precisely the slip-resistant ability, the most controversial feature of a floor in service. Slipperiness of tiles is usually interpreted relatively. In some areas there is an increased risk of slipping that depends not only on interaction with slippery materials, but pedestrian behaviour and type of footwear also. Furthermore surface texture should be considered to have a great influence. Taking into account the presence of a contaminant on the surface, which can cause a walking person to lose footing, loss of traction can be predicted. Measurements of frictional properties of floor coverings is essential in risk assessment of slip and fall accidents. For determining friction a precise examination is necessary, which approximately simulates the physical forces of walking and can be repeated at any time under the same conditions. The objective of this study was to determine and to assess the affecting factors that can possibly change slipperiness of coverings. In the research 8 different types of glazed ceramic tiles were chosen. Firing time and temperature were key variables during manufacturing and there was also difference in glazing operation and decoration application. Laboratory slip resistance tests were conducted using Skid Resistance Tester, where Pendulum Test Value (PTV) was measured under dry and wet conditions. The results of PTV measurements showed that the variation in surface structure determined slipperiness of glazed ceramic tiles. Surface roughness, an important contributor to slip resistance, was significant due to the fact that production technology defines the surface quality of a flooring material. Arithmetical mean deviation (Ra) and maximum height of the assessed profile (Rz) were measured using a profilometer according to EN ISO 4288. With the quantification of roughness parameters diversity in the characteristics of the surface was evaluated.

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Exploring waste-based body formulations for porcelain stoneware tiles produced at lower sintering temperatures

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Keywords: waste recycling, porcelain stoneware, ceramic tiles

Waste recycling in vitrified ceramic bodies is getting a growing concern in the literature, where a wide range of residues have been proposed as raw materials for porcelain stoneware tiles, with promising results in terms of base properties.[1] However, drawbacks arose about technological behavior of waste-bearing bodies and actual cases of transfer to the tile-making industry seem to be limited to cannibalization of residues of the ceramic process itself.[2,5] The target of introducing high amounts of end-of-life residues is particularly challenging because of the fast innovation rate in the tile industry, that is shifting current expectations towards large ceramic slabs. The present contribution relates preliminary results of the MATER_SOS project[6] which is aimed at testing the chances for an actual industrial symbiosis involving the recycling chain in the Emilia-Romagna region, Italy, where the Sassuolo-Scandiano ceramic district is situated. The analysis of regional waste flows led to select various typologies of wastes which for characteristics and amounts appear to be potentially suitable as ceramic raw materials, mostly glasses, ashes and sludges, some well-known (e.g. soda-lime glasses, rice husk ash) and others less investigated (e.g. wood combustion ash). A dozen samples of residues were characterized (chemical and phase composition, particle size distribution, thermal properties) and used as fluxes in replacement of feldspathic raw materials (from 20% to 60%) in a standard porcelain stoneware batch. Bodies underwent a laboratory simulation of the industrial tile-making processing in order to test their technological behavior in milling, pressing and firing stages. Every waste has been classified through a technological profile summarizing compositional features and effects on grindability, compressibility and sintering by means of variation indexes based on particle size distribution, bulk density, firing shrinkage and water absorption. The main advantages achievable with waste-bearing batches is about the temperature of maximum densification that can be reduced of tenths degrees depending on the residue. General drawbacks are the tendency to have lower bulk density (symptom of close porosity) and a darker color after firing. Deviation from the tolerable range in the industrial practice may occur in specific cases (e.g., excessive slip viscosity with combustion ashes). Nevertheless, technological properties usually do not scale linearly with the waste percentage and frequently escape from the additivity rule, thus making every waste type a case-study and suggesting caution in batch design.

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Poster presentations

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Effects of hollow micro glass sphere materials for developing lightweight porcelain tile

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In building materials market, there is a growing trend for lightweight products recently. Porcelain tile has many superior properties but its high density limits the usage of it as façade cladding material especially for large sizes. This study aims to decrease the density of porcelain tile by occurring of closed porosity using hollow micro glass spheres (HMGS) with different particle size. After preparing the samples, sintering behaviour was simulated by contactless optical dilatometer in order to obtain information about expansion characteristics. Microstructural evolution (pore formation, morphology and size etc.) of the body were investigated by SEM for all the particle sizes. Results show that it is possible to obtain porcelain tile body less dense by 25% with appropriate water absorption, strength and deformation according to the standard product.

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Alumina coatings on C35 steel: a numerical modelling of the interface Al_2O_3/steel for characterizing the coating adherence

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Keywords: numerical simulation, FEM, tensile adhesion test, fracture mechanics, alumina coating, steel

The C35 steel substrates used were alumina-coated via thermal plasma spraying. Before coating, the steel surface was pre-oxidized in CO_2. The pre-oxidized samples exhibited coatings adhesions of 82 ± 7 MPa. This good result was attributed to the "crystallographic bonding", which is characterized by the structural continuity of the chain: steel/α-Fe/wüstite/magnetite/γ-Al_2O_3/α-Al_2O_3. The adhesion measurements were obtained utilizing the new technique of the "silver print test" that consists in the painting of a part of the samples surface with a silver paint, before coating. The rupture of the coatings occurred at the surface of the substrates, or inside the wüstite layer.[1]

A numerical approach using the finite element method is investigated in order to optimise junction parameters. First, a multi-layered system is defined in the elastic domain for very small strain, as seen in Fig. 1. Three layers are superimposed with successively the alumina top coat (300 µm depth), the wüstite grains (2 µm depth) and the C35 steel substrate (1 mm depth). The shape of the included wüstite grains allowed the study the effect of the roughness at the wüstite/steel interface, on the energy release rate and on the stress intensity factors. Then the preferential crack trajectory is chosen, based on the experimental observations (the cracks appeared both at the alumina/wüstite boundary and at the steel/wüstite one). Whereupon, a thermo-mechanical approach based on the same model including the influence of internal stress appearing during cooling or thermal cycling, wüstite growth, and creep on the stress concentration, is considered.

Finally, the use of the pre-programmed subroutine called "DEBOND" permits to study the influence of the fracture criterion on the crack trajectory. This modelling allows to highlight the main parameters influencing the stresses of the interfacial zone, in order to minimize them.

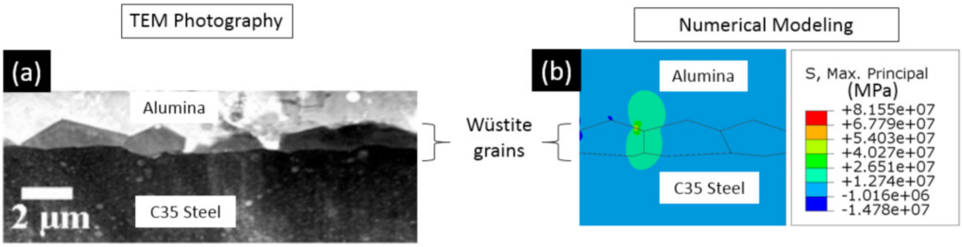

Fig.1. TEM micrograph of the interfacial zone alumina/wüstite/C35 steel (a) and corresponding numerical modeling (b), from Ref. 1

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Influence of the $ZrSiO_4$ and ZnO on the whiteness and physical-mechanical properties of industrial ceramic sanitary-ware

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Keywords: physical-mechanical properties, whiteness, FTIR, SEM, DTA/TG, ceramic sanitary-ware

The object of this study is to improve the whiteness and physical-mechanical characteristics of sanitary glazes. The glazes were prepared using the traditional ceramic substrate by spraying and then thermally treated in industrial tunnel kiln at temperature of 1250 °C. The obtained glazes were characterized by FTIR spectra and were observed by SEM to study microstructure the glaze-ceramic. The whiteness characteristics of the glazes obtained by instrument Micro color colorimeter data station. The important phase for sanitary ware is the mechanism of interaction body-glaze, this mechanism determines the physical-mechanical and aesthetic properties of the products ceramics sanitary-ware for this study we used DTA/TG.

The chemical durability of glazes was evaluated in acidic $C_6H_8O_7$, Hydrogen peroxide and Potassium permanganate $KMnO_4$ solutions. The results showed the improvement possibility of the whiteness (up to 87%) and flexural strength (55.06 MPa).

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Effect of WC grain morphology on the diamond coating adhesion in tungsten carbide tool

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Keywords: diamond coating, grain morphology, adhesive strength, tungsten carbide, mechanical interlocking

CFRP (carbon fiber reinforced plastics) have been used as the composite materials with a very high strength-to-weight ratio and rigidity, which properties are required in aerospace and automotive parts. Special cutting tools are necessary to process the CFRP-composites into the final shape parts efficiently. It is widely believed that the diamond coating tool is the most suitable for them. The most critical problem for the application of CVD diamond tool is the adhesion strength between the diamond film and tungsten carbide. Various techniques for controlling and improving the adhesion have been reported, including chemical etching, sandblasting and thermal treatment. Although a rough and corrugated WC-Co surface contributes to enhancing the adhesive strength by mechanical interlocking, the diamond cutting tools produced by this technique is still not satisfactory for cutting CFRP.

In this study, we focused on the evolution of each WC grain morphology instead of the surface roughness of the pre-treated WC-Co substrate. The shape of WC grains after pre-treatments (multi-steps etching) was observed by using SEM and the hot filament CVD was employed to deposit nanocrystalline and micron-size diamond films. The adhesion strength of diamond films was estimated by sandblast peeling. In order to investigate the cutting performance of the diamond coating tools, cutting tests were conducted on as-deposited diamond coated drills with a work-piece of CFRP plate. The tool-life and adhesion of deposited diamond film on the WC-Co tools appear to be critically dependent on the WC grain morphology.

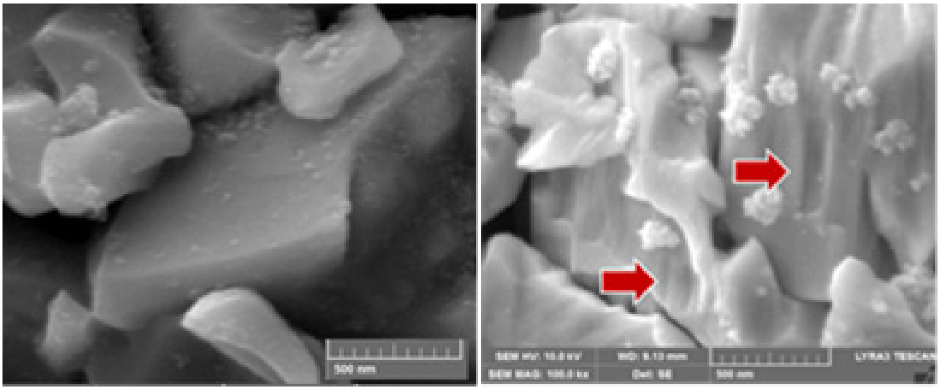

Fig. 1. WC grain morphologies of the pre-treated tungsten carbide tools

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An industry-oriented classification of fluxes for ceramic tiles

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Keywords: ceramic tiles, feldspar, flux, technological classification

Fluxes are fundamental ingredients of bodies and glazes used to manufacture ceramic tiles. They play a primary role during firing, giving rise by melting to the vitreous phase that governs the viscous flow sintering process. Feldspars and feldspathoids are quintessentially the most common ceramic fluxes, even though a much wider range of minerals (e.g., talc, wollastonite, sericite, dolomite) is utilized as flux in highly vitrified bodies (porcelain stoneware) vitrified and semi-semivitrified bodies (stoneware) up to porous bodies.

The main problem in planning mining activities and correctly evaluate the present market and future demand of ceramic fluxes is the lack of a clear identification of what is needed by the tilemaking industry. In fact, there is no standard definition and classification of ceramic fluxes. Current terminology in the field of ceramic tiles encompasses commercial definitions, local terms, and rock names, not always referred to the international geological nomenclature. Therefore, there are often ambiguities when linking a given flux name with a certain composition. Thus, no univocal correspondence exists, in general, between common flux terms and actual chemical and mineralogical composition.

The igneous, sedimentary and metamorphic rocks, which are the sources of ceramic fluxes, are classified according to geological schemes based on mineralogical (modal) analysis or chemical features. However, these classifications have little technological significance and no way to be systematically applied in the ceramic sector. On the market, feldspathic fluxes are roughly distinguished in sodic, potassic and mixed feldspars. Nepheline syenite and feldspathic sands are often considered in separate classes. Further fluxes are commonly referred to a given commodity (e.g., talc, wollastonite, basalt, pumice) even though these names are not always correct under the geological and petrographic viewpoints.

In order to overcome the limits of current terminology, a new, industry-oriented classification is here proposed and applied to the wide range of fluxes utilized in the production of ceramic tiles. The main goal of this general classification of ceramic fluxes is to unambiguously describing any flux by a simple coding, based on the chemical composition only, which should have technological and commercial significance. This classification makes use of a few parameters able to discriminate between alkaline fluxes (based on feldspars and felspathoids), alkaline-earth fluxes (prevalently consisting of Mg and Ca silicates and carbonates) and special fluxes (containing significant amount of lithium, boron, phosphorus or fluorine). The alkaline fluxes are classified, by the equivalent amount of feldspars and the alkali ratio, in: foid-bearing, feldspathic, quartz-feldspathic and feldspar-bearing fluxes. The alkaline earth fluxes are classified, based on their alumina content and the alkaline earth ratio, in magnesian, magnesio-calcian, calcio-magnesian and calcian fluxes. Examples of classification of industrial minerals, representative of different geological sources and used by the ceramic industry in various countries, are given for both alkaline and alkaline earth fluxes.

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A study for glass-ceramic glaze modified by brass powder waste to obtain metallic effect

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Keywords: brass waste, glass-ceramic glaze, metallic effect

Ceramic products have good technical properties such as thermal and acoustic insulation, scratch resistance besides inert to weather conditions as well as. In other words, corrosion of metals due to weather conditions (air, water, steam, ice) is not observed in ceramic parts. In addition, numerous decorative techniques can be applied to ceramics when compared to metal plates. On the other hand, unique metallic reflections of metals increase aesthetic perception. For this reason, different compositions and techniques have been developed to create products with superior properties by combining the aesthetic qualities felt by metals such as metallic reflection-luminescence, and other advantages of ceramic products. In the related study, methods have been developed to separate the brass powder which is formed during the sanding of brass parts formed by casting method, to evaluate it for decorative purpose in the production of ceramic tile.

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Usage of bandirma colemanite wastes in the production of matte opaque frits and glossy opaque glaze

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Keywords: colemanite waste, frit, glaze

Every year large quantities of wastes are formed during the productions of boron compounds by the Eti Mine Boron Company of Turkey. The disposal of wastes cause economical loss, some technical and environmental problems. In the present study, Bandirma colemanite enrichment wastes (the rich B_2O_3 content of the waste) were employed as a raw material into the production of matte opaque frits. The objective of the study was to reduce boric acid consumption and to substitute the wastes with the B_2O_3 present in frit composition, not only for developing a sustainable production but also providing an economical benefit. Frit is the main component of the glaze, which highly used in numerous applications such as; tiles, sanitaryware products, enamels, kitchenwares and so on. Laboratory scale production is carried out according to the basic principles of producing frit. Frits is subjected to various characterization tests which can be arrayed as; mineralogical, microstructural and thermal analysis. The result of frits showed that usage of wastes does not affect the crystallization and microstructure of the frits. Even though there have been increases in the brightness values, decreases in the surface roughness and whiteness values of the frits, these differences do not have a negative effect on usage of frit. Besides that newly produced frits used in a glossy opaque glaze recipes. The final product, in this study; new glazes tested EN ISO 10545 tests includes surface abrasion, chemical resistance, resistance to thermal shock and stains. When compare the results of the analysis of glazes with the standard glaze, it can be show that there is no differences with the standart test results. By this study, it can be seen that frits prepared with colemanite wastes can be easily used in glossy opaque glaze recipe without leading to any surface failure or fault and can be adopted into the current industrial production.

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Increasing casting rate by increasing gel buildup

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Keywords: sanitaryeare, gel buildup, casting rate

Slip casting method is used in sanitaryware production and it is known to be a suitable and inexpensive shaping process to produce material with high green densities and micro structural homogeneity, even for complex geometries. One of most important manufacturing measure is *cast rate*, which is the thickness of the cast achieved during a specified time in the plaster or polymer mold. A higher cast rate results in quicker casts and it means more efficient production. Many of the parameters affect the casting rate like particle size, density and thixotroph of the slurry and properties of molds. In this work, thixotrophy of slurry increased as adding bivalent cations like salts ($CaCl_2$ and $MgSO_4$) with constant of other paramters.

Rate of buildup is measured for determine the casting rate. Because, rate of buildup is a measure of the speed at which the viscosity increases and is therefore also a measure of the rate at which the colloids are immobilized within the gel structure. Bivalent cations were added in the slurry as increasing rate and rheological properties were measured with Brookfield viscosimeter. According to the measuring results of rate of buildup and casting rate, $CaCl_2$ salt is more effective agent for increasing thickness of products because of high thixotropy. It is observed that casting rate increased 30% according to the standard slurry.

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Enhanced catalytic activity of CeO_2-V_2O_5-ZrO_2/WO_3-TiO_2 based for De-NO_X catalyst

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Nitrogen oxide (NO_X) are generated (emission) from high temperature combustion gases such as thermal power plants and ships, it cause various environmental pollution problems such as greenhouse effect and smog. The selective catalytic reduction (SCR) is the most effective NO_X control system. The commercial catalyst was consist of anatase TiO_2 as monoliths, V_2O_5 and WO_3 as active component. However, this type is applied a narrow temperature area of 300–400 °C. Therefore, we studied to synthesis the catalyst using for wide temperature window by addition of ceria and zirconium.

In this present study, synthesis of catalyst were performed by hydrothermal and impregnation method. And, using the carbon material to improvement the catalyst component dispersion. We confirmed the promotion effect of catalyst according to dispersion of catalyst component.

The catalyst was characterized by scanning electron microscopy (SEM) and Transmission electron microscopy (TEM), X-ray diffractometer (XRD), X-ray fluorescence (XRF) in order to analyze the surface and components, the physical-chemical characteristics about measurement of specific area were by Brunauer–Emmett–Teller (BET). Also, the De-NOx activities were measured by Fixed-bed Reactor.

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Amorphization and valence state of tungsten doped ceria/titania

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Keywords: thermal stability, interstitial tungsten, local atomic structure, non-stoichiometry, NO_x conversion

Tungsten (W) has received attention as a co-catalyst with CeO_2 for improving the catalytic activities of TiO_2 based catalysts. Chen et al. reported that tungsten could be a solid solution with CeO_2, resulting in a higher NO_x conversion property.[1] We examined the solid solution behavior of W in CeO_2/TiO_2 catalyst in terms of local atomic structure. The Ce-L^3 and W-L^3 edges were analyzed by extended x-ray absorption fine structure (EXAFS) spectroscopy. Tungsten ion should be in an interstitial site of CeO_2 since a bond distance between W and Ce was about 1.4Å. The inter planar spacing of ceria (111) in tungsten doped CeO_2/TiO_2 was expanded about 5.7% compared with CeO_2/TiO_2. The interstitial tungsten has affected in amorphization of the ceria nanoparticles because tungsten and cerium have a large amount of difference in ionic radii, which occurred severe lattice distortion. Interstitial tungsten also enhanced the thermal stability of ceria, which was confirmed by TEM_EDS mapping. We investigated the increase of Ce^{3+} ratio on the surface of the catalyst resulted from tungsten addition. Since the Ce^{3+} ratio is a major factor affecting the catalytic activity in SCR reaction, the increase of Ce^{3+} ions have influenced on NO_x conversion as one of chemical changes in company with the structural changes such as amorphization of ceria.

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Investigation of thermal expansion mismatches in fine fire clay ceramic sanitaryware

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Keywords: thermal expansion, ffc, ceramics, chamotte

Vitreous ceramics are the materials consist of clay, kaolin, feldspar and quartz, are sintered with a glazed surface at around 1250 °C. These ceramics are commonly called as sanitaryware and they are used in hygienic parts of everyday life such as closets, washbasins, shower stalls, urinals. Two different slips are used in the production of ceramic sanitaryware. One of them is a slip of fine fire clay (FFC) while the other is vitreous slip. Large size products are usually produced with FFC sludge, which generally require less deformation behaviour. The most important reason is use of chamotte material, which is actually sintered clay, it provides low deformation during sintering. In this study, thermal expansion behaviour was investigated depending on the amount of chamotte material. The main purpose of such a study is to reduce the gap of glaze-body expansion in the production of FFC. The value of body and glaze expansions were measured by using dilatometer. It was observed that expansion difference was high enough to cause crack formation. One of the ways to prevent crack formation is to increase the thermal coefficient of glaze. However, this solution may degrade the quality and brightness of surface as well as water absorption properties. Instead, the thermal coeffient of body was reduced and this method has been seen as a more seamless application. For this reason, the thermal expansion behaviour of new recipes have been investigated by reducing the amount of chamotte in the FFC slip. It was observed that the expansion value of body is decreased with decreasing chamotte amount. In contrast with this finding, deformation value of the body has started to increase with chamotte addition.

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Preparation of copper-plated graphite powder, and the sintering behavior of its composite with copper

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Keywords: DC-motor brush, electroless plating, copper, graphite, sintering, composites

To reduce the inhomogeneity from density difference in copper-graphite composite, which is a material system for DC-motor brushes, copper is deposited on graphite surface via electroless plating, and then the copper-plated graphite mixed with pure copper powders is pressed

and sintered to produce a final compact. Here, we identified the optimum electroless plating condition for a large amount of copper deposition, and used it to prepare composite powders with pure copper. We compared the sintering behavior of the copper-plated graphite/copper composite powder with that of pure graphite/copper composite powder. The results show that the copper-plated graphite/copper composite significantly enhanced the sinterability of the composite powder, along with the homogeneity of the sintered compact.

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Model to predict dustiness of ceramic raw materials

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Keywords: particulate matter, dustiness measurement, minerals, prediction model

A wide variety of raw materials employed in the ceramic industry were selected and characterised, including more than twenty samples of quartzes, feldspars, nephelines, carbonates, dolomites, sands, zircons and alumina. The dustiness of these samples, ergo their tendency to generate dust when they are handled, was determined using the continuous drop method.

This study presents a physical characterisation of these samples and an assessment of the influence of some material parameters on its dustiness. In this regard, the obtained results show that dustiness may significantly be affected by particle size distribution.

Moreover, a model to predict dustiness has been developed. This model is based on the hypothesis that, for a given test (i.e. the energy applied to the powder remains constant), dustiness depends on the fraction of particles in the bulk material which can be emitted, and the ability to release these particles.

In this regard, dustiness is defined as the ratio between the mass of generated dust with a specific size and the mass of tested material. Meanwhile, relative emission can be defined as the ratio between the mass of generated dust with a specific size and the mass of particles with this size in the bulk material. The introduction of the relative emission instead of the dustiness as an adjustment parameter in the proposed model has allowed not only a better goodness of the obtained fits but also a better comprehension of the apparently contradictory results reported in previous studies.

These finding suggest that these discrepancies could be due to the fact that the relative emission is directly related with the easiness of the material to release dust (bulk material parameters) and energy applied (device and parameters of dustiness test), whilst dustiness also depends on the fraction of particles susceptible to be emitted.

The developed model let to estimate dustiness from only particle size distribution data. The goodness of the fit is quite good and the fact that only particle size distribution data is required is an important advantage regarding its applicability because it does not require additional or sophisticated tests (these data are commonly known by the raw materials suppliers and users).

This information is deemed essential for establishing the most efficient preventive and/or corrective measures to reduce the generation of fugitive emissions of particulate matter during powders processing, both into the outside atmosphere (air pollution) and inside the facilities (occupational health).

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High feed rate suspension plasma spraying of ceramic materials using water stabilised plasma

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Keywords: air plasma spraying, water stabilised plasma, suspension

Plasma spraying is a well-established technology for preparation of unique protective and functional coatings. Various materials such as metals, cermets, and ceramics may be deposited. Standard approach of plasma spraying is based on introduction of powder material into the plasma jet, where the powder is melted and then deposited onto the coated part, where it forms continuous coating. Alternatively, it is possible to use suspensions of fine particles dispersed in appropriate liquid (e.g. water or ethanol) as a feedstock, rather than using dry coarse powders. Such coatings prepared by suspension plasma spraying often exceed coatings prepared by standard plasma spraying and have high potential in various industrial applications. When using standard APS torches with typical power 40–60 kW, the suspension federate is limited to small amounts of liquid (about 30 ml/min), since additional heat is required to process the liquid carrier decreasing the heat available to melt the powder particles.[1] As an alternative to standard gas-stabilised APS torches, we present in this study suspension deposition with high-enthalpy hybrid water stabilised plasma torch (WSP-H) which combines of water stabilisation and gas stabilisation principles, bringing along high power of the torch, up to 160 kW.[2] Suspension plasma spraying using WSP-H torch allows us to use considerably higher feed rates (more than 100 ml/min) and therefore thick coatings may be formed in much shorter time than in the case of low feed rates. Deposition of coatings using WSP-H suspension plasma spraying can be achieved from various feedstock materials and the coating microstructures can be tailored to fulfil the needs of various applications by choice of deposition conditions; from dense coatings suitable for wear protection to porous coatings with low thermal conductivity and high thermal shock resistance.[3] The coatings from selected materials, such as Al_2O_3, TiO_2, Cr_2O_3 and YSZ, were deposited on rotating carousel with integrated temperature monitoring which enabled effective cooling and repeatability of the spraying process. The obtained coatings were analysed by means of SEM, XRD and their microstructures and mechanical properties are discussed to demonstrate the viability of the newly developed process.

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Thermomechanical properties and fracture of resin-bonded-sand cores. experimental study and application in aluminium foundry

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Keywords: granular materials, mechanical properties, fracture, sand-core, foundry, thermal degradation

Sand cores are used to produce internal cavities of metallic cast parts with complex shapes like automotive cylinder heads. Foundry cores are granular materials made of sand grains aggregated with binder bridges. In the cold box coring process, the binder is a polyurethane resin. It is noteworthy that during the casting of the liquid metal, the polymer binder is seriously damaged. This kind of materials has been poorly investigated so far. This study aims for a better understanding of the mechanical behaviour and fracture of cores subjected to various loads and thermal ageing. Particularly, the focus is on the decoring step, which consists in removing the sand by hammering and vibration of the metallic part after casting. This major project, generated from the collaboration of the aluminum casting company Montupet, and two laboratories Centre des Matériaux (CdM) and MATEIS, includes both experimental and numerical activities in order to model the decoring step of cylinder heads based on empiric data. Here, the experimental part of the work is presented.

This presentation will deal with the experimental characterization of sand cores, especially the links between the thermal degradation of the binder, the microstructure and the mechanical properties will be pointed out. The damage and breaking mechanisms depending on the kind of loads get also our interest. The influence of the binder is primordial and though modifications in its nature, proportion or intrinsic properties will change deeply the behavior of the material.

Various cycled or monotonous mechanical tests have been performed on as-received and heat-treated materials for this purpose in order to examine the response of the material subject to compressive, bending or shear stress. A decrease of these mechanical properties has been observed at room temperature after a heat-treatment at temperatures higher than 200 °C, in relationship with the binder degradation during such heating. A particular attention has been paid to crack propagation. In particular, some compressive tests have been followed *in-situ* by X-ray tomography, permitting to determine the evolution of the strain field during the test. All these information will nourish a finite element model of the decoring step.

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Flame resistant composite panels processed from preceramic prepregs

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Keywords: preceramic prepregs, pyrolysis, Basalt reinforced Ceramic Matrix Composites (CMC), Continuous Fiber Ceramic Composite (CFCC), laser flash analysis (LFA), cone calorimetry

The objective of EEE-CFCC project (www.eee-cfcc.it) is the development and characterization of low cost Basalt reinforced Ceramic Matrix Composites[1] (CMC) for flame resistant panels, heat shields and complex shaped for thermostructural applications in transports up to 600 °C. In particular, thermoplastic polysiloxane mixtures were used to produce comparatively cheap basalt-based preceramic prepregs, which can be shaped using standard procedure employed for polymeric matrix composites (PMC) and may then be cured and pyrolysed in inert atmosphere (24 h at 700 °C). The composite material can withstand his own weight up to 1200 °C, although basalt fibers loose most of their mechanical properties beyond 600 °C. Laser flash analysis (LFA), providing direct measure of thermal diffusivity up to 1250 °C and, indirectly, specific heat and thermal conductivity, according to the cogent European harmonised Standards[2,3], was employed to evaluate achievable fire resistant ratings. These data are crucial for further dynamic modelling activities aiming at simulating fire scenarios and thermal behaviour of the whole ceramic structure. TG-DTA, XRD and SEM were used to study weight and phase changes upon heating. In some cases, the composite material in the cured state is even more interesting, being flame retardant and superior to pyrolysed material in term of room temperature mechanical strength. This uncured state was studied by cone calorimetry and 4 point flexural strength measurements. The application of an 80 µm electrospun Nomex® layer was tested to achieve additional flame resistance. The ignition delay of the different solutions was compared according to test conditions EN 13501.

Acknowledgement
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Innovative ceramic tiles to enhance buildings energy efficiency

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Keywords: ceramic tiles, phase change material, energy efficiency

To face the overwhelming increase on the CO_2 emission levels demanding directives have been implemented by the European Commission limiting the Union's energy consumption.[1] To cope with these directives new and exciting building components must be developed, since buildings are responsible for nearly 40% of the energy consumption in the European Community. One very exciting approach is the incorporation of phase change materials (PCMs), which can store and release energy. Ceramic tiles are an extensively used material in construction yet PCMs incorporation into tiles is uncommon. In this investigation PCMs were directly incorporated into lightweight ceramic tiles[2] and then their thermal performance was evaluated. Results demonstrate that this innovative material present improved thermal performance in comparison with conventional ceramic tiles, mitigating the energy consumption inside buildings by decreasing the operation time of cooling/heating devices.

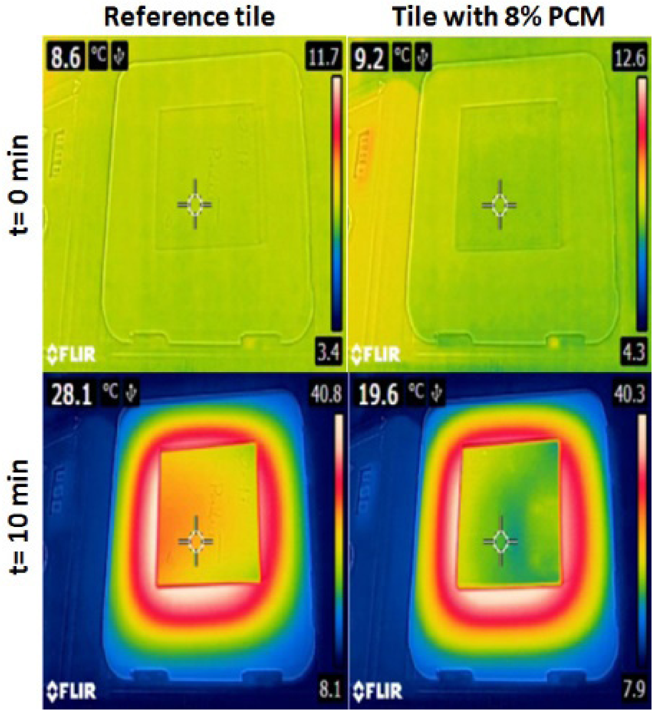

Fig. 1. Temperature evolution for the different tiles heated in a hot plate: without PCM (reference) and with 8 wt.% PCM content

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Modelling powder distribution of powder injection molded green bodies

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Keywords: segregation, powder injection molding (PIM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), numerical simulation

Powder injection moulding (PIM) is a set of process that combines the shape forming process of plastic injection moulding with powder metallurgy. Most commercial injection moulding software focuses on plastic injection moulding simulation. A few have progressed to allow powder injection moulding (PIM) simulations to be carried out. These software enables the visualization of shear rate and powder concentration distribution to predict the potential moulding defects. These defects are caused by the segregation between powder and binder during moulding which leads to inhomogeneity in the green bodies. A numerical model has been developed using a commercial software, Moldex3D, to simulate the injection stage of silicon nitride-based ceramics. The Cross-WLF model based on experimental data of the feedstock is employed in the numerical model. Simulated results from the numerical model have been compared with experimental results. The powder distribution results from the simulation is compared with powder distribution analysis of green bodies using thermogravimetric analysis and differential scanning calorimetry.

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Geopolymers incorporating silicate waste

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Keywords: geopolymers, waste, fly ash, red mud, waste glass

Geopolymers are being primarily developed for the construction industry as a substitute for traditional Portland cement, which requires extremely high temperatures during manufacturing, with consequent high energy dispersion and emissions.[1]

Geopolymer technology enables not only the reduction of CO_2 emissions within the cement industry, but also to use waste materials that are not currently deployed in other fields but are abundant and urgent to dispose of.

Working towards this purpose, fly ash, a residue generated during coal combustion in thermal power plants, and red mud, a by-product in the aluminum production, are used as aluminosilicate source.

The innovation of this work lies in the use of soda lime waste glasses, in addition to fly ash and red mud, in order to substitute relatively expensive chemical reagents such as like water glass and sodium hydroxide that are generally employed in geopolymerization reaction.

The red mud and fly ash based geopolymers were prepared with different amounts of glass and different NaOH molarity. The mechanical resistance of the new materials was assessed by compressive strength test after 28 days of air cooling. Spectra have been acquired through Fourier transform infrared spectroscopy (FTIR) and crystalline phases have been detected by X-ray diffraction (XRD) analysis. Helium pycnometry and microstructural characterization, including pore size and crack distribution analyses by scanning electron microscopy (SEM), were carried out. Moreover leaching tests were conducted to assess the stability and sustainability of the geopolymers.

The performance comparisons were made between the new compositions, and geopolymers made using commercial sodium silicate and traditional construction materials.

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Development of continuous self-cleaning enamel using slag as raw materials

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Keywords: enamel, slag, self-cleaning, domestic ovens

One kind of enamel that has been developed for domestic ovens is the self-cleaning one. The systems of continuous self-cleaning are layers of porous silica applied to metallic materials which absorb the splashed grease marks that are produced in the utilization of roast food in the oven, which are decomposed afterwards by the action of oxide catalytes and by the temperature rise. This research carried out a study about the utilization of iron cast slag in the cupola oven for the production of self-cleaning enamels, which will be applied to ovens in domestic stoves. Thus, there would be a raw-material cost reduction and, consequently, an environmetal impact decrease caused by the slag waste. The formulations used consisted of a blend of commercial self-cleaning enamels (X e Y) and slag enamel ranging at the rate of

20% to 80% of the slag enamel (EE). The samples were based on: chemical analysis, X-ray diffractometry, X-ray fluorescence, optical microscopy, and sweeping. In the enamel preparation, the size and distribution of particles, viscosity, and, density were controlled. The final product was analysed considering its resistance to abrasion and impact. The self-cleaning property was assesed by determining the oil absorption. By using a self-cleaning enamel layer of 250 µm to 300 µm with 40% of slag enamel (EE), it is possible to obtain 5 self-cleaning cycles of second degree according to the ISO STANDARD.

Acknowledgment
Authors are thankful to UTFPR/DAMEC, UEPG/CLABMU and the financial support of Atlas Eletrodomestics, CAPES/PNPD and CNPq.

T08: The ceramics genome: modelling, simulation and *in-situ* experimentation

Invited lectures

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In situ observation of the heat-induced phase transformation of 3D hierarchical niobium oxide nanostructures with atomic resolution

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$Nb_3O_7(OH)$ nanostructures, which captivate due to their complex morphology consisting of highly-ordered nanowire networks, are attractive candidates for green energy applications such as solar-driven hydrogen production and solar cells. Their structural and morphological stability at elevated temperatures is crucial for their application and therefore studied at the atomic scale as a function of atmosphere.

The study reveals a strong effect of the presence of oxygen on the phase transformation, which reflects the ability of niobium oxide to form suboxides and accommodate oxygen deficiency via structural strain. *In situ* heating experiments in the transmission electron microscope are used to study the thermal and structural stability of the $Nb_3O_7(OH)$ nanostructures in the absence of oxygen. The initial $Nb_3O_7(OH)$ nanowires exhibit a defective region in their interior which develops during the synthesis to compensate for the off-stoichiometric chemical composition. This region serves as origin for the formation of dislocations observed at 450 °C which move through the crystal lattice towards the surface of the nanowire with a speed of 5.9 ± 1.3 nm/min. The *in situ* phase transformation starts at 750 °C featuring the formation of pores in the nanowires to compensate for the volume difference of the initial $Nb_3O_7(OH)$ crystal phase and the formed oxygen-deficient niobium oxide phase. In the presence of oxygen no pores are observed in the *ex situ* calcined sample which was identified as monoclinic Nb_2O_5. Independent of the atmospheric conditions the $Nb_3O_7(OH)$ nanostructures demonstrate a surprisingly high thermal stability of their crystal structure as well as their complex morphology which is preserved up to 850 °C.

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Ab initio modelling of structure and properties of cements

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Keywords: cements, CSH crystals, *ab initio* calculations, electronic structures

Cement and concrete are among the most important materials throughout the human history. They possess extremely complex composition and structure at various spatial scales. Realistic structural models, especially at the atomic-scale are much needed to understand from bottom-up building block level on how the cementitious materials perform. We have been investigating the electronic structure and bonding of a large number of calcium silicate hydrates (CSH) mineral crystals using *ab initio* method.[1] Our results reveal a wide range of intricate bonding types (covalent, ionic and hydrogen bonding), which is pivotal for critical analysis of spectroscopic measurements and construction of realistic C-S-H models at larger scale. We advocate the use of the total bond order density (TBOD) as the ideal quantum mechanical metric for assessing crystal cohesion of cements and should replace the conventional criterion such as the Ca/Si ratio.[2] A rarely known orthorhombic CSH phase Suolunite is found to have higher cohesion (TBOD) than Jennite and Tobermorite, which are traditionally considered to be the backbone of hydrated Portland cement. We have now extended our *ab initio* modeling to Al-substituted crystals (CASH models) for a more complete description for cements at nanoscale.

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Importance of soft processing (= low-energy production) of advanced ceramic materials for sustainable society

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As well as organic and/or bio- materials, advanced inorganic materials, most of metallurgical materials, semiconductors and ceramic materials have been used in wide area of applications like structural, mechanical, chemical, electrical, electronic, optical, photonic, biologi-

cal, medical, etc. Most of them except for bio-minerals have never been produced in natural processes via biological systems. Thus they have generally been fabricated artificially and/or industrially by so-called high-technology, where high temperature, high pressure, vacuum, molecule, atom, ion, plasma, etc. have been used for their fabrications, then consumed huge amount of resources and energies thus exhausted huge amounts of wastes: materials, heats and entropy.

Considering the lowering of total energy consumption, we have challenged to fabricate those advanced inorganic materials with desired shape/size/location, etc. directly in low energetic routes using aqueous solutions since 1989 when we found a method to fabricate $BaTiO_3$ film on Ti substrate in a $Ba(OH)_2$ solution by Hydrothermal Electrochemical[HEC] method at low temperatures of 60–200 C. We proposed in 1995 an innovative concept and technology, “Soft Processing” or “Soft Solution Processing,” which aims low energetic (= environmentally friendly) fabrication of shaped, sized, located, and oriented inorganic materials in/from solutions. It can be regarded as one of bio-inspired processing, green processing, or eco-processing. When we have activated/stimulated interfacial reactions locally and/or moved the reaction point dynamically, we can get patterned ceramic films directly in solution without any firing, masking nor etching. Direct Patterning of CdS, PbS and $CaWO_4$ on papers by Ink-Jet Reaction method and $LiCoO_2$ by electrochemically activated interfacial reactions. Furthermore, we have succeeded to fabricate BaTiO3 patterns on Ti by a laser beam scanning and carbon patterns on Si by plasma using a needle electrode scanning directly in solutions. Successes in TiO_2 and CeO_2 patterns by Ink-Jet Deposition, where nano-particles are nucleated and grown successively on the surface of substrate thus become dense even below 300 C will be presented. Nano-structured films will be also talked. A recent novel subject, Soft Processing for various nano-carbons including Graphene and functionalized Graphene, will be introduced. Where we have succeeded to prepare functionalized Graphene Ink via successive processes under ambient temperature and pressure conditions.[3–6]

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Bio-inspired functional materials converted from nature species

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Keywords: bio-inspired materials, bio-templates, butterfly, wood, agricultural wastes

Biological materials naturally display an astonishing variety of sophisticated nanostructures that are difficult to obtain even with the most technologically advanced synthetic methodologies. Inspired from nature materials with hierarchical structures, many functional materials are developed based on the templating synthesis method. This review will introduce the way to fabricate novel functional materials based on nature bio-structures with a great diversity of morphologies, in State Key Lab of Metal Matrix Composites, Shanghai Jiao Tong University in near five years. We focused on replicating the morphological characteristics and the functionality of a biological species (e.g. wood, agriculture castoff, butterfly wings). We change their original components into our desired materials with original morphologies faithfully kept. Properties of the obtained materials are studied in details. Based on these results, we discuss the possibility of using these materials in photonic control, solar cells, electromagnetic shielding, energy harvesting, and gas sensitive devices, et al. In addition, the fabrication method could be applied to other nature substrate template and inorganic systems that could eventually lead to the production of optical, magnetic, or electric devices or components as building blocks for nanoelectronic, magnetic, or photonic integrated systems. These bio-inspired functional materials with improved performance characteristics are becoming increasing important, which will have great values on the development on structural function materials in the near future.

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Bioinspired optical structure for enhancement infrared absorption

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Recently, an increasing number of researchers have directed their attention to the wings of lepidopterans (butterflies and moths) because of their dazzling colors. According to one previous study, these iridescent colors are caused by periodic structures on the scales that make up the surfaces of these wings. These materials have recently become a focus of multidiscipline research because of their promising applications in the display of structural colors, advanced sensors, and solar cells. This work will provide a broad overview of the research into these wings. Specifically, the review focuses on characterization and simulation of bio-inspired optical materials templated from lepidopteran wings scales.

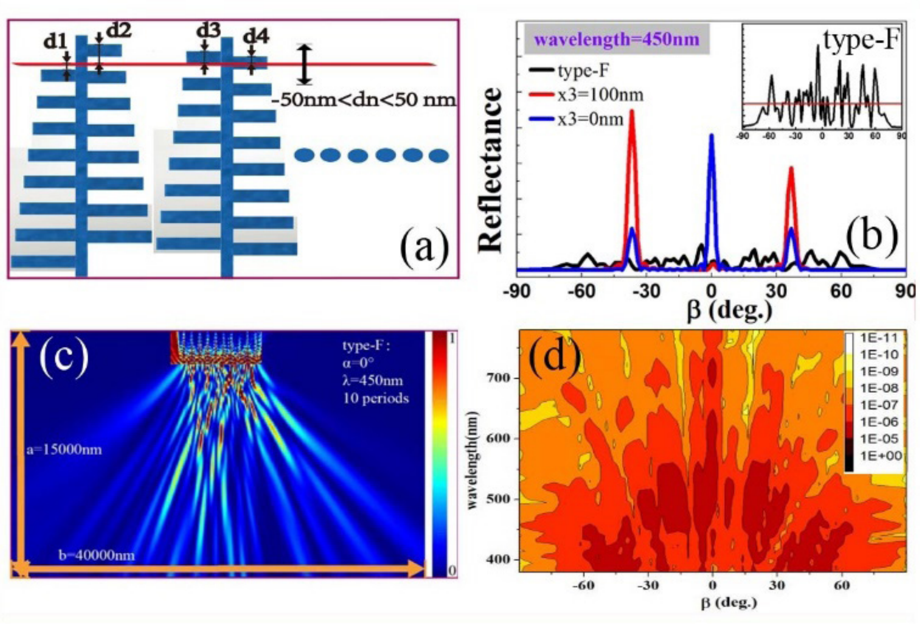

Fig. 1. The Model and Angular dependence of the reflection intensities. (a) the Parameters of model (b) 2D β-Reflectance line plot under the wavelength of 450 nm (c) field maps (d) 2D β-wavelength filled contour plot of angular dependence of the reflection intensities

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Oral presentations

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In situ HT-ESEM observation of sintering first stage of MO_2 (M = Ce, Th, U) microspheres

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Keywords: HT-ESEM, sintering, modelling, oxides, actinides

As a key-step in the elaboration of numerous ceramic materials over a wide range of applications, sintering of oxide compounds has been studied for years. If grain growth processes were investigated thanks to experimental works and calculations, the elaboration of necks during the first step of sintering was generally assessed only through numerical models, frequently based on simple configurations (two spherical single crystals in contact). In order to complement such numerical approaches, the elaboration of necks during the sintering of MO_2 microspheres (with M = Ce, Th and U), herein used as model compounds of nuclear fuels, was experimentally observed by High Temperature Environmental Scanning Electron Microscopy (HT-ESEM).

In a first step, the study of the morphological modifications occurring within a single grain during heat treatment at high temperature (typically in the 1000–1300 °C range) led to determine the variation of the number of crystallites included in the polycristalline microspheres and the attached mechanisms[1]. Mechanical rearrangement of the crystallites was generally pointed out for short heating times and associated to low values of activation energies, while solid-state diffusion was found to occur for longer durations. In parallel, the conditions required to reach spherical single crystals grain were evaluated.

The kinetics associated to the evolution of neck, contact angles and centers displacement during the sintering of two microspheres were then evaluated[2,3]. In this case, the evolution of polycrystalline assemblies and of single crystals was studied in parallel and led to determine the driving diffusion mechanism. The comparison of the results with that supplied by the SALAMMBO model then allowed us to estimate the bias associated to the polycristallinity of the powders or to the existence of mesoporosity within the microspheres.

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High temperature characterization using novel thermo-optical measuring devices

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Keywords: *in-situ* characterization, thermo-optical measurement TOM, high temperature materials, refractories

Predictable and reliable high temperature performance is critical for materials like refractories, kiln furniture, heat exchangers etc. In order to minimize energy consumption, maintenance or damages the best available material has to be chosen. In order to gain better and more realistic data the Fraunhofer-Center HTL has developed Thermo-Optical Measuring (TOM) devices for more than 20 years. The TOM method is based on advanced sensor technique which is applied in well-defined and controlled temperature fields and combined with specific software tools for data evaluation. Recent developments are driven by higher resolution, larger samples sizes and additional measurands.[1–3] Two new TOM devices, *TOM_wave* and *TOM_air*, will be presented which allow the *in-situ* measurement during thermal cycling, creep or sintering as well as characterization of high temperature properties.

TOM_wave is a combination of a 1750 °C high temperature furnace and a 600 W CO_2-laser with variable light paths. It allows for different laser heatings of samples which are customarily pre-heated in the furnace: one and two side sample irradiation, variable laser focus and power. TOM_wave measures thermo-physical properties like thermal conductivity, thermal cycling behavior and hot thermal shock resistance. The so-called hot thermal shock by laser heating is better defined than the customary quenching of hot samples in cold liquids or gases. Sample damage is monitored *in situ* during thermal cycling using sound emission analysis. Thermal conductivity is obtained using the laser flash method. Based on laser and pyrometer characteristics samples can be measured without coating. Large samples can be measured by using inverse FE-simulations of the 3-dimensional heat propagation.

TOM_air is designed for precise measurements of sample deformation during sintering, uniaxial loading or due to inhomogeneous green-bodies, temperature fields or interaction with support material. Thermo-mechanical properties like uniaxial viscosity and viscous Poisson ratio can be measured in load and temperature controlled experiments.

Latest developments will be presented by current data on thermal conductivity, thermal shock as well as creep behaviour of ceramics.

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In situ study of the oxidation of ZrB_2 and HfB_2-based ceramics through laser-induced fluorescence from BO_2

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Keywords: UHTC, LIF, ZrB_2, HfB_2, BO_2

The Ultra-High Temperature Ceramics (UHTC) are a class of materials of growing interest. For applications like hypersonic flights, re-entry vehicles or propulsion, these materials are expected to sustain very high temperatures (>2000 °C) in very corrosive and oxidizing atmospheres. The most promising materials are ZrB_2 and HfB_2-based composites. When SiC is added to the diboride, the material develops a multi-oxide scale composed of a MeO_2 skeleton and a glassy borosilicate layer at high temperatures. Stability of this glassy borosilicate layer is the key in ensuring the protection of the underlying materials. Most of the studies dealing with UHTC oxidation are *post-mortem* studies, meaning that characterization of the sample is performed after the oxidation test. Very few *in situ* studies are published, some authors use high-temperature X-Ray diffraction[1] or optical emission spectroscopy[2]. In this study, the laser-induced fluorescence (LIF) technique is used to probe BO_2 radicals in the gas phase above the heated sample in air atmosphere. This provides an *in situ* and real-time monitoring UHTC thermal oxidation.

Various sample compositions (ZrB_2, ZrB_2-20 vol % SiC, HfB_2-20 vol % SiC and HfB_2-20 vol % SiC-3 vol % Y_2O_3) are heated with a 2 kW CO_2 laser, in a custom-made chamber. The sample surface temperature is measured using an optical pyrometer. Samples are heated up to 1650 °C in air flow at 1 bar. The chamber is equipped with fused silica windows for laser diagnostics.

LIF of BO_2 is performed in the $A^2\Pi_u$ - $X^2\Pi_g$ electronic system with laser excitation at 547 nm and detection of the fluorescence at 580 nm. A tunable dye laser pumped by a frequency doubled pulsed Nd:YAG laser is used to promote BO_2 in the $A^2\Pi_u$ excited state. Monitoring BO_2 fluorescence signal throughout the heating ramp gives insights on the thermal stability of the boria glassy phase (at low temperatures, when SiC is not oxidized) and then of the borosilicate layer. This signal is first correlated with the reaction of B_2O_3 with air, and then to the external borosilicate layer. These *in situ* diagnostics allow us to propose more precise oxidation mechanisms with temperature. Afterwards, samples are characterized with SEM/EDS to confirm the oxidation mechanisms.

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Identification of mechanical properties of perovskite membranes of type $La_{(1-x)}Sr_{(x)}Fe_{(1-y)}Ga_{(y)}O_{(3-\delta)}$ versus temperature and oxygen partial pressure by inverse method

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Keywords: mechanical properties, MIEC, creep, I-DIC

Among materials proposed in the literature for oxygen transport membranes, $La_{(1-x)}Sr_{(x)}Fe_{(1-y)}Ga_{(y)}O_{(3-\delta)}$ perovskites are some of the most promising materials.[1] In service, these materials are exposed to high temperature and oxygen partial pressure gradients that are at the origin of their thermal and chemical expansion. To ensure mechanical reliability and avoid membrane breakage induced by mechanical constraints, it is then important to characterize the mechanical properties of these materials from room temperature to service temperature and for different atmospheres.[2,3] Recently, a set of experimental protocol using I-DICs methods was proposed to determine elastic properties in air at room and high temperature (900 °C).[4] In this study the mechanical characterization set-up and the I-DIC routine has been enhanced to performed test for different atmospheres and to identify creep properties. The present routines are based on home-made subroutines and a coupling between finite elements methods and the DIC program. The optimisation algorithm for the parameters identification is a modified Levenberg-Marquardt.[5] Then, the Young modulus, the poison's ratio and tensile strength of $La_{(1-x)}Sr_{(x)}Fe_{(1-y)}Ga_{(y)}O_{(3-\delta)}$ perovskite materials were determined at 1000 °C in air, nitrogen and argon gas firstly. Secondly, creep parameters were determined in air at 1000 °C from a power law creep model. To consider the influence of oxygen partial pressure at high temperature, the creep model proposed by Bretheau[6] is investigated.

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Experiment-based, predictive simulation of ceramic high-temperature processes

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Keywords: high temperature processes, process simulation, *in-situ* characterization

The quality and reliability of ceramic parts is strongly related to the thermal processing conditions a material is exposed to on its way from green body to dense sintered product. A merely empirical optimization of temperature profile and other processing parameters is usually very time-consuming, and often ends up with thermal cycles which consume significantly more time and energy than optimally required. Most existing approaches to do these optimizations by numerical simulations suffer from the need for one or more adjustable parameters within the models used.

To overcome these limitations and enable reliable quantitative predictions, the Fraunhofer HTL has developed an approach to model the behaviour of ceramics during thermal processes on the basis of precise *in-situ* measurements of the relevant process kinetics. The *in-situ* data are obtained using specialized thermo-optical measuring (TOM) systems[1]; the data are then used in the form of a kinetic field[2] as input for finite element simulations. These simulations can, for instance, provide predictions of sinter shrinkage and possible final shape distortion as a function of applied time-temperature cycle. This knowledge is particularly helpful for the design and processing of additively manufactured ceramic parts, whose final shapes cannot be corrected by machining.

In this contribution, the quality of the simulation approach is demonstrated on the sintering of pure alumina ceramics. The finite element sintering model uses TOM *in-situ* results obtained by special optical dilatometry and cyclic loading dilatometry, and can predict stresses and sinter shrinkage during any time-temperature cycle which is in the range of the measured kinetic field. As well, the expected final 3D geometrical shape of an arbitrary ceramic part can be calculated. In addition, it will be shown that this modeling concept can successfully be transferred to other thermal processes like debinding or dehydroxilation, where besides a kinetic field for the rate of weight loss further experimental input like knowledge about exo- or endothermic processes is required.

Altogether, the method of thermal process simulation presented here enables a comprehensive optimization of ceramic production processes with respect to energy efficiency, processing time and product quality.

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Theoretical modeling the magnetic properties of $(Cr_{2/3}M_{1/3})_3AX_2$ (M = Ti, V, A = Al, Si, P, S, Ge, Ga, X = C, N) tailored by chemical compositions

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Keywords: MAX phases, magnetic properties, first principles

Please note that the whole text should fit to this single page $M_{n+1}AX_n$ (MAX) phases belong to a group of nanolaminated ceramics, which have the unique layered crystal structure. The Cr or Mn containing MAX phases were found to be magnetic materials, attracting great interests due to the combination of nanolaminated structure and magnetic properties, which has promising functional application in spintronics or as the self-monitoring smart coating. Most of the discussed magnetic MAX phases are belong to the group of M_2AX. However, Cr_2TiAlC_2 is recently reported as magnetic materials and been synthesized experimentally. Previous studies also show the solid solution method is a strong tool to develop new MAX phase from the pure MAX phases which are considered to not exist before. In this work, the magnetic properties of Cr containing $(Cr_{2/3}M_{1/3})_3AX_2$ solid solutions were studied from first principles. The results show that magnetic moments of the solid solutions are mainly contributed from the Cr atoms. The chemical compositions strongly effected the local magnetic moments of Cr atoms due to changing the number of valence electrons and the Cr-Cr atomic plane separations. This result can provide an insight on tailoring magnetic properties of MAX phases by tuning the chemical compositions through solid solution method.

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Poster presentations

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Modeling of functional properties of microwave dielectric ceramics: study-adapted materials informatics approach

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Keywords: microwave dielectric properties, materials informatics, machine learning, quantitative composition-structure-property relationship, data curation, miltitask learning, relative permittivity, temperature coefficient of resonant frequency

During the past decades the hurtling growth of technologies related to wireless communication resulted in the development of wide spectra of new dielectric materials for microwave applications. These inorganic materials have to meet three main requirements: high permittivity for possible device miniaturization, high quality factor (low loss) for frequency selectivity and near zero temperature coefficient of resonant frequency for temperature stability. Ceramics related to different structure-types are widely investigated in this concern as the candidates for the components of communication systems because of their attractive microwave properties. This study encompasses the information on the compounds related to complex perovskites, wolframites, columbites, ixiolites, aeschynites, and euxenites as the data basis for the development of predictive quantitative models establishing the chemical composition-structure-microwave dielectric property relationships.

The data curation procedure is considered in this study as one of the key aspects of the model development, where two conceptually different approaches are represented in order to aid the expert decision for the cases where different data is published for the same compound. Another feature of this study is the attempt to adopt the idea of multitask learning in order to share the information gained from one structure-type among the other ones as well as to assist the compromise solution in reaching the balance between the contradictory microwave properties for new compounds. Both approaches are intended to demonstrate the possibilities of machine learning in speeding-up the process of the development of new compounds with tailored properties as well as the assisting the experimental data analysis.

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FEM of the factors affecting nanoindentation in the coated systems

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The factors affecting nanoindentation were studied experimentally and by finite element method (FEM) on around 1 um thin hard W-C coatings deposited by High Power Impulse Magnetron Sputtering (HiPIMS) technique on softer steel (12050) substrate. Nanoindentation was performed by Berkovich indenters with three different tip radii in continuous stiffness measurement (CSM) mode and the indents were observed by scanning electron microscopy, atomic force microscopy and focus ion beam. The nanoindentation was simulated by 2D axisymmetric FEM model using sharp tip and experimental tip radii. The experimental and FEM results showed that the hardness and modulus depth profiles of hard coating/soft substrate system strongly depend on the radius of the indenter tip, ratio of the tip radius to coating thickness (*R/t*) and on the ratio of the yield strengths of coating/substrate (σ_c/σ_s). The correct measurement of nanohardness and indentation modulus of thin hard coatings on softer substrates requires the limits for the ratios *R/t* and σ_c/σ_s are fulfilled. The determination of these limits is a valuable contribution to the standardization of CSM method for nanoindentation on coated systems.

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Microstructure characterization of silicon carbide/boron nitride composite by precession electron diffraction technique in transmission electron microscope

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Keywords: precession, electron diffraction, silicon carbide, boron nitride, TEM

Structure property relationship has significant importance in materials science, especially the orientation between the phases present in the structure. Electron backscattered diffraction (EBSD) technique in scanning electron microscope (SEM) is widely used for characterization and visualization of orientation difference between the grains. To overcome the limitations of EBSD, especially the resolution, transmission electron microscope (TEM) based techniques like precession electron diffraction (PED) had been developed.[1] This technique involves a scanning of nearly parallel nano probe over the specimen and at each point diffraction spots are collected while the probe is tilted away from the optical axis in order to minimize the dynamical diffraction. This movement of the beam is created by the scan generator

(DigiSTAR™ P1000, NanoMEGAS) and collected electron diffractions by the external CCD then indexed through template matching algorithm with theoretical patterns in a software (ASTAR™).[2,3]

In the present work, SiC with 7 wt% h-BN additive composite material produced by spark plasma sintering (SPS) method is characterized by TEM/STEM and precession electron diffraction (PED) techniques. Transmission electron microscopy sample is prepared by conventional mechanical polishing followed by Ar-ion beam milling. Electron transparent sample is examined by using 200 keV field emission TEM (JEOL-JEM2100F) equipped with STEM high angle annular dark field (HAADF) detector (Fischione-Model 3000) and energy dispersive X-ray (EDX) spectrometer (JEOL-JED2300T). The TEM phase and orientation mapping results are obtained at NBD mode 0.5 nm and the probe is scanned in a user specified area over the sample up to 0.7° of precession angle and obtained diffraction patterns are analyzed with software (ASTAR™ V2).

TEM and STEM-HAADF results showed that microstructure of the composite system has micron sized SiC and h-BN grains with an amorphous phase that contains yttrium, aluminum and oxygen elements. Due to the mass difference, there is a sharp contrast change between the present phases in TEM and STEM-HAADF results and EDX results confirms the contrast difference in TEM and STEM-HAADF images. TEM and STEM results also showed that, liquid phase that is formed during SPS process is present between not all SiC particles but some of them and this result is concluded as the selective wetting of liquid phase on SiC surfaces.

In this study, apart from the crystallographic orientation and phase maps of the composite structure, the crystallographic relationship between SiC and BN particles during synthesis and wetting behavior of liquid phase around SiC particles are investigated by the application of PED technique at different precession angles (from 0° to 0.7°). It is also important to emphasize that indexing parameters have a great influence on the orientation mapping results. Thus, in this study it is also tried to find out the optimum indexing parameters to have the best indexing results which is quantified by the index and reliability values.

Acknowledgements

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Correlation composition-processing conditions to optimize cement clinker quality

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Nowadays challenges in ceramic materials processing are closely related to the integration of all factors contributing to process efficiency. Practically, efficiency could be expressed as obtaining the best quality for the material with a minimum expenditure of materials, energy, fuels and manpower, thus lessening the costs and the imprint on the environment. When dealing with industrial processes with outcomes of up to 10000 t/day – such as clinker processing – the efficiency level becomes highly significant.

The solution to this challenges is to consider an integrated approach that can involve most – if not all – of the contributing factors, thus minimizing loss by accurately correlating these factors. In this work, two leading selections for a cement plant, i.e. raw materials and thermal processing conditions are being included into an integrated approach, that translates into: selecting the most appropriate thermal history and the best corresponding raw materials from available ones.

The aim of this research is to find out the exact influence of these two factors that affect clinker quality. It has to be found, also, whether all these factors do affect not only the clinker quality but also microstructural features, such as grains size and shape, and minerals proportions in clinker. A total of 9 series (3×3) of combinations of materials composition – processing conditions were used.

Clinkers were analyzed by using various methods such as: Scanning Electron Microscopy (SEM), Optical Microscopy, X-Ray powder diffraction (XRD). Free CaO was measured as an indicator of the clinker quality.

Experimental showed that free CaO and clinker mineral composition clearly depends on both materials composition and thermal histories. Optimal combination of factors within the available possibilities has been clearly identified, with reasonably small efforts. Although the numbers (resulted values) are not universally applicable, given the specificity of each cement plant’s features, our findings can be used as a roadmap procedure to select the best combination possible.

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The effects of tin bath entrance design on molten glass flow during float process

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Keywords: float process, tin bath, multiphase modeling

One of the most widely employed procedures for flat glass manufacture is float process, proposed by Pilkington. Nowadays, there is great demand for thinner float glass of high optical quality. In the float process, the molten glass moves out of the melting furnace and flows into an enclosed bath of molten tin through its canal and spout, spreads out on the surface of the molten tin incessantly. The forming of the glass ribbon takes place during passage of the glass through tin bath, where the glass is stretched to achieve the required size and cooled down until the surfaces are hard enough. The most important stage of float process is the glass forming in tin bath.

When the molten glass flows into the tin bath from spout, most of the glass flows forward in the direction of the float bath outlet, but a small amount flows backward. The part of the float tank in which the glass flows backward is called wet back region. The glass appearing in the wet back region can cause defects in the glass and need lead to the sidewall of tin bath.

In this study, a multiphase flow model including molten glass, tin bath and protective atmosphere was established using the FLUENT software. The flow phenomena of molten glass when spouted over a lip onto the tin bath under protective atmosphere were simulated and analysed. The influence of wet back tile and restrictor tile design on flow behaviour of wet back flow was investigated. Simulation indicates that the molten glass in the wet back region flows outward into the extreme edges of the glass ribbon and depends on the length of wet back tile and angle of restrictor tile.

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T09: Boron-based ceramics

Invited lectures

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Preparation of boride-based eutectic composite by melt-solidification

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Keywords: boride, SiC, eutectic, one directionally solidification, laser

Since borides have high melting temperature, high mechanical strength and stability at high temperature, they are promising structural materials. Various boride-based composites have been fabricated by solid-state sintering such as hot press and spark plasma sintering.[1] However, fully dense composites are often difficult to fabricate due to low diffusion coefficient and covalent nature. It was also too hard to melt because of their high melting temperature often more than ~3000 K. On the other hand, laser or electron-beam technology is developing, and the high-temperature can be easily produced by laser. Boride-based composites can be fabricated by melt-solidification using laser. By scanning laser and sequential powder loading, melting and solidification, additive production or 3D printing of ceramic materials can be realized. One-directionally solidification is particularly useful to control microstructure of ceramic composites improving mechanical properties.[2] Borides are often corroded in oxidizing atmosphere at high temperature forming volatile B_2O_3, while silicon carbide (SiC) is not oxidized due to protective SiO_2 formation. Therefore, boride-SiC eutectic composite can be promising high temperature structural materials. In this study, we will present several boride-SiC eutectic composites by melt-solidification using laser and arc melting. VB_2-SiC is a quasi-binary eutectic system, whose eutectic composition is 55 mass%VB_2. By arc melting, SiC phase dispersed in VB_2 matrix with labyrinth-like lamellar structure. The SiC and VB_2 phases have a relationship of SiC(111)//VB_2(1-210) and SiC[01-1]//VB_2[0001]. The Vickers hardness show the maximum of 22.2 GPa (load: 9.8 N) at the eutectic composition. CrB_2-SiC is also quasi-binary eutectic system, whose eutectic composition is 80 mass% CrB_2. At the eutectic composition, thin lamellar SiC phase dispersed in a CB2 matrix. The eutectic temperature of the CrB_2-SiC system could be relatively lower than other boride-SiC system, and thus CrB_2-SiC eutectic composite was melted by laser (Nd:YAG laser, 180 W). By scanning laser, CrB_2-SiC eutectic composite was easily melted and solidified one-directionally along the scanning direction. CrB_2(0001) was perpendicular to the scanning direction.

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Correlation between microstructure and mechanical properties of boron suboxide B_6O ceramics; a TEM study

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B_6O is a potential candidate for superhard materials with a hardness of 45 GPa measured on single crystals. In recent studies it was found that mixtures of Al_2O_3/Y_2O_3 can be utilized as an effective sintering aid. Therefore, liquid phase sintering of B_6O can be achieved with such oxide additives. Microstructure evolution as a function of additive composition during SPS/FAST processing and resulting mechanical properties were investigated in detail. A strong dependence of the resulting microstructure and the corresponding mechanical response was found. The material revealed characteristic triple junctions filled with amorphous residue composed of B_2O_3, Al_2O_3 and Y_2O_3, while no clear evidence of grain-boundary films was observed along internal interfaces. Mechanical testing revealed on average a hardness of 33 GPa, a fracture toughness of approximately 4.5 $MPa(m)^{1/2}$ and a strength value of 520 MPa. Scanning electron microscopy (SEM) and conventional as well as high-resolution transmission electron microscopy (TEM) analysis allowed for the correlation of the intrinsic microstructure and local distribution of sintering additives with the measured mechanical properties, in particular, with the fact that, independent of additive composition and volume fraction, no further increase in fracture toughness could be achieved.

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Combustion synthesis of refractory ceramics

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Keywords: combustion synthesis, high-propagation high temperature synthesis, ceramics, boron nitride, boron carbide, silicon nitride, silicon carbide

Combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) is an attractive technique to fabricate a wide variety of advanced compounds in forms of powders, bulk materials and near-net shape articles.[1] The characteristic feature of the CS approach is the self-sustained propagation of a chemical reaction through the heterogeneous mixture of the precursors. The temperature in the combustion front can reach quite high values (2000–4000 K) and the velocity of its propagation typically in the range 0.1–10 cm/s. Ceramics were among the first materials produced by SHS.[2] They include boron and silicon nitrides (BN, Si_3N_3), boron and silicon carbides (B_4C, SiC).[3] Recently cubic modification of boron nitride (c-BN) was produced by combination of CS and shock-wave. The goal of this review is summarized and critically discussed the results for direct CS of these ceramics, including synthesis conditions, mechanisms of microstructure formation, as well as material's properties. It is also an attempt to prove that combustion-based approach provide unique efficient routes for production of these refractory compounds.

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PCBN – supermaterial for abrasive and non-abrasive applications

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Since its first synthesis 40 years ago Polycrystalline Cubic Boron Nitride has established itself as a unique cutting tool material for machining of hard ferrous materials. High Pressures (4 to 6 GPa) and relatively high temperatures (1400 °C to 1600 °C) are required to sinter typical grades. Complex ceramic binder structures form the matrix around cBN grains of various sizes. These binders present challenges and opportunities for the product, process design and applications. This paper will give an overview of the history of PcBN synthesis and sintering, typical structures, material classifications, properties and a couple of case studies of abrasive applications. Hardened Steel and Gray Cast Iron Machining will be described to highlight critical and interesting tool-workpiece interactions. The final section includes discussion on the opportunities for PcBN outside of cutting; for example Friction Stir Welding and PcBN as a functional High Voltage Insulator material.

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B_4C based ceramic composites prepared by spark plasma sintering

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Boron carbide ceramics posses low density, high hardness, high wear resistance, high neutron absoption cross section, high melting temperature and high corrosion resistance to chemical attack. Due to these outstanding properties, they found wide application in industry such as cutting tools, blasting nozzles, armor materials, nuclear reaction control rods. However low self diffusivity of constituent elements of B_4C and high melting temperature make difficult to obtain fully densified B_4C ceramics. Beside poor sinterability, another major drawback of B_4C is its brittle feature. To overcome these problems many studies have been attempted by using various sintering techniques and additive materials.

In this talk, we will discuss the effect of various additives such as metals (Al, Si, W), oxides (Al_2O_3, SiO_2, TiO_2, Y_2O_3,), carbide (SiC), boride (TiB_2) and carbon nanotubes on sinterability and some properties on spark plasma sintered B_4C ceramics.

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Processing and properties of B_4C-based systems combined with TiB_2 and SiC

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Boron carbide is one of the lightest and hardest ceramics. Properties such as high melting point, high elastic modulus, high corrosion resistance to chemical agents and high neutron absorption cross section have generated a great interest in B_4C – based ceramics. As a result, this carbide is currently used in many advanced application fields, including cutting tools, high temperature thermoelectricity conversion, armor materials and nuclear industry. In spite of that, B_4C is not exploited to its full potential mainly due to its brittleness and extremely poor sinterability. As many other covalent type carbide ceramics, temperature in excess of 2000 °C and/or pressure assisted techniques are required to obtain the full densification.

In this talk, we first explore different approaches to the processing and sintering of B_4C with the aim to enhance the densification. Then we focus on the B_4C – TiB_2 system that is particularly attractive because the addition of TiB_2 allows not only an improvement of fracture toughness and strength, but also a better machinability, thanks to the possibility of using the EDM technique. We analyze the effects of: -different TiB_2 content on the composite properties, -further secondary phases used to improve either sinterability (such as WC), or high temperature properties/oxidation behavior (such as SiC). Finally, we compare the properties of these materials with reference B_4C-based materials, discussing advantages/drawbacks of different processes.

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Thermoablative resistance of ZrB_2-SiC-WC ceramics at 2400 °C

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Keywords: borides, UHTCs, microstructure, oxidation

Although ZrB_2-SiC ceramics have been extensively researched for applications at ultra-high temperatures (>2000 °C), it is well known that at these temperatures the SiC oxidises actively yielding a gaseous sub-oxide, SiO, rather than the protective, passive oxide product, SiO_2. This limits the high-temperature range of SiC-bearing ceramics for ultra-high temperature applications. In this presentation, dense ZrB_2-20vol%SiC ceramics with and without 5 vol% WC additions have been consolidated by spark plasma sintering at 1950 °C under an axial pressure of 60MPa. Apart from the mechanical properties, the presentation will focus on the thermoablative resistance of sintered ceramics at ultra-high temperatures. Results show that the addition of 5 vol% WC has been shown to effectively eliminate the active oxidation of SiC in ZrB_2-SiC ceramics, even when exposed to an oxyacetylene flame at 2400 °C. In contrast to the porous and fragmentary surface observed with ZrB_2-SiC ceramics tested under the same conditions, a dense oxide surface layer was observed that is believed to have resulted in decreasing pO_2 in the layers beneath. This had the effect of changing the chemistry of the system and hence the composition of the phases produced. Clear evidence of the presence of SiO_2 was observed, thus indicating that the oxidation of the SiC had been passive rather than active. A full volatility diagram for WB at 2400 °C was derived, and existing volatility diagrams for ZrB_2 and SiC were extended to the same temperature, in order to develop a theoretical understanding the active mechanism. The significantly improved ablation resistance of ZrB_2-SiC-WC is consequently mainly attributed to a competitor transition from tungsten boride (WB) to metallic tungsten in the oxygen partial pressure range 10^{-8} Pa to 10^{-3} Pa, which retards the occurrence of the active oxidation of the SiC phase.

Oral presentations

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In-situ formation of VB_2/VC composite powders from oxide raw materials via powder metallurgy processes

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Keywords: vanadium boride/vanadium carbide, milling, annealing, composite powders

Vanadium borides have superior properties such as high melting point, high hardness, high wear resistance and good chemical stability. They are generally used as materials in high temperature applications due to their advanced thermal and mechanical properties.[1–3] Not only vanadium borides, but also vanadium carbides are also attractive for many industrial applications related with the high hardness, high temperature strength and excellent thermal stability at high temperatures.[4,5] In ceramic materials, addition of a second phase developed the fracture toughness and strength of a single phase ceramic material.[6] Also, boride/carbide hybrid ceramics can exhibit improved mechanical properties than those of individual characteristics.[7]

The aim of the present study is the *in-situ* synthesis of vanadium boride and vanadium carbide composite powders by using powder metallurgy routes. VB_2/VC composite powders were synthesized from the V_2O_5, B_2O_3 and C powder blends via the carbothermal reduction which were assisted by mechanical milling. Powders blends prepared in the stoichiometric amounts were milled up to 5 h in a high energy ball mill (1200 rpm) by using hardened steel vials and balls with 10/1 ball-to-powder weight ratio. Milling step reduced the crystallite size, increased the uniformity of the distribution and increased the reactivity of the starting powders. Mechanically milled and also activated powders were annealed at different temperatures in a tube furnace under Ar atmosphere for 12 h to produce single phase VB_2 and VC powders. Annealing temperatures were determined as 1400, 1450 and 1500 °C with 10 °C/min heating and cooling rates. Annealed powders were characterized by X-ray diffractometer (XRD) to determine the yielded phases and phase transformations. In the case of using annealing temperature of 1400 °C, VB_2-V_3B_4-V_2B_3/VC hybrid powders were obtained. Besides, Rietveld analyses were performed in regard of the XRD patterns to determine the approximate percentages of the phases. However, annealing temperature of 1400 °C is not enough to the formation of the most stable VB_2 as a single phase in the structure in addition to the VC. Also, morphologies of the synthesized powders were investigated by using scanning electron microscope/energy dispersive spectrometer (SEM/EDS). Also, particle size distributions of the synthesized composite powders were measured by using of laser diffraction technique.

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Effect of titanium diboride on properties of functionally graded boron carbide-titanium diboride-aluminium composites

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Keywords: functionally graded materials, spark plasma sintering, infiltration, mechanical properties, ceramic-metal composites

In this study, the effect of titanium diboride on the properties of functionally graded boron carbide-titanium diboride-aluminium composites was investigated. Boron carbide-titanium diboride powder mixtures containing 0 to 30 weight % titanium diboride were partially sintered at 1700 °C for 5 minutes by spark plasma sintering.

Functionally graded materials were designed by considering the porosity content of the boron carbide-titanium diboride pellets after partial sintering, and their titanium diboride content. An aluminium-12 weight % silicon alloy was then infiltrated into the partially sintered functionally graded preforms at 1200 °C for 10 minutes via pressureless melt infiltration. Phase analysis of the functionally graded composite layers were characterized by x-ray diffraction, and their microstructure was investigated by using a scanning electron microscope attached with an energy dispersive x-ray spectrometer. Hardness and compressive strength values, and densities of the functionally graded composite layer were measured.

Results obtained indicate that titanium diboride addition has a positive effect on both the sintering behavior of boron carbide, and the hardness and compressive strength of the produced boron carbide-titanium diboride-aluminium functionally graded composite layers. Furthermore, it was determined that the amount of residual porosity in the produced functionally graded composite layers was always well below 1%. Hardness and compressive strength values changed gradually in moving from front to rear surface of the functional graded composite materials.

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Sintering and properties of $AlB_{12}C_2$ – based materials

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Keywords: aluminum dodecaboride-based materials, hardness, fracture toughness, bending strength, compressive strength, structure

This article focuses on the formation of $AlB_{12}C_2$ – based ceramics from the submicron α-AlB_{12} powder with C and TiC additions under hot pressure (30 MPa) and high quasihydrostatic pressure (2 GPa) conditions at 1200–2100 ºC. The interrelations between materials properties and structures are under the consideration.

The results of the present study allowed us to conclude that the fracture toughness of α-AlB_{12} (98 wt.%, porosity 1.59%, density 2.58 g/cm^3) was lower than that of the $AlB_{12}C_2$ – based composites ($AlB_{12}C_2$ = 70 wt.% BN = 14 wt.% Al_2O_3 = 16 wt.%, porosity 5%, density 2.42 g/cm^3) prepared by hot pressing (at 30 MPa). The fracture toughness (estimated under 49 N-load) of $AlB_{12}C_2$ – based composite was 7.6 MPa·m$^{0.5}$ and the material Vickers hardness was about 20.1 GPa while the fracture toughness of α-AlB_{12} prepared under the same conditions was K_{1C} = 4.2±0.5 MPa·m$^{0.5}$ and hardness H_V = 24.1 GPa (at 49 N-load). The fracture toughness of α-AlB_{12} sintered under high pressure (2 GPa) conditions was as well lower than that of $AlB_{12}C_2$. Addition of carbon (17 wt.%) to α-AlB_{12} and hot pressure synthesis leads to the formation of the composite material ($AlB_{12}C_2$ = 86 wt.% and AlN_H = 14 wt.%, porosity 0.13%, density 2.7 g/cm^3) with K_{1C} = 5.9±1.4 MPa·m$^{0.5}$ and Vickers hardness H_V = 23.6±2.8 GPa (at 49 N-load).

The results of SEM studies showed that the main matrix phase of the $AlB_{12}C_2$ – based material (sintered at 1950 ºC, 30 MPa and which demonstrated high mechanical characteristics) high deficit of Al and some deficit of boron as compare to $AlB_{12}C_2$ stoichiometry, while boron in rather high amount was present in the secondary phase having Al_2O_3 structure. The increase of concentration of Al-B-O-based phase with Al_2O_3 structure up to 5 wt.% (according with the results of Rietveld refinement of the X-ray pattern) in $AlB_{12}C_2$ – based material correlated with the higher fracture toughness (4.2±1.3 MPa·m$^{0.5}$). The material synthesized from α-AlB_{12} and 20% TiC at 1950 °C contained after synthesis 74% $AlB_{12}C_2$, 22% TiB_2 and 4% Al_2O_3, its hardness was H_V = 28.9 GPa, fracture toughness K_{1C} (49 N) = 5.2 MPa·m$^{0.5}$, bending R_{bs} = 633 MPa and compressive R_{cs} = 640 MPa strengths, density ρ = 3.2 g/cm^3.

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Novel catalytic synthesis of boron nitride nanotubes at low temperatures

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Keywords: BNNT, catalyst, CVD

Boron Nitride Nanotubes (BNNT) have been the most popular inorganic nanotubes for the last 20 years, after carbon nanotubes. BNNTs are structurally analogous to carbon nanotubes. However, their chemical difference to carbon nanotubes makes them more advantageous on many aspects such as chemical stability, thermal stability (oxidation resistance up to 1100 °C), piezoelectricity, neutron screening, and super hydrophobicity. Moreover, as opposed to the semiconducting or metallic carbon nanotubes, BNNTs, owing to the partially ionic character of their bond structure, are wide bandgap (5–6 eV) insulating materials. Because of all those unique properties, BNNTs are candidate materials for nanoelectronics (nano insulating material, nanosensors), optical applications (Deep-blue and infrared lasers), magnetic applications (targeted drug delivery), biomedical applications (biosensors, tissue scaffold), energy applications (hydrogen storage), ceramic-glass composites and polymeric nanocomposites. However, the most important drawback of BNNTs lie in the challenges of synthesizing them with high purity and amount. Chemical Vapor Deposition (CVD) technique is advantageous in the sense that it is possible to produce high amounts of material with high purity. Hence, CVD is a technique of importance in industrialization of BNNTs, and is considered as the primary technique in BNNT synthesis. However, the catalysts used in BNNT production only function at temperatures at and above 1100 °C.[1,2] Here, a novel alkali based catalyst is produced and used in vapor trap CVD synthesis of BNNTs. The catalyst works at temperatures as low as 750 °C. The catalyst is characterized via XRD. The structural characterization of BNNTs were conducted by XRD and Raman Spectroscopies, the size of the nanotubes were determined with SEM, wall structure was determined with TEM and chemical composition analysis was carried out with EELS measurements.

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SHS of TiB_2-B_4C powder mıxtures

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Titanium-diboride (TiB_2) is an important and promising transition metal boride with its unique properties such as high strength, hardness, durability, melting point, wear resistance, thermal conductivity and low electric resistivity. Boron Carbide (B_4C) is one of the hardest materials known, ranking third behind diamond and cubic boron nitride. It is the hardest material produced in tonnage quantities. Originally discovered in mid-19th century as a by-product in the production of metal borides, boron carbide was only studied in detail since 1930. TiB_2 and B_4C are are being used in various industrial areas from space technology to nuclear industry owing to combination of their unique properties. Present study was conducted in two main stages: Self-propagating high-temperature synthesis (SHS) reactions and leaching. TiO, Carbon black, B_2O_3 were used as starting material to produce TiB_2-B_4C powders by SHS. The metal oxide powders have over 97% purity and 150 µm average grain sizes. For thermodynamic analysis of system Fact sage 6.4 software was used, in order to determine probable phases at different temperatures. The reaction mixtures were weighted on a precision scale and mixed thoroughly 15 minutes in a turbula mixer and powder mixtures (approximately 150 g) were charged into Cu crucible and compacted. W (tungsten) wire was placed at the top of copper crucible and the reaction realized by passing current through the wire. After initiation, a highly exothermic reaction became in a self-sustaining mode and propagated throughout the SHS mixture. The obtained SHS products were discharged from the crucible after cooling. At the end of the SHS process leaching step was applied to eliminate undesired Mg based phases. The hydrochloric acid solution was prepared with TiB_2-B_4C SHS powders. The samples were characterized by using Atomic Absorbsion Spectrometer, X-Ray Diffraction, X-Ray Fluorescence, Scanning Electron Microscope and EDS techniques.

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Production of IV-B group boride composite ceramics via SHS

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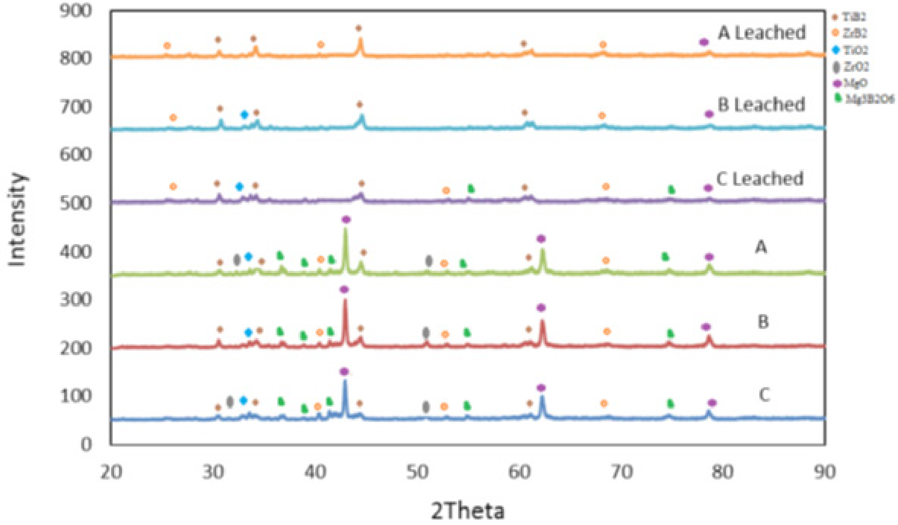
TiB_2 and ZrB_2 are important metal borides. They are being used in various industrial areas such as space technology, nuclear industry owing to their unique physical properties such as high thermal/electrical conductivity, high melting point and low density. In the SHS experiments, a mixture of ZrO_2, TiO_2, B_2O_3 and Mg powders were used in order to produce advanced ZrB_2-TiB_2 composite ceramic powders. The metal oxide powders have over 97% purity and 150 µm average grain sizes. In the experimental set TiB_2-ZrB_2 composite powders produced by SHS and leaching processes. In this experiment set TiB_2 and ZrB_2 ratio changed and optimum conditions determined, initial conditions and results of these series present in Table 1.

Table 1. Initial conditions of ZrB_2-TiB_2 SHS experiments

No	Zr/Ti	$ZrO_{2\ (g)}$	$TiO_{2\ (g)}$	$B_2O_{3\ (g)}$	$Mg_{(g)}$	SHS Product(g)
1	90/10	23.20	2.96	41.90	31.92	90.00
2	80/20	20.64	5.92	40.12	33.33	90.30
3	70/30	18.04	8.89	38.32	34.31	71.90
4	60/40	15.46	11.85	36.53	36.14	71.80
5	50/50	12.89	14.82	34.74	37.54	91.20
6	40/60	10.31	17.78	32.94	38.95	94.90
7	30/70	7.73	20.74	31.20	40.40	57.00
8	20/80	5.15	23.71	29.30	41.72	97.50
9	10/90	2.57	26.67	27.57	43.16	60.30

After the SHS experiment again leaching process made, Fig. 1 indicates leached and unleached products of ZrB_2-TiB_2 composite powders.



A%40 ZrB_2 %60 TiB_2 – B%50 ZrB_2 %50 TiB_2 – C%60 ZrB_2 %40 TiB_2

Fig. 1. XRD Graphs of Unleached and leached ZrB_2-TiB_2

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A study of novel PcBN tool materials in interrupted machining applications

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Keywords: polycrystalline cubic boron nitride, PcBN, interrupted machining, properties, tool life

Polycrystalline cubic Boron Nitride (PcBN) materials are increasingly being used to make tools for high speed machining of various alloys, including hardened steels. Next generation PcBN materials need to out-perform existing PcBN materials as well as ceramic and coated carbide grades in terms of tool life and predictability of performance. In the quest for next generation PcBN tool materials, different materials processing technologies are employed to manufacture novel grades. Testing of these materials in application tests is costly and time consuming. This study presents novel PcBN materials, with performance superior to current commercially available grades in interrupted applications. This paper also presents an observed correlation between Vickers micro-indenter crack length distributions and tool life of these variants in moderately interrupted applications. This work has resulted in new PcBN tool material solutions, as well as a significant saving in cost and time for screening of new PcBN variants in moderately interrupted machining applications.

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Effect of calcium carbonate addition on the gel precursor synthesize of boron carbide

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Keywords: carbothermic reduction, boron carbide, gel precursor

Boron carbide (B_4C) is an expensive material, commercially synthesized by the carbothermal reduction at high temperature. However, this technique results in excessive free carbon residue in the final product due to the boron loss. To minimize boron loss during synthesis, additional assistive compounds can be added into the system and afterwards these additives are easily removed to obtain purified end-product. Citric acid (CA) has frequently used as a carbon source to synthesize B_4C but studies showed that despite the high synthesising temperatures, high amount of residual carbon still exist in the system.[1–3]

In this study, B_4C was synthesized with using of gel precursor technique that was prepared in a single step process and by the carbothermic reduction via reaction of boron oxide from boric acid (H_3BO_3) and carbon from citric acid ($C_6H_8O_7$). Effect of calcium carbonate addition and its optimum amount on the residual carbon content have been investigated systematically.

The gel product was characterized by means of Fourier Transform Infrared Spectroscopy (FTIR) and Thermal Analysis (TG/DTA) to prove of gel formation. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) have been used to analyse phase formation and morphology of the synthesized powders. It was found that $Ca_3B_2O_6$, CaB_2O_4 phases were formed as transitional phases and all of them were easily removed via acid leaching from the end product. The optimum synthesis conditions for the formation of B_4C without free carbon residue were determined as 1400 °C for 10 h in an argon flow and the ratio of $CaO:B_2O_3=1:3$.

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Modification of B_4C ceramics surface by the intense electron beam and ion plasma sputtering

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Keywords: boron carbide ceramics, spark plasma sintering, intense pulsed electron beam, metallization, microhardness, fracture toughness

B_4C ceramics has been sintered by SPS technique using powder mixture of two fractions: 90 wt% of submicrometer fraction (average size of B_4C particles 0.55 microns, JSC Uralinvest, Russia) and 10 wt% of nano-scaled one (average size of B_4C particles 46 nm, Plasmachem GmbH, Germany). Relative density of sintered ceramics was 99.2%; microhardness 36.5 GPa (Vickers pyramid indentation using the microhardness tester PMT-3M LOMO); fracture toughness 5.6 MPa*m$^{1/2}$ by Niihara's formula.[1] Ceramic samples were irradiated with a low-energy intense pulsed electron beam (IPEB, energy 15 keV, energy density 5–30 J/cm^2, pulse duration 100 μs, pulse frequency 0.3 s^{-1},) in residual argon atmosphere (10^{-2} Pa). TEM (JEM-2100F JEOL), SEM (SEM-7500F JEOL) analysis showed that the irradiation caused the formation of a full-dense surface layer (thickness of 15 microns) with microstructure having micro-twins and nanoscale interlayers along the boron carbide crystalline interfaces. Fatigue tests were performed before and after irradiation using ultra-microhardness tester DUH-211S Shimadzu (up to 50 loading cycles by 10 mN indentation load with 5 s time exposure; size of loading pyramid tip was 10 nm). After 10 loading cycles surface of the irradiated ceramics had microhardness of 27 GPa while non-irradiated one showed microhardness decreasing up to 17 GPa. So the surface layer hardening of the irradiated ceramics has been shown.

Ti film (thickness of 0.5 micron) was deposited on the B4C ceramics by the ion-plasma sputtering.[2] It was found that irradiation of Ti film/B4C substrate by the IPEB lead to formation of metal-enriched mixed system (α-Ti)+TiB_2 in the surface layer (thickness of 5–7 microns) having improved plastic properties. The irradiated metallized Ti/B_4C surface was not fractured under Vickers pyramid indentation at load of 1.96 N while at the same testing the initial B_4C ceramics showed the cracks and had fracture toughness of 5.4 MPa*m$^{1/2}$.

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Design-synthesis-evaluation of hard coatings for industrial applications

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Hard-phase films have been extensively applied in various parts with superior mechanical properties like high hardness, wear resistance, low friction, etc. for the applications in machining, die-casting processes. Recently, the electrochemical applications of DLC, diamond films are spotlighted for waste-water treatments.

(1) Nanocomposite films: Various new materials for the multi-function are designed. For example, various ternary, quaternary, and quinary nano-structured films in the (Ti, Cr, Mo, Al, Si)-(B, C, N) system are compared in sense of not only hardness but also other properties of corrosion, oxidation, friction etc. for the structural applications.

(2) DLC and BDD films for the waste-water treatment: Diamond- like carbon (DLC) and boron-doped diamond (BDD) films have superior chemical stability and electrochemical properties. For the applications of waste-water treatment, the hard layers should have ideal interlayer structure and those multi-layered structure must show the excellent properties such as mechanical stability and electrochemical properties.

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Preparation and characterization of oxidation behavior of YB4-SiC ceramics

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Keywords: YB4, synthesis, oxidation

Yttrium tetraboride (YB4) powders were synthetized via four reactions including: direct synthesis from elements (1), reduction of yttrium oxide with boron (2), boron carbide reduction method (3) and combined boron carbide/carbothermal reduction (4) at 1500 °C, 1700 °C and 1900 °C for 2 hours in vacuum. Powders were characterized by X-ray diffraction analysis and scanning electron microscopy. Pure YB4 was successfully synthetized using combined boron carbide/carbothermal reduction method. Secondary phases, especially Y2O3, YB2 or YBO3, were found in powders prepared using other three methods.

YB4 powder synthetized via reaction (4) was used for preparation of composites with 20, 30 and 40 wt% of SiC. YB4-SiC composites were densified using hot-pressing technique and subjected to oxidation test up to 1650 °C. Weight changes after oxidation were measured and the thickness of formed oxide layer was evaluated by scanning electron microscopy. Electron dispersive spectroscopy and X-ray phase analysis was used to identify the phase composition of samples after oxidation.

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Reactive spark plasma sintering of boron carbide nanostructured ceramics

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Keywords: ceramics, boron carbide, high-energy ball milling, mechanical activation, reactive sintering, spark plasma sintering

Boron carbide (B_4C) based ceramics possess a unique set of physical and mechanical properties, such as low density, high melting point, high elastic modulus, high neutron absorption cross-section, and chemical durability. However, due to the strong direct covalent bonds between the boron and carbon atoms, it is difficult to consolidate the B_4C ceramics, which limits applications.

Since direct reaction between boron and carbon is exothermic one may use combustion synthesis (CS) method for fabrication of B_4C compound.[1] Spark plasma sintering (SPS) is an advanced consolidation process by combination of uniaxial pressure and powerful DC pulsed current to fabricate bulk materials.[2] SPS is widely used to produce boron carbide ceramics. However, the majority of these works were dedicated to SPS of B_4C powders.[3,4] In this work, we developed a method for one-step fabrication of pure boron carbide bulk ceramics from the elements, i.e. boron and carbon. This, so-called, reactive spark plasma sintering (RSPS) method consists of CS of B_4C from elemental precursors combined with simultaneous spark plasma sintering.[5–7]

It was also demonstrated that preliminary high-energy ball milling (HEBM)[8] of the B+C powder mixture leads to the formation of B/C composite particles with enhanced reactivity. Using these reactive composites in RSPS permits tuning of synthesized B_4C ceramic microstructure. Optimization of HEBM + RSPS conditions allows rapid (less than 30 min of SPS) fabrication of B_4C ceramics with porosity less than 2%, hardness of ~35 GPa and fracture toughness of ~ 4.5 MPa· m $^{1/2}$.

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Oxidation behavior of iron boride coatings

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In the present work, microstructure, phase constitution and high temperature oxidation kinetics of iron boride coatings prepared by diffusion boronizing have been studied. Low carbon steel S235JRG1 was powder-boronized by B_4C at 1273 K for 45–150 min. Iron boride layers with a distinct tooth-like microstructure were produced. The layers were found to be composed of Fe_2B and FeB in unequal amounts. The oxidation behavior of the layers was studied by simultaneous thermal analysis in a flowing synthetic air for 21–24 h at 873–1173 K. Parabolic oxidation kinetics has been found. At 1173 K, two successive parabolic periods were observed, followed by a breakaway oxidation behavior. The experimental rate constants were found between 1.04×10^{-9} and 3.78×10^{-6} $kg^2\ m^{-4}\ s^{-1}$, depending on temperature and oxidation time. The activation energy for oxidation is 93 kJ mol^{-1}. The oxide scales of the iron boride coatings are characterized. Possible oxidation mechanisms are discussed and implications towards high temperature stability of iron boride coatings are presented.

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Contribution to the thermodynamic study and oxidation behavior of HfB_2-SiC ultra-high temperature ceramics

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Keywords: UHTC, HfB_2-SiC, Spark Plasma Sintering, oxidation

Ultra-High Temperature Ceramics (UHTCs), more specifically diborides of the IVb group, are potential candidates for a large variety of applications, in particular as structural materials for thermal protection of hypersonic vehicles exposed to high temperatures (> 1800 °C) and to oxidation[1].

The aim of this work consists in elaborating ultra-high temperature HfB_2-SiC ceramic composites used as structural materials for several applications, such as aeronautic and aerospace areas and to understand oxidation mechanisms involved during their entry into the atmosphere. The sintering of these materials at different compositions has been carried out by Spark Plasma Sintering (SPS). This process is used to obtain fully dense materials (> 98% relative density) with fine grains, at lower temperatures and shorter dwell times than conventional techniques (natural sintering, hot pressing)[2]. In order to favor densification and to obtain a homogeneous distribution of both phases in the final material, a study on the raw powders granulometry has been necessary. An optimization of sintering conditions (applied load, temperature and its hold time, heating rate) has been subsequently carried out in order to elaborate fully dense samples by using parameters adapted to their environment. Obtained bulk bodies have been oxidized at several temperatures with a solar furnace to approach conditions to which hypersonic vehicles are subjected. Oxidation mechanisms have been highlighted through the study of the oxidized layers by combining X-ray diffraction analysis (XRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectrometry (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). This work was helped by the obtaining of kinetic data during oxidation tests. In order to supplement this study, a first thermodynamic approach of the Hf-B-Si-C system has been made through the modeling of ternary diagrams, the aim being to constitute a coherent data base of this quaternary system.

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Influence of the chemical composition on the mechanical properties of spark plasma sintered boron carbide ceramics

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Keywords: boron carbide, Spark Plasma Sintering, microstructure-property relationship, stoichiometry

Due to its excellent mechanical properties (i.e. high hardness and high Young's modulus) and its low density, boron carbide is a promising ceramic phase which can be used as shielding materials. These physical properties result from unusual characters of B-B and B-C bonds. Boron carbide phase exists over a wide range of stoichiometry, i.e. from 8 to 20 at.% of carbon.[1,2] Niihara et al.[3] have shown that this variation of stoichiometry modifies the mechanical properties (hardness and Young's modulus). Indeed, these authors observed an increase of the Vickers hardness with the rise of carbon content in the crystalline structure of boron carbide. Enhanced mechanical properties were obtained for C/B ratio of 20 at.%. However, the measured hardness depends on the stoichiometry of the boron carbide phase, but can also be altered by the existence of secondary phases located at the grain boundaries. Since Niihara et al.[3] have clearly demonstrated it, the excess of carbon in boron carbide samples leads to a decrease of the hardness and the Young's modulus. Indeed, boron carbide powder is usually synthesized via the carbothermal route of boron oxide, which can lead to the presence of residual reactants in the powders (e.g. free carbon, boron acid, boron oxide).

Consequently, this work firstly aims at characterizing the chemical composition of different powders batches by using coupled analytical methods (i.e. XRD analysis and Rietveld refinement to give lattice parameters, standard addition methods to quantify the amount of free carbon, XPS). Then, dense monoliths with fine microstructure were elaborated using the Spark Plasma Sintering process. The manufacture of dense specimens enabled to study the relationships between the chemical composition (i.e. stoichiometry, influence of secondary phases) and the mechanical properties, without being altered by the presence of residual porosity. The mechanical response was characterized at two different scales by nano- and micro-indentation measurements in order to elucidate the influence of the stoichiometry of boron carbide phase from the one of secondary phases on the mechanical properties.

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Microstructural design of melt infiltrated boron carbide – aluminum ceramic – metal composites via spark plasma sintering

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Keywords: boron carbide, spark plasma sintering, ceramic–metal composite

Like other composites, ceramic–metal composites enable tailoring their properties with special techniques and/or optimization of production parameters. B_4C–Al ceramic–metal composites are attractive materials due to their good mechanical properties and lightweight. One of the simplest and effective methods to produce high ceramic volume fraction B_4C–Al composites is metal melt infiltration method. On the other hand, this method requires strict control of each production step to prevent the formation of deleterious reaction products which may seriously degrade mechanical properties. Enhancement of material properties could be achieved by controlling the microstructural progress. Studies suggest that a co–continuous microstructure may improve mechanical properties of composite.[1] This study focuses on how to enhance the properties of such composites by controlling the progress of microstructure.

Spark Plasma Sintering (SPS) provides effective sintering at lower temperatures and shorter times than conventional sintering methods. Besides, it is reported that partial SPS of B_4C may provide a continuous ceramic network.[2] Same starting powders were also preformed by cold isostatic pressing and used as reference samples. The partially sintered co-continuous preforms as well as the reference specimens were-after having adjusted processing parameters so as to yield the least amount of reaction products-melt infiltrated with an Al-Si alloy via the pressureless melt infiltration method. Microstructure of the composites was investigated by SEM and phase analysis was performed with XRD. Physical and mechanical properties of composites were characterized by water immersion method, hardness and compression tests, respectively. Findings were evaluated in terms of preforming method, starting powder and infiltration conditions. The results obtained indicate that a proper microstructural design enabled the achievement of a co–continuous ceramic–metal network, which in turn enhanced both hardness and compressive strength of the produced composites.

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Ultrahigh pressure deformation and Raman spectra of boron carbide and its polymorphs

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The ceramic boron carbide (B_4C) is known for its exceptional refractory properties, hardness, strength, and impact resistance. Interesting properties of boron carbide include its polymorphism and susceptibility to amorphization, a solid-state phase transformation induced by high pressures. The present study is a coordinated experimental and modeling effort on the behavior of this unique material with the goal of optimizing its crystal structures for enhanced performance. First, the rate-dependent response of the amorphized zone and the evolution of its structure beneath indented surfaces in micro-grained and nano-grained boron carbide were investigated. Using Raman spectroscopy, the consequences of amorphization are addressed with regard to volumetric changes in the amorphized material and the stress state in surrounding regions. To determine the origin of the amorphization process, numerous density functional theory (DFT) simulations were performed to comprehensively identify and quantify the structures formed in boron carbide specimens fabricated by hot pressing and spark-plasma sintering. To offer insight on the kinetics of amorphization, simulated deformations were performed on representative polymorphs using DFT. Analysis of their response to high hydrostatic compression and homogeneous shear has provided new insight into their bonding behavior and Raman spectral shifts at the atomic level. These studies have enabled excellent comparisons with experimental data from high-pressure environments up to 50 GPa, especially those of Hugoniot response. We have demonstrated that increases in hydrostatic pressure cause high-wavenumber Raman peaks to shift higher while low-wave number peaks shift lower, as observed in prior experimental investigations reported in literature. Finally, this study reveals that introducing dopants into the large volume of “cage space” in the virgin B_4C structure may improve the stability, amorphization resistance, and therefore mechanical performance of boron carbide. Overall, these results provide new insight into the links between polymorph crystal structure, deformation response, and Raman spectra while simultaneously laying the foundation for polymorph-level design of boron carbide.

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The importance of using borosilicate in geopolymer incorporating waste

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Keywords: boro-aluminosilicates, Inorganic polymers, spectroscopy

Geopolymers, as cement-like materials, gained a lot of attention in the last decades as natural replacement of Portland cement.[1,2] In fact, the production process of this material is free of CO_2 emission, the major cause of the climate change. In this issue, Portland cement covers the 8% of the annual emission of carbon dioxide in the atmosphere.[1] The production of geopolymers incorporating wastes seems competitive to reduce the cost of production, and help to empty the landfills.[2]

In this research work, fly-ash, a by-product from a bohemian power plant, and recycled borosilicate glass (BSG) from pharmaceutical purposes were employed as primary aluminosilicate sources for geopolymerization. The innovation in using BSG is the dissolution of borates prior polycondensation, which was expected to take part in the final network as the alumina does. By this way, a boro-alumino-silicate polymer is finally formed. Fourier Transform Infrared (FTIR), among all, confirmed the presence of a resonance at about 830 mm^{-1}, associated to the vibration of tetrahedral borate (BO_4), being this configuration the only admissible to arrange in the product of the polycondensation. ^{11}B NMR conducted on both BSG and geopolymer confirmed the quasi-total depletion of trigonal borate (BO_3) inside the BSG in favour of a tetragonal one in the geopolymer.[3] This proved that not only the borosilicate successfully dissolved in the basic solution of sodium hydroxide, but also borate species rearranged in a more appropriate configuration and linked to the aluminosilicate network. ^{29}Si NMR analysis carried out on geopolymer sample revealed a large presence of $Q_4(nAl)$ environments, associated to a highly structured networking (3D cross-linked), which in turn involve better mechanical properties.[2] This means that the insertion of borates in geopolymers is helpful for a better polymerization of the microstructure.

Acknowledgements

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Preparation of B_4C-HfB_2-SiC eutectic composite by arc melting

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Keywords: arc-melting, eutectic boride and carbide, Vickers hardness, fracture toughness, electrical conductivity, thermal conductivity, thermal expansion coefficient

B_4C-HfB_2-SiC based composites may possess the excellent combination properties of B_4C, HfB_2 and SiC, such as extraordinary mechanical, electrical and thermal properties, and may be applied as a new generation of ultra-high temperature structural materials, *e.g.*, cutting tools, plasma-arc electrodes, furnace elements, rocket nozzles and sharp leading edges of propulsion system. In the present study, B_4C, HfB_2 and SiC based composites were prepared by arc melting. The effects of the composition and microstructure on microstructure, mechanical, electrical and thermal properties were investigated.

B_4C-HfB_2 binary composites were prepared by arc melting using B_4C and HfB_2 as raw materials. At the composition of $70B_4C$-$30HfB_2$ (mol%), the uniform and fine eutectic microstructure in large area was obtained. The lamellar and regular eutectic microstructure was composed of B_4C matrix with HfB_2 phase about 1 μm in thickness. The Vickers micro-hardness of B_4C-HfB_2 composites significantly increased with increasing B_4C content and showed the maximum value of 31.2 GPa at the eutectic composition. The fracture toughness of B_4C-HfB_2 composites had the maximum value of 5.9 MPa $m^{1/2}$ around the eutectic composition. Both the electrical conductivity and thermal conductivity of B_4C-HfB_2 composite increased with the increase of HfB_2 content and decreased nearly concomitantly with increasing the temperature. The electrical conductivity and thermal conductivity of B_4C-HfB_2 eutectic composite were 7.43×10^4 to 8.94×10^4 Sm^{-1} in the range of 298-800 K and 16 to 18 $WK^{-1}m^{-1}$ in the range of 298-973 K, respectively. The thermal expansion coefficient of B_4C-HfB_2 composites showed the highest value of 7.18×10^{-6} K^{-1} in the range of 293–1273 K at the eutectic composition.

B4C-HfB2-SiC ternary eutectic composite was also obtained by arc melting. The ternary eutectic composition of 45B4C–15HfB2–40SiC (mol%) was first identified with a lamellar eutectic texture. HfB2 about 500 nm in thickness and SiC about 700 nm in thickness were uniformly dispersed in B_4C matrix of the eutectic composite. B_4C-HfB_2-SiC composites showed the highest Vickers micro-hardness of 35.7 GPa and highest fracture toughness of 6.5 MPa $m^{1/2}$ at the eutectic composition, which were both higher than that of B_4C-HfB_2 eutectic composites. The electrical conductivity of B_4C-HfB_2-SiC composites increased with the increase of HfB_2 content and nearly keep constant (0.937×10^4-1.09×10^4 Sm^{-1}) from 298 to 800 K at the eutectic composition. The thermal conductivity of B_4C-HfB_2-SiC composites increased with the increase of HfB_2 content and the decrease of B_4C content and decreased with increasing the temperature. B_4C-HfB_2-SiC eutectic composite had the minimum thermal conductivity, which decreased from 32 to 23 $WK^{-1}m^{-1}$ with increasing the temperature from 373 to 973 K. The thermal expansion coefficient of B_4C-HfB_2-SiC composite increased with the increase of HfB_2 content and the decrease of SiC content and showed the maximum value of 6.42×10^{-6} K^{-1} in the range of 293–1272 K.

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Effect of functional additive on the SHS of TiB_2

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Optimum production condition of TiB_2 via SHS was discussed on "Self-propagating High Temperature Synthesis of TiB_2" article.[1] In order to enhance these results, the experiments were carried out with the addition of NaCl and $MgSO_4·7H_2O$ as catalysts.

In the present study, SHS of TiB_2 ceramic powders was investigated. TiO_2 and B_2O_3 powders were mixed with 90%, 100% and 110% of stoichiometrically required amount of Mg powders. SHS experiments were conducted under both air and argon atmospheres to determine the optimum process atmosphere. The effects of functional additive (NaCl and $MgSO_4·7H_2O$) were also carried out with the various addition rates of catalysts. SHS products were leached in HCl media to purify their TiB_2 contents. Fig. 1 (A) presents, XRD Patterns of Unleached and Leached SHS Products Synthesized under Argon Atmosphere and Stoichiometrically 100% Mg Additon with Increasing NaCl Addition Rate, (B) shows $MgSO_4·7H_2O$.

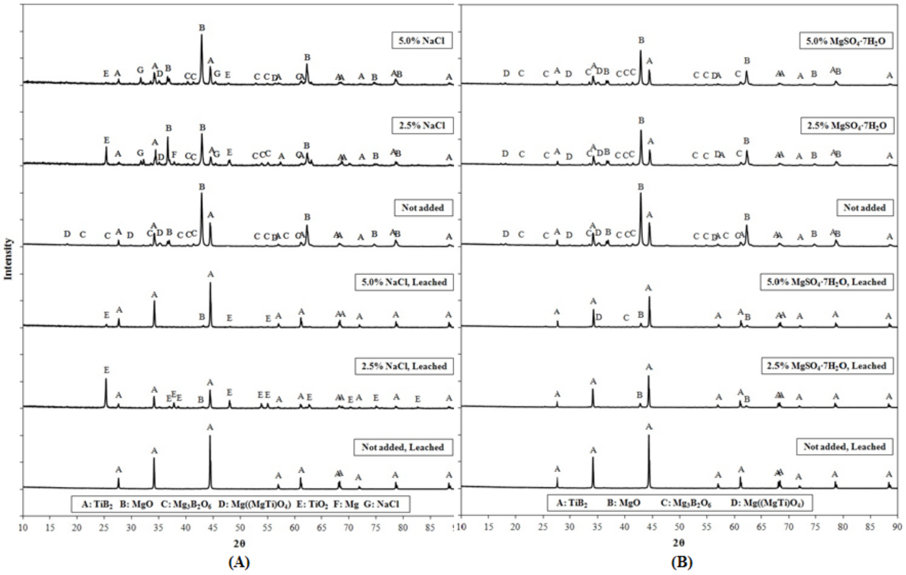

Fig. 1. XRD Pattern of SHS Products

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Poster presentations

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HfB_2, ZrB_2 and $Hf_{0.5}Zr_{0.5}B_2$ solid solution UTHC ceramics: processing by SPS and mechanical properties

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Keywords: ultra high temperature ceramics, SPS, HfB_2, ZrB_2, $Hf_{0.5}Zr_{0.5}B_2$, ring-on-ring

Mechanical properties of Spark Plasma Sintered (SPS) HfB_2, ZrB_2 and their $Hf_{0.5}Zr_{0.5}B_2$ solid solution were studied both at room and high temperatures. For SPS, 300g of pure HfB_2 and 300g of pure ZrB_2 powders (starck grade B) were ball milled in a planetary ball mill for 6 hours. To make 50/50 Hf-Zr-B solid solution, 150g of pure HfB_2 and 150g of pure ZrB_2 were also ball milled together for 6 hours. WC 250 ml lined vial and 5–10 mm in diameter SiC balls were used for milling in the ethanol as a liquid media. After the batch preparation, pure HfB_2 and ZrB_2 samples were sintered at 2100 °C, while $Hf_{0.5}Zr_{0.5}B_2$ solid solution was densified at 5 different temperatures between 1900 °C to 2300 °C in order to determine the optimal temperature for its densification. After sintering of 21 mm in diameter and 6mm in thickness pellets, the samples were machined into 20 mm in in diameter and 2 mm in thickness disks, which were further used for the study at room and high temperatures of the properties by Resonant Ultrasound Spectroscopy. The Young's, shear and bulk moduli, along with Poisson's ratio were measured up to 1000 °C. At the same time, an attempt is being made to measure the biaxial strength of these ceramics using ring-on-ring biaxial strength testing technique. In order to accomplish the measurement, the ring-on-ring testing jig is currently being designed and manufactured, and after it is produced, the biaxial strength of HfB_2, ZrB_2 and their 50/50 solid solution will be measured.

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Study of structure and mechanical characteristics of hot pressed α-AlB_{12} with C and TiC additions

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Keywords: AlB_{12}, mechanical characteristics, hot pressing

The samples of α-AlB_{12}-based materials were prepared from α-AlB_{12} submicron powders synthesized from hexagonal boron nitride. Blocks of 40 mm in diameter and 15 mm in height were manufactured under hot pressing conditions (pressure 30 MPa, temperature up to 2200 °C) using inductive heating in the graphite dies covered inside by hexagonal boron nitride (in order to isolate manufactured materials from graphite). The samples 9–30 mm in diameter and 5–10 mm in height were manufactured under high (2 GPa) pressure at 1200–1400 °C temperatures. The sintered materials were isolated from the graphite heater using containers from hexagonal boron nitride.

The additions of carbon (17 mass/%) to the α-AlB12 lead to the formation of $AlB_{12}C_2$ and fracture toughness increase, the material density increased just slightly. The additions of TiC to α-AlB12 and sintering at 1950 °C under 30 MPa lead to the formation of $AlB_{12}C_2$ as well and, in parallel, to the formation of TiB_2. The mechanical characteristics (hardness, fracture toughness, bending and compressing strength) of the sample 6 were rather high, but, besides, the density increased up to 3.2 g/cm^3. After sintering of the same α-AlB_{12} and TiC mixture under high pressure (2 GPa) at comparatively low temperature 1200 °C the $AlB_{12}C_2$ was not formed and the sample consisted from α-AlB_{12}, TiC and some AlN. The higher sintering temperature (1400 °C) under high pressure (2 GPa) did not lead to the formation of $AlB_{12}C_2$, as well, but the formation of TiB_2 and disappearing of TiC has been observed. Unfortunately, mechanical characteristics of both samples were low. It should be mention that parameters 1400 °C and 1h at 2 GPa were the limit of our equipment.

The structure of material synthesized from α-AlB_{12} and 20% TiC according X-ray phase analysis contained 74 wt. % of $AlB_{12}C_2$, 22 wt. % of TiB_2, and 4 wt. % of Al_2O_3, while SEM microprobe study revealed three main phases with the approximate stoichiometers $Al_{0.17}B_{4.55}C_2O_{0.04}N_{0.21}$, $TiB_{2.58}C_{0.8}Al_{0.02}$ and $Al_2O_{3.79}$ $B_{2.04}C_{0.8}$.

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Infiltrated TiB_2-steel composites

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Keywords: TiB_2, infiltration, composites

Melt infiltration is one of the attractive techniques to fabricate ceramic–metal composites with a wide range of mechanical properties. If molten metal wets ceramic particles free infiltration approach may be applied. It was established experimentally that the wetting angle in the TiB2-carbon steel (0.7wt.%C) system of about 20° at 1450 °C is adequate for free infiltration. Thermodynamic analysis of the interaction between TiB_2 and molten steel was performed and its results were taken into account to determine parameters of the infiltration process. SPS-processed TiB_2 preforms with 30vol% porosity were successfully infiltrated with molten 1070 steel at 1450 °C under 10-4 torr vacuum. The infiltrated composites were heat treated at 900 °C and quenched in oil. The Young modulus (of about 500 GPa) did not change as after quenching, while hardness value increased form 1500 HV to 1900 HV for infiltrated and thermal treated composites, respectively. The effect of thermal treatment on the hardness value was attributed to the microstructural changes in steel matrix (form pearlite to martensite).

T10: Cultural heritage

Invited lectures

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Non-invasive on-site analysis of enamelled pottery, glass and metal. State of the art

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For more than a decade, the strong miniaturisation of electromagnetic sources and detectors led to the availability of different portable instruments, namely Raman microspectrometer,[1–3] X-ray Fluorescence handheld analyzer[4] and UV-visible spectrometer[5]. These instruments inform on the phase/structure, elemental composition and chromophores, respectively.[6,7] At the time of their production enamelled wares were advanced materials and their micro- and nano-structure carries a lot of information about their making process, important information to distinguish genuine from copy, or to trace technological exchanges.[3–8] We present a review of the state of the art of the non-invasive study of coloured artefacts and discuss representative examples of innovation or of technological transfer.

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Characterization of the Medieval pottery from the Studenica Monastery, Serbia, a UNESCO World Heritage Site

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Keywords: Medieval pottery, petrography, SEM-EDS, FTIR spectroscopy, high resolution XRPD, multivariate statistical analysis

Medieval ceramics found in fortified towns and sacred places in Serbia are well-described by archaeologists. However, systematic archaeometric studies of ceramic production have recently started.[1,2] This work focuses on the characterization of pottery excavated at the Studenica Monastery, in central Serbia. Founded in the late 12th century, Studenica was the cultural and spiritual center of medieval Serbia, but also a spiritual and architectural model through centuries. Archaeological investigations identified two clearly distinct cultural horizons: the first (from the late 12th until the late 13th century) and the second (the 14th and the first half of 15th century). Investigated pottery from the first cultural horizon consisted of undecorated and unglazed cooking pottery while tableware was rare, and from the second cultural horizon subject of investigation were unglazed and glazed vessels, both cookware and tableware, including vessels decorated with sgraffito and painted motives. Mineralogical and chemical composition and production methods of investigated pottery were determined combining petrography, scanning electron microscopy with energy dispersive spectrometry, Fourier transform infrared spectroscopy, high resolution X-ray powder diffraction, multivariate statistical analysis. The studied pottery is composed of fragments of quartz, feldspars, micas, pyroxenes and rock fragments (quartzites, schists, granitoids, volcanics, peridotites, serpentinites, etc.) and matrix which shows different degree of crystallinity – from crystalline to amorphous. The firing temperature was estimated to be about 600 ^{o}C for the most of cookware and in the range of 850–1000 ^{o}C for tableware. Multivariate statistical analysis of FTIR and high resolution XRPD data, together with mineralogical and petrographical analyses did not show significant differences among samples from two cultural horizons indicating continuous pottery production process from XII until XV century.

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Transmission electron microscopy: emerging investigations for cultural heritage materials

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Keywords: cultural heritage, imaging, ancient material, TEM

Transmission electron microscopy with its various imaging modes and its analytical abilities is now an indispensable tool for chemical and structural characterization at the nanoscale of all types of materials. One of the main advantages of this technique is that it generates an image that enables us to determine atomic structure and perform highly localized chemical analysis, make individual measurements on nano-objects and undertake the chemical and structural study of interfaces and extended defects. This is certainly one of the best techniques for characterization at this scale currently available. Cultural heritage materials do not differ fundamentally from other materials except that they are more heterogeneous with a more complex and imperfect structure[1]. In addition, many of them contain nanoparticles or have a nanoscale structuration, which play a significant role in their physical properties or are rich in information concerning their manufacture. TEM techniques are thus well suited to investigate them especially because the developments of these last decades afford both a more efficient sample preparation and faster data recording[2]. Without TEM techniques, it would be impossible to reveal the true nature of lusterware of ruby glass. They have also played a major role in the determination of optical and mechanical properties as well as the manufacture of the *Terra Sigillata* slips. Their contributions were also essential in the study of prehistoric pigments or to understand the chemical transformation of some painting pigments. These successes should encourage more and more people to used TEM techniques for characterizing divers cultural heritage materials. The use of advanced techniques, currently largely employed in physical sciences, such as ASTAR technique, structural determination from electron diffraction or electron tomography should likewise grow and open new perspectives.

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Oral presentations

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Preliminary results on polished surface of Phoenician red slip ware

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Keywords: Red Slip Ware, Phoenician pottery, optical microscopy, X-ray diffraction, scanning electron microscopy

Red Slip Ware is a typical Phoenician production characterized by a shiny deep red slip which is considered an important cultural marker that followed the spread of Phoenicia across their Mediterranean colonies. Despite its archaeological relevance, this ceramic has not yet been widely studied. Therefore, a selected number of samples unearthed in the Phoenician-Punic site of Motya (Sicily, Italy), dating back from the 8th to 5th century BC, have been analyzed. The archaeometric characterization of the slipped surface has been performed using optical microscopy, X-ray powder diffraction and scanning electron microscopy. The aim is to explore the procedure used in the preparation, application and firing of the superficial layer and to characterize the internal body. Petrographic analysis shows a predominance of sub angular-rounded fragments of quartz along with minor amount of K-feldspar and nodules of iron oxides as inclusions in the ceramic bulk; whereas the slip is characterized by a fine grained structure with few and fine sized inclusions of quartz and K-feldspar. EDAX spectra highlight that the red slip and the internal body of the vessels have similar elemental compositions, but with the coating Fe-enriched. Mineral assemblage and in particular the presence of neoformed phases, i.e., K-feldspar, hematite and gehelenite, allows estimating the maximum temperature of firing of these artefacts in the thermal range 850–950 °C in oxidizing conditions. In addition, the accessory minerals, i.e, rutile and zircon, can be considered important markers to identify the provenance of raw materials. The comparison with data from a previous study on Motyan ceramics allows hypothesizing a local supply of raw materials involved in ceramic productions.

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Geochemical characterization of Medieval pottery from the Auvergne region of France by portable X-ray fluorescence analysis

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Since 2000, several excavations and testing projects have been conducted on medieval sites in the highlands of the Auvergne (France). The sites are interpreted as farms, isolated or grouped in hamlets, occupied beetween the end of the 10th century and the end of the 12th century.

Ceramics were recovered at all sites. A major question we have is whether the ceramics were made locally on the sites themselves or if some or all were imported. Further, we hope to address areal and regional interactions. While architecture across the sites is variable, and we are currently developing a typology to address this, the ceramic forms are quite uniform, at least macroscopically. To test our questions, we conducted portable x-ray fluorescence (pxrf) analysis on pottery recovered from each site to characterize the chemical composition of the paste. Preliminary analysis suggests significant inter-site variability, and we suggest that ceramic manufacture and use during the Medieval here was very localized at the household and hamlet level.

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Jun ware colours: chemistry and nanostructure

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A selection of Jun wares found at Juntai and Zhiyaochang and Liujiamen kilns, official kilns from the court, at Yuzhou City, Henan Province in China, showing various colours and appearances are analysed. The main novelty of this study is that the nanostructure is revealed from polished areas of the glazes by a Focus Ion Beam (FIB) attached to a Scanning Electron Microscope (SEM). The main advantage of this procedure is that the size and volume fraction of the liquid-liquid nanostructures may be quantified at different areas of the glaze showing different colours and optical effects. Differences between the different kiln productions are highlighted and the origin of the colours and appearances discussed in terms of chemistry and nanostructure.

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18th and 19th century garden ceramics: investigation of manufacturers' stamps in relation to compositional change

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In England, in the eighteenth Century, the fashion for a neo-classical style in architecture created a growing demand for a range of classically-inspired products. Because the production of stone items was both time-consuming and expensive, the necessity of finding a cheaper alternative to stone resulted in the exploration of clay-based substitutes. Using a ball clay from Dorset, UK, an artificial stone called Coade stone was introduced by Mrs Coade in 1769. It is actually a stoneware ceramic and was used to create both architectural decoration and garden ornaments. The Coade factory in Lambeth was in existence until 1840 but, following its closure, other manufacturers emerged – such as Blashfield, Pulham and Doulton – who produced similar materials during the 19th century.

The artefacts produced by these manufacturers are now considered of great historic value so their correct identification is important, not only for the historic record, but also for the provision of the necessary evidence to carry out informed conservation. Although many of the products are stamped with a manufacturer's mark, some have no indentation. As the sale and copy of moulds was common practice at the time, stylistic considerations do not provide reliable identification of unsigned artefacts, making scientific identification necessary.

Research by the authors has shown that by using X-ray fluorescence (XRF) analysis to produce trace and bulk element profiles, it is possible to identify, and differentiate between, the signed products of Coade, Blashfield and Doulton. Further research has shown that Pulham products can also be identified by this method. However, these long-lived businesses have had various phases of manufacture as indicated by changes in their stamp design. In order to have confidence in our differentiation methodology, it is important to ascertain whether a change in stamp reflects a compositional change in the product.

From elemental profiles, and subsequent multivariate statistical techniques, it is shown that for Coade and Pulham products, a change in stamp does not reflect the use of a different source material, and is likely therefore to indicate a change in management. In contrast, for Blashfield and Doulton products, a change in stamp reflects a significant compositional change, which is indicative of geographical or technological variation.

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A multi-analytical investigation of the Cucuteni pottery technology from Eastern Romania

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Keywords: pottery technology, Cucuteni-Trypillia civilization, SEM-EDX analysis, XRD analysis, magnetic and dielectric measurements

The aim of this paper is to investigate the relationship between the emergent complexity of the Cucuteni-Trypillia civilization (V–IVth millennia BC) and the specialization of their ceramic craft production as it is reflected by increasingly homogeneous products. Traditionally, this question has been addressed by traditional archaeological methods (typology, style and context analysis) and only a few interdisciplinary studies have been published.[1,2]

In order to evaluate the technological parameters of the ceramic production we engage a robust methodological approach to the analysis of ceramic sherd assemblages, including painted and unpainted pottery, consisting in a combination of analytical techniques. We have used Energy Dispersive X-ray spectroscopy (EDX) for spot analysis of the matrix and temper of pottery samples from sites across the eastern region of present-day Romania. X-ray diffraction (XRD) and magnetic and dielectric measurements were used to explore the firing temperature and the effects of distinctive tempering agents on the mineralogical transformations due to different firing parameters. The microscopical investigation for detailed study of groundmass microstructure (low magnification) and the degree of vitrification (high magnification) was determined by Scanning Electron Microscopy (SEM) analysis.

By determining the chemical and mineralogical composition and the magnetic and dielectric characteristics of the potshards it was possible to determine the similarities and differences between different groups of pottery determined macroscopically. In addition, the investigation of pottery production process clearly indicated the technological choices made by the potters regarding raw material selection, paste recipes and firing process.

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Chromatic characteristics of traditional Korean copper glaze with the addition of copper oxide and sintering atmosphere

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Keywords: material, glaze, copper oxide, color

The copper-red pottery was the first traditional Korean technique which colorized the red by the reduction atmosphere sintering at high temperatures i.e. more than 1200 °C in the 12th century of Goryeo Dynasty. This study aimed at analyzing the factors which affect the copper-red glaze coloration and understanding the influence of the copper oxide addition and sintering condition on the glaze coloration. As the addition of copper oxide increased under the oxidation condition of 0, 0.3l/min of the LPG supply, the color was created to Green and Green-Yellow, respectively, with CIEa* value of '-' and CIEb* value of '+'. The CIEa*b* distribution was developed in proportion to '+' value in 0.5 and 0.7l/min, the reducing atmosphere and showed the Red group. The copper oxide was reacted with the CO gas and reduced to Cu_2O or Cu with the increase in the LPG supply and it was judged that the specimen was under the composite influence of Cu nuclei aggregation, metal Cu Globule and Cu_2O. This study purposed to establish the technical basis to restore the traditional copper-red glaze by understanding materials and process technology of Korean copper-red glaze.

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Combined spectroscopic analysis to study ceramics

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Keywords: Raman spectroscopy, XRF spectrometry, ceramics, archaeometry

The study of ceramics in the field of cultural heritage is not only done by archaeologists and conservators. Nowadays, also natural scientists such as physicists, chemists and geologists are involved in their investigation, using different analytical techniques. Information about the structure and composition helps towards identification and classification of the material in terms of provenance determination[1] and production processes[2].

Next to Inductively-Coupled-Plasma mass-spectrometry (ICP-MS), X-ray diffraction (XRD), and infrared (IR) spectroscopy[3] also Raman spectroscopy[4] and X-Ray Fluorescence (XRF) spectrometry[5] are widely applied to investigate the composition of ceramic materials. These two analytical methods are considered as complementary as Raman spectroscopy provides molecular information while XRF spectrometry gives elemental information about the composition of the investigated material. Both techniques are non-invasive and allow analysis of the material on micro-meter scale.

For the application of both techniques, both laboratory and mobile instrumentation is developed. Whether measurements are done in laboratory environment or *in situ* analysis is performed depends on the material (shape, size, location, value) and the research question. The combined application of both spectroscopic techniques is discussed through several case studies.

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Poster presentations

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Data-driven ancient ceramics studying – case of Fanchang Kiln

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Keywords: EDXRF, chemical feature, Fanchang, Jingdezhen, random forests

The energy dispersive X-ray fluorescence (EDXRF) is used to determine the chemical composition of celadon body and glaze in Fanchang kiln and Jingdezhen kiln. Forty typical shards in four cultural eras were selected to investigate the raw materials and firing technology. Random forests, a relatively new statistical technique, has been adopted to identify chemical elements that are strongest explanatory variables to classify samples into different cultural eras and kilns. The results indicated that the contents of Na_2O, TiO_2, and SiO_2 vary in celadon bodies from Fanchang and Jingdezhen, which implies that local clay was used to manufacture celadon bodies in Jingdezhen kiln as a new type of celadon. By comparing the chemical composition in glaze, we find that the chemical elements and firing technology of Jingdezhen kiln are very similar to those in Fanchang kiln, especially for late Tang dynasty. This study reveals the inheritance between Jingdezhen kiln and Fanchang kiln, and explains the differences between two kilns.

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T11: Refractories

Invited lectures

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The main role of silica gel technology on alumina castables

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Keywords: castable, installation, sol-gel bonding, microstructure, hot mechanical properties

The use of unshaped refractory products is continuously increasing due to their well know advantages: Time saving during shutdowns, less storage area needed, quick response from manufacturing plants to customers, better performance together with lower prices and less CO_2 emissions during production.

The fundamental issue to ensure the optimum performance of castables is the installation method. In this sense, the rheological behavior of castables has to be adjusted depending on the specific installation method. This goal is achieved by the careful selection of additives and their amount. As examples, additives have to assure the adequate flowability of the castable during the pumping step in shotcreting, the appropriate setting time of the gunning systems, or the tixotropy showed by the LCC products.

Due to their critical role to make the installation step robust and safe, a number of different additives are nowadays present in the market.

In addition to rheology optimization, a main point to consider is that most of these additives would also have an influence on the development of the microstructure of the castables at high temperature, especially on phase development.

In this work, after a short overview of the role of additives on installation methods a comparison between two different model systems based on "no cement bonding" using silica to obtain sol-gel bonding in cold conditions is done. One of them contains a colloidal stabilized suspension and the other one, based on the "all-in-bag" idea, uses functionalized microsilica particles. The rheological behavior together with the high temperature microstructural evolution and mechanical behavior are discussed.

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Reflections on refractory materials and their evaluation

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Survival of the refractory area is based on new products with engineered microstructures. Nature presents examples of designs and evolution proof structures that should catch our attention and interest. Nevertheless, mimicking nature also poses new challenges on how to adapt and analyze these novel materials. Would, for example, the usual refractory mechanical tests be sufficient to evaluate a lamellar structure with kinked and stable crack propagation? If most of our community is not yet familiar with the importance of R curve profile, are we prepared to measure the effects of K_I, K_{II} and T factor with the temperature? Sometimes, we see the challenges only for the advanced refractory microstructure designs, but are we aware that even our traditional currently used tests are far behind what represents the actual conditions faced in the working environment? In order to take us out of our comfort zone, do we really know how to measure the maximum working temperature of refractory materials? This talk will present some of the challenges ahead for producing and characterizing the refractories to come and those that we are used to, but we still do not understand why they perform well, based on our characterization processes. Along this continuous journey of looking at the future and the past, we know, rephrasing T.S. Elliot, that "the end of our exploring, will be to arrive where we started and know the place for the first time".

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Applied research on and application of refractory materials in an industrial environment

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Keywords: refractories, value in use, fem modelling

Refractories are of critical importance for an energy-intensive industries such as iron and steel making, the production of refractories constitutes the demand for novel materials with improved characteristics and superior technological and economic performance. The refractory research is a truly interdisciplinary endeavor requiring knowledge and expertise from diverse academic disciplines as well as contributions from the steel industry itself.[1]

The aim of the paper is to sketch a picture of different aspects in the refractory research approach within an international steel company bridging the gap between the need from day to day production and a the long term solutions academics can offer. In an industrial environment a refractory engineer should be able to deliver both direct support to the plant as well develop experimental techniques and perform long term research bearing in mind the needs of the company.

In this paper a few examples of recent research will be discussed, ranging from direct support to middle and long term research supported by fundamental research programs of academia.

From an end user point of view maintaining close relationship to refractories dedicated universities and companies is of vital importance to operate production processes at a high level. A network like FIRE (The Federation for International Refractory Research and Education) is an excellent vehicle to achieve this goal in our experience.

FIRE with its unique multi-cultural and multi-disciplinary composition is able to exactly draw on desired skills and provide a unique framework for furthering refractory education within the context of multi partner research programs.[2]

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Oral presentations

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Granulated RTP magnesia stabilised zirconia for refractories

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Keywords: zirconia, MgSZ, magnesia stabilised zirconia, refractories, granulation

Magnesia stabilised zirconia is a widely used material for refractory applications. Typically either a pre-stabilised MgSZ (e.g. fused and crushed) or a mixture of monoclinic zirconia and magnesium oxide is used as raw materials. These raw materials are mixed with binders, granulated and shaped to refractory parts. In this study different granulation methods are compared to produce a ready-to-press MgSZ using MgO and monoclinic ZrO_2 as raw materials. During sintering (at 1650 °C) the MgO reacts with the zirconia to form a magnesia stabilised zirconia (*in-situ* stabilisation). In this paper a comparison between spray dried and mechanically granulated material is presented and discussed. For the mechanically granulated material a design of experiments was done in order to optimise the granulation parameters and type and amount of organic additives. Also different particle size distributions of the raw materials (especially of the used monoclinic zirconia) were used and several binder systems were studied and their effect on the properties was evaluated.

The produced granulated material was uniaxially pressed to cylindrical parts. Special focus was taken on the analysis of pressing curves as well as the green and sintered properties.

The sintered specimens were analysed in terms of density, microstructure and porosity. Finally a comparison with parts produced from spray dried $MgO\text{-}ZrO_2$ granulates is presented.

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An improved corrosion and thermal shock resistant sintered mullite-zirconia refractory

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Keywords: refractories, mullite-zirconia composite, andalusite, zircon, thermal shock, corrosion, incineration

Mullite-zirconia composites are commonly used as refractories due to their excellent properties such as high strength and fracture toughness as well as good thermal shock and corrosion resistances. The aim of the present research is to propose an improved corrosion resistant and thermal shock resistant mullite-zirconia refractory. Generally, mullite-zirconia refractory raw material is industrially produced through a fusion process by melting a mixture of zircon and alumina in an electric arc furnace. Zirconia crystal grains are dispersed in a mullite matrix. A glassy phase is additionally present.

In the present work, a new sintered mullite-zirconia raw material has been developed on basis of andalusite, alumina and zircon. During sintering, the formation of mullite takes place in different ways. The primary mullite formation results from decomposition of andalusite ($SiO_2.Al_2O_3$) into mullite ($2SiO_2.3Al_2O_3$) and silica (SiO_2). The secondary mullite formation is effected by the reaction of alumina (Al_2O_3) and the silica (SiO_2) from the decomposition of zircon ($ZrSiO_4$) and the excessive silica from the decomposition of andalusite. The mullite-zirconia refractory composite has a mineralogical composition comprising 69% to 72% (percent by weight) mullite and about 19% (percent by weight) zirconia. The microstructural build-up consists essentially of fine zirconia particles homogeneously distributed in a mullite matrix, wherein the average particle diameter of the zirconia particles is preferably less than 5 μm. The thermal shock resistance of the composite was tested by heating the samples up to 1200 °C and subsequently cooling to room temperature. The effect of the thermal shock was proved by means of ultrasonic transmission technique. The thermal shock resistance of the composite increases with the first and second thermal cycling and stays constant afterward, whereas the thermal shock resistance of other materials like cordierite or alumina begin to decrease from the first thermal shock. Different industrial refractories based on mullite-zirconia raw materials have been elaborated and characterized. The corrosion resistance against molten slags was tested in comparison to the commercially refractory bricks. It was found that the molten slag penetrated the commercially refractory bricks deeply, whereas for mullite-zirconia bricks very low penetration-depth was measured. In summary, this new family of mullite-zirconia refractories presents high thermal shock and corrosion resistance against molten slag and is well suitable for different applications such as the incineration of wastes.

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Hercynite as active spinel

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Hercynite is a representative of *sensu lato* oxide spinel compound with a semi-structural formula $[Fe^{2+}]^{Td}[Al_2]^{Oh}$, where T_d and O_h indices designate tetrahedral and octahedral positions in the spinel structure, respectively. $FeAl_2O_4$ melts at 1780 °C and possesses a low thermal expansion coefficient, which make it applicable as modifying component in basic refractories for cement rotary kilns. What distinguishes hercynite from other alumina spinels is its distinctive behaviour at elevated temperature, sometimes called "activity of hercynite". This work aims to show activity of single phase hercynite and hercynite substituted by low Mg^{2+} and Mn^{2+} ions content.

In this work hercynite and its solid solutions were prepared by a technique utilizing arc plasma (*Arc Plasma Synthesis*, APS) in arc plasma facility SpekoArc300. This method was found to be an effective route in obtaining hercynite spinels of relatively low inversion parameters.

Thermal activity of pure hercynite was investigated on both bulk and powdered sample in order to reflect its behaviour during the operation and to get the near-equilibria conditions, respectively. The bulk samples were kept at temperatures 600 and 1000 °C, for various periods of time, and then subjected to examinations by X-Ray Diffractometry (XRD) for phase identification, Scanning Electron Microscopy with Energy-Dispersive Spectroscopy (SEM/EDS), Electron Probe Micro-Analysis with Wavelength-Dispersive Spectroscopy (EPMA/WDS) for microstructure analysis. Additionally, Mössbauer Spectroscopy was used for determination of iron ions oxidation state and their local chemical symmetry as well as for confirmation of ferrous/ferric ions-containing phases in a decomposed material.

The powdered samples of pure and substituted hercynite were examined by High Temperature X-Ray Diffractometry (HTXRD) up to 1200 °C. HTXRD results showed a gradual decomposition of hercynite proceeding *in situ* during measurements. This was manifested by the change in phase composition, which finally led to obtain the most thermodynamically stable αAl_2O_3 and αFe_2O_3 phases. In general, these final phases were being formed through the stage transformations of less stable transitions phases accordingly: $\gamma\rightarrow\delta\rightarrow\theta\rightarrow\alpha$ for Al_2O_3 and $\gamma\rightarrow\alpha$ for Fe_2O_3. The detailed and complete hercynite decomposition mechanism was demonstrated in this work. SEM observations showed a final hematite of an unusual scalenohedral morphology. The significant difference in the influence of Mg^{2+} and Mn^{2+} on hercynite decomposition were found and presented.

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Degradation of silicon carbide based refractories in CFB plants under co-combustion conditions

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Keywords: silicon carbide, corrosion, co-combustion, refractory, CFB, thermodynamics

Producing energy in efficient and environmentally clean way is certainly one of the biggest challenge for humankind towards a sustainable development. The energy mix composed by fossil fuel, is still the major contributor. Biomass combustion or co-combustion is surely one of the most promising energy source, together with hydro, solar, wind, to mitigate greenhouse emission.[1]

The request of flexibility concerns not only the tendency to partially substitute coal with biomass with the subsequent need to optimize this multi-fuel combustion but also to have flexible power plant performance so to facilitate the use in conjunction with power generation from renewables.

However, biomass has significant different compositions[2,3] and its combustion releases ashes slag[4] which can be aggressive for the power generation plants in particular for the refractories lining their combustion chamber.

Silicon carbide, as brick or castable system, is generally used when a high resistance to thermal cycling is required for its low thermal expansion and high thermal conductivity hence good thermal shock resistance.

In the present case the analysis of SiC based refractories, after testing in Circulating Fluidized Bed (CFB) pilot plant under co-combustion conditions, showed a curious degradation behaviour, apparently inexplicable, but undoubtedly obeying to the thermodynamics of the system. To validate this system, laboratory tests were conducted under controlled conditions which reproduced the same degradation behaviour of SiC based refractories already observed in pilot campaigns.

Acknowledgement
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High temperature mechanical characterisation of *in situ* forming spinel-alumina castables, using magnesia or magnesite as raw materials

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Keywords: thermomechanical, spinel, alumina, magnesia, magnesite

Alumina-spinel castables are used as steel ladle lining because of their superior slag and thermal shock resistance compared to alumina materials. In high alumina castables, spinel can be introduced as preformed spinel grains or by *in situ* reaction between alumina and magnesia or a precursor, at service temperature, from 1100 °C. *In situ* formed spinel materials exhibit a microstructure which is favorable to very good corrosion resistance. The reaction also leads to a thermal expansion due to density difference between the product and reagents with as result a good thermal shock resistance. However it always exists a need to master the composition and to understand the thermomechanical behavior at service temperature and mainly the relation with composition. In this work, four alumina-magnesia, cement bonded castables were tested at high temperature with two different methods: strength and Young's modulus. As a reference, a high alumina castable was also investigated. The effect of several parameters: composition, addition of magnesia or magnesite (carbonate), impurities and microsilica addition were investigated. Strength was determined by bending strength at temperature ranging from room temperature to 1550 °C. Strength resistance and the stress-strain curves were recorded. Young modulus was measured with the resonant frequency technique from room temperature to 1500 °C. Microscopic observation and XR diffraction were also introduced to support the discussion and conclusions of the work. Results demonstrate the real effect of parameters on high temperature mechanical behaviour, mainly sintering, phase transformations and liquid phase appearance versus temperature. The alumina castable exhibits a linear behaviour at room temperature and a limited nonlinear behavior at high tem-

perature (1000–1500 °C). With magnesia addition, and depending on composition (magnesia or magnesite addition, magnesia content, presence or not of microsilica), at high temperature, the elastic modulus decreases and the non linear behaviour extends. Depending on the temperature, materials exhibit a high ductility which is favorable to a good thermal shock resistance. Results also allows relating a refractoriness limit (drastic fall of mechanical resistance) versus composition.

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Microsilica as anti-hydration agent for basic refractory castables

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Keywords: MgO castables, microsilica, hydration, brucite

Magnesia castables have been drawn a great attention in refractory industries, however they have not widely been used. The major challenge is volume expansion and cracking due to brucite ($Mg(OH)_2$) formation during MgO hydration - a phenomenon commonly called “slaking”. In this paper, the focus is on understanding the effect of microsilica on the hydration behaviour of MgO that allow us to develop crack-free MgO castables. The flow-, set- and hydration-behaviour during dry-out and curing have been studied. SEM and XRD techniques were used to characterize the phase composition and microstructure after the dry-out process and the results demonstrate that microsilica suppresses the hydration process of MgO. A minimum of 3wt% microsilica is necessary to inhibit the hydration of MgO in lab-scale specimens, while more microsilica is needed for industrial-scale samples. By controlling the MgO hydration and dry-out behaviour, magnesia castables based on the MgO-SiO_2-H_2O bond system have been developed; a perfect 600kgs block was produced with no problems.

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Development of aluminium titanate/porcelain ceramic matrix composites having high thermal shock resistance

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Porcelain represents one of the most known and common ceramic material, formulated from a mix of clay, feldspar and quartz, sintered at temperatures between 1200 °C and 1400 °C, to form a glass-ceramic composite. Aluminium titanate (Al_2TiO_5) is known for its excellent thermal shock resi stance, resulting from the low thermal expansion coefficient, low thermal conductivity, low Young's modulus and for its good chemical resistance. In the present work, aluminium titanate/porcelain ceramics composites with different percentages of Al_2TiO_5 (up to 50 wt%)were prepared by uniaxial pressing and then fired at temperature between 1200 °C and 1300 °C. The microstructural, mechanical and thermal properties were characterized. Thermal shock resistance behaviour under water quenching of the as-prepared ceramics was also evaluated. The results revealed that the addition of aluminium titanate to porcelain matrix improves the properties of the aluminium titanate/porcelain ceramics and that the thermal shock resistance tended to increase with increasing aluminum titanate content . This composite represent an optimum candidate to be used as refractory in the process of metal casting.

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Impact of surface functionalization of carbon-bonded filters on steel cleanliness

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Keywords: ceramic foam filters, carbon nanotubes, alumina, non-metallic inclusions

Non-metallic inclusions in cast metal parts often have a negative impact on properties such as fracture toughness, tensile strength and fatigue resistance. Foundries require high purity metal melts in order to limit the casting repairs and possibly avoid rejected castings. This can be achieved by applying a filtration process after the ladle treatment. In the case of steel, ceramic foam filters (CFFs), especially those based on zirconia and carbon-bonded alumina, have been successfully employed for years.

Understanding the interactions between filter material and molten steel is essential to improve the purity of cast products by filtration. Using a special steel casting simulator, carbon-bonded alumina filters were immersed in a steel melt which contained artificially-generated endogenous alumina particles. Uncoated and MWCNTs-coated ceramic filters were dipped and rotated for 10 and 300 seconds in the melt at 1650 °C. For alumina-coated filters, chemical reactions at the filter/steel interface under quasi-static conditions were investigated using spark plasma sintering (SPS) equipment. In addition, samples of the solidified steel were taken after the immersion tests and analyzed by electron microscopy. The population of detected inclusions was classified in terms of size and chemistry in order to compare the filtration efficiency of the different carbon-bonded filters.

Microstructure and phase analyses revealed that interfacial reactions between filter and molten steel result in an a few hundred nanometers thin layer on the filter surface. During a “reactive” stage, large plate-like alumina structures are formed on top of this layer. Thereby, material is transported from the carbon-bonded material underneath (i.e. gaseous reaction products) as well as from the molten steel (i.e. precipitating particles and endogenous inclusions) to the filter/steel interface. The growth of these alumina particles stops as soon as the carbon supply, which triggers the dissolution and precipitation processes at the interface, is cut off. From that point on, endogenous inclusions are collected (“active” stage). In general, it seems that the filters are most efficient during the reactive stage, i.e. as long as the interfacial reactions take place.

Investigations of the steel samples after the test suggest various filtration effects, regarding size as well as chemical composition of the remaining inclusions. Considering the total number of inclusions, our alumina-coated and MWCNTs-coated filters deliver filtration efficiencies from about 70% up to over 90%. These values are significantly higher than those achieved with state-of-the-art filters.

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Investigation of the mechanical and thermomechanical properties of carbon-bonded alumina refractories with reduced carbon content due to nano- and microscale additives

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Keywords: nanoscaled additives, silicon, carbon-bonded alumina, semi-conductive material, reduced graphite

This study investigated the combined effect of nanoscaled additives (carbon nanotubes and nanoscaled alumina) and semi-conductive silicon on carbon-bonded alumina with a reduced primary carbon content of 20 wt%. It focused on the initial cold modulus of rupture and its evolution on exposure to thermal shock. The use of the single additive groups or their combination yielded an increased initial strength compared to the reference without additives. It was shown that the combination of the additives resulted in a material that exhibited no statistically significant decrease of the cold modulus of rupture in up to five thermal shock cycles. To understand these effects, physical properties (total porosity, open porosity, true density) were observed. The data showed that the microstructural reactions were complex. The combination of all additives caused a decrease in the open porosity. The available data of the true density analysis matched partly with the possible reactions. Especially the formation of SiC whiskers was considered to be important during the coking process and the thermal shocks. Furthermore, it was proposed that a deposition of carbon because of oxidation processes followed by reactions with the additives, especially the semi-conductive silicon, occurred, which might have a self-healing effect on the refractory matrix.

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Investigation of the influence of metallic additives on the thermomechanical properties of carbon-bonded refractory composites

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Keywords: refractories, thermomechanical properties, carbon, antioxidants

Alumina-carbon refractories are widely used in the continuous casting of steel, e.g. for ladle shrouds, monoblock stoppers and submerged entry nozzles. They are responsible for the steel flow control and its protection against oxidation. To improve their own oxidation resistance, several metallic additives such as Al, Al-Si and Al-Mg are added as antioxidants. In this study, the influence of those antioxidants on the thermomechanical behaviour of carbon-bonded refractories was studied. Model materials having simplified composition compared to the real industrial ones were investigated so as to facilitate comprehension of mechanisms responsible for the modification of mechanical properties. Behaviour of both cured (before pyrolysis) and fired (after pyrolysis) materials was studied. The evolution of Young's modulus during firing was followed thanks to an ultrasonic pulse echography device. Damage occurrence within the material was investigated by the acoustic emission technique. X-ray diffraction measurements with Rietveld refinement enabled identification and quantification of phases after firing. Stress-strain curves were obtained by tensile testing at room temperature. Obtained results show that the carbonaceous binder undergo transformation into pyrolytic carbon and that micro-cracks in material's matrix are created during firing. It results in a non-linear stress-strain behaviour. What is more, metallic additives react with carbon and gases emitted from the binder to form new ceramic phases which rigidify the refractory. Antioxidants are added to carbon-bonded refractories so as to protect all forms of carbon from oxidation. Nevertheless, this study showed that even a small quantity of metallic additives may significantly modify their mechanical properties and thus have an influence on their reliability and performance.

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Poster presentations

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Geopolymer matrix composites as innovative sustainable refractories

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Keywords: geopolymer, ceramic refractory, sustainability, thermal shock resistance

Geopolymers are nowadays considered as one of the most attractive materials from the sustainability point of view as they can be made by using secondary raw materials and cured at room temperature.[1] Besides this, geopolymers may be characterised by high technical performances that can be tailored and improved, for instance by designing geopolimer matrix composite materials.

The present work aims to develop innovative and sustainable refractory geopolymers for industrial applications. Different carbon fly ash based geopolymer mixes were optimized to withstand high temperature by adding milled refractory scraps coming from industrial production of alumina-based refractory rollers. Geopolymerization was carried out at low temperature ($20 < T < 80$ °C) followed by a room temperature curing.

The processing, microstructure and properties of geopolymer composites have been investigated. The thermal stability was assessed by heating microscope analysis, dilatometry and thermal exposure in muffle furnace. In addition, electron microscopy studies (SEM/EDS) and mineralogical quantitative analyses (XRD Rietveld-RIR method) were performed. Results showed that the microstructure of fully reacted geopolymers consists of an amorphous and porous matrix with embedded alumina-based particles.

The investigated materials are able to resist to thermal shock above 800 °C, remaining microstructurally stable.

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The influence of silica colloidal on properties of castables bonded with calcium aluminate cement

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Keywords: calcium aluminate cement, silica colloidal, workability, green mechanical strength

Calcium aluminate cement (CAC) has been used as one of the most common binders in the field of refractory castables. However, there are some drawbacks for refractory castables bonded with CAC, in which the low mechanical strength during curing process is a big problem. The use of silica colloidal as a binder for refractory castables has attracted great interest due to its gelling properties in recent years, but the bad workability and low green mechanical strength during demoulding process have greatly constrained the silica colloidal application in refractory castables. In this work, the combined binder of CAC and silica colloidal has been made to overcome the above disadvantages. The workability, apparent porosity and bulk density, cold modulus of rupture (CMOR) and cold compressive strength (CCS) of castables were measured. Phase and microstructure evolution were characterized by the techniques of XRD and SEM. The results showed that with a fixed ratio of water/cement, the flow values decreased with the content of silica colloidal addition increasing. The apparent porosity change of castables was very limited at the temperature range of 110 and 1100 °C; however, it was decreased drastically when the heating temperature rose to 1600 °C, and both the CMOR and CCS were increased by more than triple. When 5.0wt.% silica colloidal was added and after heating treatment at 1100 °C, the CMOR and CCS of castable samples were increased from 5.8 MPa and 56.75 MPa to 20.9 MPa and 152.42 MPa, respectively. The XRD study indicated that the addition of silica colloidal didn't change the mineral phases of castable samples after heating treatment. The investigation of microstructural characteristics by SEM revealed that a network structure was formed in the castables with the addition of silica colloidal at 1100 °C, whereas it was a loose structure in the castables without addition of silica colloidal. It was found that the nanosized SiO_2 particles of silica colloidal were not only filled into the pores in the castables to obtain high packing density, but also promoted the hydrate formation in the pores due to its nucleation effect. The gelling effect of silica colloidal and hydration process of CAC together improved the mechanical strength of castable samples at the temperature range of 110 and 1100 °C. Therefore, the combined binder of silica colloidal and CAC can be considered as a promising alternative binder for refractory castables.

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Effect of testing conditions on the thermal diffusivity measurements of nuclear fuels via the flash method

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Keywords: thermal diffusivity, flash method, nuclear fuel, uranium, ceramic

The nuclear fuel is a ceramic produced by powder metallurgy route. The knowledge of its thermal conductivity is a fundamental data for a better prediction of the fuel performance in reactor. The thermal conductivity is derived from a thermal diffusivity measurement, whose value may be affected by parameters such as the origin of the powders, the fabrication process used, the fraction of porosity of the sintered fuel....and must be measured accurately.

Within the Fuel Studies Department, the Uranium Fuels Laboratory has acquired a thermal diffusivity Light Flash Apparatus (LFA HyperFlash 467, manufactured by the Netzsch company) to complete its range of characterization capabilities devoted to nuclear fuels.

The device implements the flash method, which is a standard method for measuring the thermal diffusivity. The test consists of subjecting the lower surface of a small and thin sample, with plane and parallel faces, to an energy pulse of very short duration (provided here by a xenon flash lamp). The resulting temperature rise (thermogram) is recorded on the opposite upper face of the sample (using here an InSb infrared detector cooled with liquid nitrogen).

The thermal diffusivity value is inferred from the interpretation of the thermal curve. The analysis software provides different theoretical models (such as those of Cowan and Cape-Lehman) for the interpretation of the experimental thermograms.

Measurements can be performed up to 500 °C under controlled atmosphere. Several samples (up to 16, depending on their geometry) can be characterized in a single test.

In the present work, aiming at a better understanding of the factors that affect thermal diffusivity measurements using the flash method, the effect of parameters related either to the specimen (coating, thickness, porosity,…) or to the operational conditions were investigated on uranium-based ceramics.

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Effect of heating conditions on the properties of bauxite refractory castable: a design of experiments study

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Keywords: low cement refractory castable, bauxite, design of experiment

The consumption of monolithic refractory materials is steadily increasing which is connected with the constantly expanding range of applications of refractory castables and the rapid development of new technologies ensuring their high quality.

Physic-mechanical properties of monolithic refractory materials are dependent on many key factors and one of them are no doubt the heating conditions.

The aim of the present study was to determine, using the 2^n Factorial Design, the relationship between the heating conditions of low-cement bauxite castable and their properties i.e. the apparent density, open porosity, permanent linear changes, as well as Young's modulus, compressive strength and bending strength at ambient temperature. The investigations were based on experimental design methods which allowed to minimalize the number of experiments and samples needed to identify the investigated relationships. To analyze the obtained results the advanced analytics software STATISTICA was applied. It have been proved that the investigated three factors i.e. heating ratio to 450 °C, dwell time at 450 °C, heating ratio to 800 °C and their interactions significantly influence the properties of bauxite refractory castable.

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The influence of $MgAl_2O_4$ spinels occurrence status on thermal properties of refractory alumina-spinel castables

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$MgAl_2O_4$ spinels-contained refractory castables possess good resistance to both thermal shock and molten slag. In this paper, $MgAl_2O_4$ spinels were introduced into the alumina-based refractory castables through spinel-contained in aluminate cement (CMA), pre-synthesis and *in-situ* formation respectively. The results showed the existence status of the spinels could have a great influence on the generation of CA_6 and the thermo-mechanical properties of the refractory castables. The spinels in CMA give rise to the higher residual cold modulus of rupture of the castable after thermal shock and better resistance to molten slag due to the particle reinforcement and excellent ions-absorbing capacity respectively. The introduction of pre-synthesis spinels powders in the castables mean the large size in the particles or crystalline and lead to the poor slag corrosion resistance. The *in-situ* formation of $MgAl_2O_4$ with large surface area could improve the slag penetration of the castables, while that also may cause the microcracks and deteriorate the corrosion resistance of the refractory castables.

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Influence of $ZrSiO_4$/SiC modifiers on “alkali bursting” effect of aluminosilicate refractories studied by heating microscopy thermal analysis and other methods

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The corrosion chemistry of SiC/$ZrSiO_4$-modified bauxite, andalusite and mullite refractories has been studied using a post-mortem approach that considers both K^+ and Ca^{2+} ions as the main corrosive agents existing in the cyclone preheater applied in the cement production line.[1,2] An industrial scale corrosion test at 4.stage cyclone preheater in Polish cement plant where the temperature reaches 1100 ºC was performed. Final results from X-ray fluorescence (XRF), X-ray Diffraction (XRD) and Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS) analysis revealed significant changes in both chemical composition and phase-mineral composition of refractory material. The transient progress of corrosion reactions was investigated as the function of distance from the face exposed to the corrosive media (hot face) to the relatively little altered middle zone of aluminosilicate refractory bricks. Chemical alterations of refractory aggregates and SiC/$ZrSiO_4$ grains were examined and discussed on the basis of phase equilibria in binary (CaO-SiO_2, K_2O-SiO_2) and ternary (K_2O-Al_2O_3-SiO_2, CaO-Al_2O_3-SiO_2) systems. Ca and K-Si-oxide phases along with Ca-aluminosilicate and K-aluminosilicates were found in the corroded refractory samples. Thus, the wear phenomenon called as "*alkali bursting*" of aluminosilicate refractories containing $ZrSiO_4$ or SiC compounds was also studied *in situ* by the heating microscopy thermal analysis.

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Fabrication of perlite insulation bricks: effect of firing temperature and perlire content

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Keywords: perlite, furnace, insulation brick, porous structure

Various insulating materials such as bricks (perlite, diatomite, mullite, vermiculite, chamotte, etc.), blocks, insulating castable masses and fibers are commonly used in order to save the energy consumption in industrial furnaces.[1,2] The purpose of this study was to determine the technical characteristics of perlite insulation bricks production in accordance with international standards (ASTM 134-84, C 182-83, C 210-85, C 93-84). In this study, 10-30% of perlite (P10, P20, P30), 70–90% of ball clay and water as the ingredients of insulation bricks were mixed. To improve the properties and reduce the firing temperature and waste transportation, 3–7% of phosphoric acid 85% w/w solution was used. The samples were shaped as rectangular cubes with dimensions of 228×114×64 mm by an extruder, and subsequently were dried and fired at 900–1100 °C. Finally, the variations in samples' properties were analyzed at different temperatures.[3] The results showed that the samples with 30 wt% perlite and 7 wt% phosphoric acid in firing temperature of 900–1000 °C reached to desirable properties including compressive strength of about 30–35 kgf/cm^2, bulk density of 0.42–0.45 g/cm^3 and applied temperature of around 1100 °C.

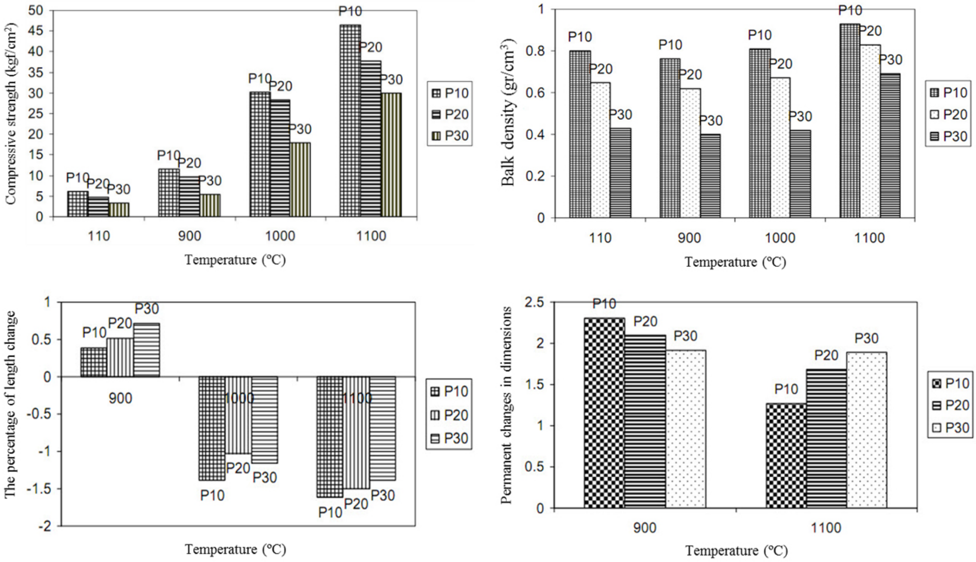

Fig. 1. Variations of physical and mechanical properties of fabricated samples with different perlite contents

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Study on magnesium silicate hydrates (M-S-H phase)

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Keywords: refractories, MSH phase, unshaped refractory materials

The magnesium silicate hydrates (M-S-H phase) has a potential wide application in refractory basic castables, as cement free bonding system. This is connected with its high bonding strength, ability to control hydration process of magnesium oxide and advantageous phase composition after heat treatment. The aim of this study was to investigate evolution of the M-S-H phase and its structure with the time.

The study pastes were composed of two kinds of raw materials: industrial oxides (sintered magnesia and microsilica) and chemically pure oxides (magnesium oxide and nanosilica) with water, in water to solid ratio equal 0.5. The obtained mixtures after preparation, has been ageing at 20 ˚C.

The samples of pastes were studied and analyzed by DTA-TGA-EGA, XRD, FTIR and NMR analysis. Performed analysis revealed that result of reaction in mixture of MgO, SiO_2 and water was a poorly crystalline product nearing to layer magnesium silicates embedded in more amorphous matrix.

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Influence of secondary components with perovskites and spinel type structure on corrosion resistance of magnesia based materials

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Keywords: refractories, corrosion, magnesia, spinel, calcium zirconate

The highest thermal expansion coefficient of MgO among all the refractory materials, low resistance to sudden temperature variations and high elasticity modulus are the main disadvantages of MgO. Therefore, it is necessary to introduction the second or more components in order to overcome these disadvantages. However, the number of components is limited because it is often connected with a low melting eutectics. For magnesia and other basic refractory materials, very interesting is the CaO-MgO-Al_2O_3-ZrO_2 tetrahedron system. It is composed of four high refractory simple oxides, which are characterized by high melting points exceeding 2000 °C. The potential phase compositions can be refractories from the MgO-$CaZrO_3$/MgO-$MgAl_2O_4$/MgO-$CaZrO_3$-$MgAl_2O_4$ systems.

The work presents the recognizing of the new phases formation as a result of the chemical corrosion between phases from this kind of the basic refractories and calcium silicates, calcium aluminates and ferrites. The XRD analysis was used to determine the phase composition. On the basis of SEM observations accompanied by the EDS chemical analysis in micro areas, changes in the microstructure was discussed. The results were discussed taking into account phase diagrams and the activity of corrosion agents. The activity of the corrosion agent – “liquidus curve slop coefficient” can be calculated as the ratio between the difference between the melting temperature of the basic oxide and the eutectic temperature and percentage share of corrosion agents in the eutectic melt.

The invariation points in the subsystem MgO-$CaZrO_3$-C_2S-C_3S reaching temperatures of 1750 and 1760 °C. The presence of Al_2O_3 and Fe_2O_3 causes a considerable decrease of the temperature of liquid phase formation. The deep of liquid phase penetration into materials can be controlled by $MgAl_2O_4$:$CaZrO_3$:MgO ratio. Replacing part of $MgAl_2O_4$ by $CaZrO_3$ improves significant corrosion resistance.

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Structure and microstructure evolution of hercynite ($FeAl_2O_4$) substituted by Ni^{2+} ions

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Hercynite represents 2-3 type spinel group with a normal cation arrangement of general chemical formula $(A)[B]_2O_4$, where () and [] indicate tetrahedral and octahedral coordination of appropriate atoms, respectively.

In this work a series of spinel compounds from hercynite $FeAl_2O_4$to nickel aluminate were obtained by the Arc Plasma Synthesis (APS). Spinel materials were synthesized in an arc plasma furnace SpekoArc300 in an inert Ar atmosphere from analytically pure oxide powders. The following stoichiometric compositions were prepared: $Fe_{1-x}Ni_xAl_2O_4$(x=0;0.3;0.5;0.7 and 0.9) by a tetrahedral substitution of Fe by Ni.

The obtained spinel materials were characterized in view of their phase identification by the powder X-Ray diffraction method (pXRD). pXRD patterns were numerically analyzed in order to determine structural parameters of spinel compounds: lattice parameter and oxygen positional parameter. Mössbauer effect in the spinel materials was measured at room temperature to determine a local coordination of Fe, oxidation state of ferrous/ferric ions and a relative Fe content in the materials. Finally, microstructure changes of hercynite were observed with the increased content of Ni^{2+} ions by the SEM-EDS technique.

Nickel ions were found to positively influence hercynite synthesis by creation of solid solution with $FeAl_2O_4$, causing a gradual decrease in Fe^{3+} content with the increased Ni^{2+} amount.

Acknowledgement
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Setting behavior of unshaped refractory materials

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Refractory unshaped materials represent a mixture of aggregate and bonding agent (or agents). They are used to produce monolithic refractory linings, preformed shapes, repair mixes, mortars and mastics.[1] Bonding agents are usually formed by hydraulic or chemical bond. Hydraulic binders solidify and harden at normal condition during about 24 hours. Setting time can be shortened or extended by using set accelerators or set retarders. Water elimination at relatively small temperature interval during its heating to working temperature is big disadvantage of hydraulic binders. The mentioned deficit might be critical for application of repair mixes, which are required to have a short setting time and short time to heating on working temperature. On the other hand, chemical binders eliminate water at larger temperature interval during heating material. So, heating can be performed with higher speed. It is necessary to optimize a composition of a refractory mixture to assure required setting time, which is determined by an application.

The aim of this work was to determine an influence of composition of two refractory mixtures with chemical bond on their workability, fluidity and primarily on setting time. Refractory castable with chemical phosphoric bond was chosen to study setting rate. Aluminosilicate, mullitic materials were chosen as an aggregate. Mixture of reactive γ-Al_2O_3 with phosphoric acid, which was hardened by magnesium oxide, was chosen as a bonding agent. A rotational rheometer was adjusted (including measurement methodology) for measurement of setting time and rheological properties of mixtures. Measurements were made using the arrangement of vane rotor-infinite medium at rotational and oscillatory regime. Influence of a hardener and other factors, as for example amount and concentration of phosphoric acid, particle size, amount of binder and aggregates, addition of flow agents and temperature on rheological properties of mixture, setting rate and properties after hardening were studied.

Second studied, unshaped material consisted of aggregates from aluminosilicate, mullitic materials again and mixture of aluminate cement with phosphoric acid was used as a binder component. Because of application of mentioned material was for purpose of repair mixes, the sticky compact consistency of the material (binder, cement, putty) had to be assured. Influence of amount and concentration of phosphoric acid, particle size, amount of binder and aggregates, addition of flow agents, temperature on rheological properties of refractory mixture, setting time and properties after hardening was studied. A certain part of calcium ions was changed by ions of calcium salts, due to requirement of adhesiveness of mixture. Strength of joint was determined by a three-point bending test after solidification and hardening.

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Perspectives of topaz rocks in the technology of aluminosilicate ceramics and refractories

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Keywords: topaz, mullite, fluoride, mineralizer, synthesis, crystallization

The total content of mullite and its structural and morphological condition (prismatic or needle-shaped particles) are important for the regulation of technical and operational properties of aluminosilica refractory ceramic. At present there are a variety of techniques to increase the yield of mullite and methods for controlling the habitus and crystal state of its particles. One of them is the use of activating addition. The perspectives of topaz application for this purpose are determined by the nature of its thermal decomposition products: acicular mullite formation and release of volatile fluoride compounds known as active mineralizers in silicate system.[1] Needle and a fibrous habit of mullite from topaz determine its relevance to the composite ceramic materials due to reinforcing role of crystalline intergrowth.

Applied to the high-alumina refractories it was established that character of topaz addition action is determined by their quantity in the composition of aluminosilicate refractory mass.

Topaz in small quantities (up to 0.5–1.0%) acts as a mineralizing additive which intensifies the process of formation of mullite prismatic habit. With the increase in the content of more than 2% topaz along with the mineralizing action serves as a crystal-forming additives. In this case it provides the nucleation of prismatic mullite (at 2–14% topaz) or synthesis of acicular and fiber mullite (if ceramic mass contain more than 14% of topaz).

Mineralizing effect of topaz additives in the clay is reduced to a complex promotional effect of gaseous fluoride released during dissociation topaz. They activate the process of mullite formation both by increasing the defectiveness of intermediate products and by acting on the rheological and reaction properties of silicate melt.

In the mixtures of mullite composition from a pure oxides mineralizing effect of small additions topaz is reduced to activate the synthesis the mullite of elongated prismatic forms due to the complex influence of products thermal decomposition of topaz - mullite and gaseous fluoride. The chemically active fluorides increase the defectiveness of the crystal lattice of reacting substances and create favorable conditions for their high temperature interaction. The action mullite from topaz is reduced to function of center crystallization during solid-phase synthesis a mullite from oxides. The introduction of topaz additives in quantities of 1–3% in a stoichiometric mixture for the synthesis of mullite reduces firing temperature (at 50–100 °C), improved mechanical strength (at 30–50%), electrical properties (enhancing dielectric strength 1.3–2 times, reduced dielectric losses at 15–30%) and other ceramic materials.

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Sialon-based refractory materials prepared from the aluminium oxynitride SHS-derived powders

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Sialons which are a specific solid solutions in the Al_2O_3-Si_3N_4 system are widely applied as refractory materials due to their good mechanical properties, high thermal shock resistance, and corrosion resistance, especially against molten metals. Dense sialon materials are obtained by pressureless sintering or by HP, HIP and SPS techniques. The starting materials for sintering are previously synthesized monophased powders or mixtures of respective oxides and nitrides usually silicon nitride and corundum. Reaction sintering can be performed also using aluminium nitride, silicon oxide and metallic aluminium and silicon powders. Such process is performed in nitrogen atmosphere. In the present work SHS-derived aluminium oxynitride with spinel structure, γ-alon, powder was used as a precursor of sialon-based materials. The γ-alon powder was mixed with different amount of silicon nitride powder and 1 mas% of yttrium oxide then compacted samples were pressureless sintered at 1750 °C for 2 h in argon. It was stated that the samples with small amount of silicon nitride in the starting powder mixture were composed of corundum and $Si_2Al_4O_4N_4$ β-sialon. An increase of silicon nitride content led to materials composed of the same sialon as a major phase with small amount of $Si_3Al_6O_{12}N_2$ X-sialon. Another β-sialon, $Si_4Al_2O_2N_6$, was the main phase in the samples with the highest amount of silicon nitride and the same X-sialon was the complementary phase. Mechanical properties of the sintered materials as well as resistance to liquid aluminum based alloys reveal strong correlations with their phase compositions. The composites containing corundum show highest hardness, strength and fracture toughness while the best performance in the liquid metals the sialon-sialon composites.

Acknowledgements
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A study on the microstructural analysis of slag corroded MgO based self-flowing castable refractories

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Keywords: MgO based castable refractories, Slag-refractory corrosion, microstructural analysis

MgO brick refractories are extensively used in basic steel production processes. However, hydration of MgO when mixed with water constitutes a problem. This study focuses on the composition of an MgO-based castable refractory composed of 94% wt. of MgO, 2% wt. of SiC and 6% wt. binder and dispersant. Self-flow test was applied to the prepared MgO based castable mass according to ASTM C 860 standard. After sufficient spread was achieved, the mass was shaped by casting into suitable moulds with 50×50×50 dimensions. Castable refractory samples were sintered by firing for 2 h at 1600 °C. Cold crushing strength test was performed on the sintered samples in accordance with the DIN 51067 (ISO ENV 1402-6) standard. Also, water absorption, apparent porosity and bulk density tests were carried out depending on the DIN 51056 and DIN 51065 (ISO EN 993-1) norms. Before starting the slag-refractory corrosion test which was done with respect to the DIN 51069 (pot method) standard, ground slag powder (<100 μm) was charged to the bottom of the pots. Slag-refractory corrosion test was conducted by heating the pots to 1600 °C with 10 °C/min heating rate and keeping at this temperature for 2 h. Castable refractory samples interacting with the slag were axially cut by using the diamond cutting tool and hence the slag penetration area was calculated. X-Ray Diffraction (XRD) and Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) studies were realized on the samples taken from the not-interacting and slag-interacting regions. In this way, the microstructure of the corrosion that occurred starting from the refractory contacting slag surfaces to the points where penetration proceeded is investigated.

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Investigation of pyroplastic behaviour of porcelain bodies with different mineralogical contents

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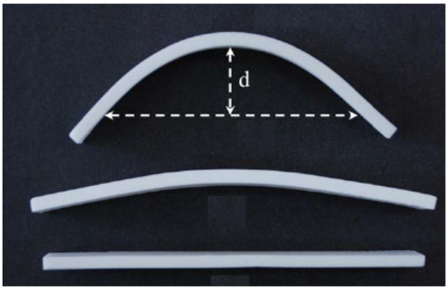
Keywords: porcelain body, pyroplastic deformation

Since the 1980s, the neogene basin of Şile has become a very important region to meet the clay reserve of Turkey as the demand for raw materials especially in the ceramic ware industry. The total reserve for ceramic clays in the region is more than 200 million tons and, it is considered to be the heart of Turkey in respect of the quality and reserves. In the district Şile, approximately 2.5 million of clays are provided to the industry per year. Ukrainian clay was used as a reference clay. Firstly, Istanbul region clays and Ukrainian Clay were characterized chemically and physically by X-ray diffraction, X-Ray Fluorescence, Fourier IR Spectroscopy and SEM. Istanbul region clays contain kaolinite, illite, chlorite and montmorillonite and accessory phases (anatase, goethite, siderite). Technogical properties and pyroplastic deformation of Ukrainian Clay and Istanbul Region Clays was investigated by using 50% clay, 40% feldspar and 10% quartz glaze porcelain body. Than effect of mineralogical content of clays to pyroplastic deformation and technological properties of bodies were investigated. It was concluded high amount of illite and montmorillonite content reduced the water absorption because of the lowering of the melting point. However, pyroplastic deformation of the bodies was reduced by adding clay which include high amount illite where increasing amount of montmorillonite affected adversely.



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T12: Art and ceramics

Invited lectures

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Self-portrait of a ceramic artist who combines Asia's East and West

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As a Turkish ceramics artist, I will describe the contemporary artistic viewpoint by exemplifying works I produce in this context. I will also talk about the curatorial duty I have undertaken in the establishment of the Turkish Museum within the Fule International Ceramic Art Museum (FLICAM) in the Shannxi Fupping Ceramic Art Village in China. This work united the most eastern and western part of Asia. Besides, I also took the curatorship of Ukrainian and Croatian museums.

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Social criticism in Turkish contemporary ceramic art

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Keywords: criticism, conceptual art, contemporary art, Turkish ceramic art

As in all works of art, the content of the work is important also in ceramics. The motivation of each artist is different. Some act with internal motivations, others are sensitive to social events. Today's ceramic artists produce very strong works and make social criticism in the name of contemporary art. In addition to global issues such as identity, subculture, gender, human rights, ecology they address topics that reflect the political atmosphere of the country, such as Gezi Resistance, cultural corruption, the values of the Republic, freedom of expression. The artist turns to witness of time and installs the events in social memory.

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Franz Collection

Franz Chen

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Franz Chen started his porcelain art brand, Franz Collection, in 2001. Chen's mission is to revive the heritage of Chinese porcelain and create eternal value for civilizations. Franz Collection has made breakthroughs in terms of porcelain form, color, and texture. These achievements are a result of combining 3D sculpting technology with traditional handicraft methods, as well as the brand's own unique glaze formula and patented "undercut demolding technique". The combination of technology, culture, and art enables Franz Collection to create artworks that deliver the values of truth, goodness, and beauty and touch the hearts of consumers worldwide.

Since its inception, Franz Porcelain has been honored with many international awards such as "The Best in Show Gift Award" and "Fashion Accessory Line of the Year" in the USA and "Best Ceramic Gift" in England. Additionally, FRANZ was awarded the "Seal of Excellence for Handicrafts" from the United Nations Educational, Scientific and Cultural Organization seven years in a row.

Franz Chen was personally awarded:
Presidential Innovation Award in Taiwan, 2014
25 Influential Chinese in Global Fashion – Forbes China, 2012
Entrepreneur of the Year 2012 Taiwan – Ernst & Young, 2012
Outstanding Porcelain Entrepreneur Award – Chinese Association of Ceramics, 2007
Creative Culture Best Contribution Award in China, 2007

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Contemporary ceramic art and traditional pottery techniques – where is the point?

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Keywords: ceramics, ceramic art, traditional pottery techniques, cultural heritage

In recent years, ceramics has regained its importance. This fact is obvious in everyday life. The ecological component of ceramics makes it a desirable material in the struggle against global pollution. This fact is obvious in the worlds of science and art as well. As a phenomenon, ceramics provides artists with multiple opportunities, relying on experimentation and new technologies. Successful results can be seen in the context of the two modules of the project entitled *Ceramics and its Dimensions* – "Shaping the Future" and "Future Lights in

Ceramics". Nevertheless, the traditional techniques and technological approaches are still attractive for contemporary artists. How does traditional pottery making enrich contemporary art ceramics? What are the achievements of the synergy of the traditional ceramic technology and artistic aspirations? What is the role of contemporary ceramics in cultural heritage protection? These are the questions that this paper will attempt to give answers to.

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Future lights – addressing the upcoming generation of ceramics and design

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Keywords: future lights, future ceramics, new designs, ceramics and its dimensions, emerging designers

The Future Lights competition has been designed for young and emerging talents in ceramics who need an appropriate platform to further their career. This competition has the intention of helping to shape and encourage the upcoming generation of ceramics and design by instilling the responsibility of progress and growth in those emerging professionals.

The Future Lights 2017 award winners will be used as a case study to illustrate the significant effects of the Future Lights competition. Further exploring how the platform opportunity is necessary in building a strong, collaborative and dynamic future which furthers the appreciation of innovation with the ceramic material in European contemporary life.

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Craftsmanship alone is not enough

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A diverse and profoundly transformable material, clay offers new designers and artists the possibility to push beyond the accepted ceramic applications into conceptually challenging contexts and outcomes.

This paper seeks to explore how contemporary artists, designers and crafts people exploit the materials traditional archetypes and production processes to comment, challenge or transform our understanding of what clay can do.

Drawing comparisons across a range of practices the paper will address the following questions; How does technological formation of clay explore craftsmanship and production values? When placed in a public context does clay allow for transformative engagement? Can we examine production values and systems through production? Does the handing down of skill from maker to maker offer opportunity for innovation? Does clays ubiquity offer transgressive, provocative opportunities?

These questions act as thresholds to a discussion about the modern context for Ceramics from education to practice and present us with the opportunity to interrogate a range of designers and makers, their work and attitudes through this lense.

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A portrait of the ceramicist as a young man: a reconsideration of a new way of promoting ceramics education, with a roadmap for developing a centre of excellence in ceramics

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A reconsideration of a new way of promoting ceramics education, with a roadmap for developing a Centre of Excellence in Ceramics.

This presentation explores the differing and often conflicting needs between young future makers, ceramic craft and design educationalists, bureaucratic government agencies and the specific needs of those economically active in the craft and design industry.

As the spirit of the young artist is enthused with an enthusiastic ‘fire in the belly’ to learn flourish and stamp their own identity upon a brave new world of adulthood, the ceramic educationalist is charged with the tricky dual role of inspiring this love of the art whilst at the same time being mindful of what might be usefully needed to survive and thrive in the future craft and design industry into 2020 and beyond.

The presentation will include a case study of how a new emerging ‘Centre of Excellence (C of E) in Ceramics’ is being developed at Thomastown in Ireland and about how in creating this new C of E the journey to re-package tried and tested traditional ways of pottery teaching can help influence the future making of a vibrant thriving ceramics industry.

Oral presentations

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Influence of chamotte addition on the physical and mechanical properties of red mud bodies

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Keywords: chamotte, red mud, mechanical properties, physical properties, slip casting

Red mud is a highly alkaline waste product composed mainly of iron oxide that is generated in the industrial production of aluminum. Used red mud contains 30–35 weight % iron oxide (Fe_2O_3). Mechanical properties and density of red mud bodies are lower than chamotte bodies. For increasing these properties 5, 10, 15 and 20 wt% chamottes were added to red mud bodies produced by 40 wt% solid content slip seperately. Slip casted samples were sintered at 900 and 950 °C.

Physical and mechanical properties were determined by measuring density, firing shrinkage, water absorption, bending strength and Vicker microhardness (HV). Structural characterization was done X-Ray diffraction method (XRD). The best physical and mechanical properties were obtained with the red mud samples containing 15 wt% chamottes and sintered at 950 °C. On the other hands, slip casted red mud samples containing 20 wt% chamottes didn't depart from the plaster mold.

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Archaeometry studies of Portuguese ceramics (pottery and tiles) produced in the region of Lisbon – 16th to 17th c.

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Keywords: ceramic pastes, Lisbon ceramic productions, XRF

Portuguese tin-glazed earthenware production is usually associated to 16th c. contexts, although findings of tin glaze ware exist from Mata da Machada kiln (1489 to 1530) and for tin glaze tiles from Santo António da Charneca (SAC) kiln, both located in the south shore of Tagus river, about 20 km away from Lisbon[1]. Moreover, cobalt blue sherds from 12th–13th c.

recovered at Silves Castle (South of Portugal) archaeological excavations[2], revealed a paste with a composition typical of clays of Miocene origin, like the ones used in Lisbon pottery productions, suggesting that Lisbon workshops were already producing tin-glazed pottery, at that time. This is an example, among many others, of the importance of ceramic pastes characterization on attempt to establish the provenance of the ancient pottery.

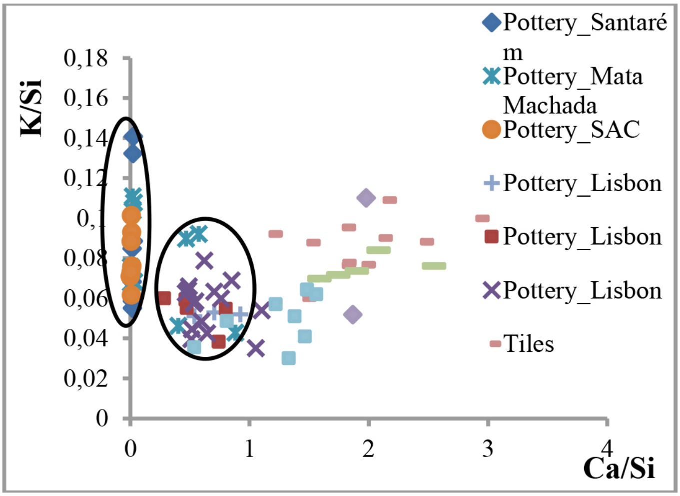

Fig. 1. Scatterplot of K/Si versus Ca/Si count ratios for the ceramic pastes of 16th-17th c. Lisbon pottery and tiles

Scatterplots of K/Si versus Ca/Si count ratios allow us to identify quite distinct groups when characterizing composition of pottery pastes, with almost no calcium in the ceramics of Mata da Machada and SAC kilns, while the production of Lisbon workshops exhibit a large range of calcium content. As far as our studies revealed, this pattern is typical of Lisbon productions. However, when we introduce the tiles (Fig. 1) it is clear that the amount of calcium presents a huge increase, indicating the use of distinct clays, with higher calcium content, and lower temperatures of firing the pastes, or an intentional addition of calcium compounds in these productions.

In this work, we present a study of representative sherds of tin-glazed productions of the Lisbon region, dated from the 16th–17th centuries, using X-ray fluorescence emission (XRF), micro-Raman and X-ray diffraction (XRD). Special focus is done on pastes composition of pottery and tiles, as well as possible clays used by potters working in this region.

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Usage of sugar beet pulp ash in stoneware body as a raw material in ceramic art

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Existing for ages as a utility or an artistic object, use of ceramic materials have expanded to vast number of areas varying from domestic use to medicine and to space technology.

Besides studies for diversification of raw materials used in ceramic body, research and development studies in ceramics also includes exploration of new inorganic and organic materials to be used as aggregates.

Providing a chance of reuse to industrial waste materials, quantities of which are increasing in a tremendous speed, have an importance not only for being an success indicator of the energy saving policy of a country, also for offering a higher utilization of resources and lastly, for economic reasons. In this study; potential of using sugar beet pulp as an ingredient in ceramic body is investigated and chemical analysis of sugar beet pulp, which is a waste product of “Konya Refinery of Sugar” manufacturing

In 21st century, where urge of consumption in modern societies surpasses the power of production, it is aimed to provide economic and ecologic outcomes with revaluation of sugar beet pulp as a raw material for ceramics in ceramic industry and ceramic art. Such reuse, as a result, saves an amount of natural resources which we are running out steadily, provides a protection for suffering environment and also becomes a new kind of raw material for ceramic artists for searching new possibilities in ceramic body.

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The color effect of magnetite and chromite in ceramic stoneware glazes

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Keywords: ceramic pigments**,** hematite, chromite, stoneware glaze, colorants

Ceramic colorants are added to a glaze or a clay to create colour. In ceramic glazes the colour is obtained by the dispersion of pigments and opacifiers. These colorants can create a multitude of colours depending on other materials they interact with. On several factors, the colouring effects of the pigments and stains depend. These factors are: nature of the raw materials, the firing temperature, time and kiln atmosphere.

The colouring metal oxides need to be subjected to various processes in order to meet stable and standard characteristics and to be ready for industrial use. And this is the ceramic stain manufacturing industry. Many different techniques and technology can be used in industrial dye production. The current market price of black paint, which is an industrial ceramic colorant, is relatively expensive.

In this study, magnetite and chromite ores were used to reduce the cost of black pigment production. These two ores, which have very low loss on ignition, have produced very effective results in the production of black pigment. Produced pigments are used in the coloring of stoneware ceramic glazes after calcination, recipe preparation and micronization. The colour and texture effect of the black dye on the ceramic glazes were investigated. The cost of dye produced from magnetite and chromite is considerably reduced compared to other pigments in the market.

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Poster presentations

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Museums as centers of diffusion of creativity, design and technique

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As institutions related to Heritage and creativity, museums can play an important role both in preserving the legacy of the past and in projecting it to the future, as well as showing new proposals and technological developments to society. The museum enjoys a privileged position to serve as a platform for dissemination in initiatives such as “Future Lights”, promoted by the European project “Ceramics and its dimensions”. The National Ceramic Museum “González Martí” in Valencia (Spain), has gained a long experience in this field through the connection between artists, entrepreneurs, training centers and specialists. The objective of our communication will be to present these experiences drawing general conclusions that can be useful for the development of the project while exposing the current situation in our social environment.

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The composition design of artistic aventurine glazes containing hematite ore

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Keywords: aveturine effect, hematite, artistic glaze

Aventurine glaze is a special type of an artistic glaze in which the separation of isolated individual crystals shimmering on the glaze surface. Crystals has the characteristic appearance of flitters, sheets or spangles suspended in a glassy phase. These types of glazes possess a high decorative and artistic value. Therefore, evaluating them on the ceramic bodies enhances the esthetical appearance and makes the final product unique. Generally aventurine effect is obtained by using high amounts of Fe_2O_3 in the chemical glaze composition. In this study, aventurine glazes are developed by contributing hematite ore raw material into the glaze formulation instead of directly using Fe_2O_3. Newly studied glazes are wet milled in a porcelain jar for 20 min and then glaze slips were applied onto both pre-fired ceramic substrates and wall tile bodies. Firings were conducted firstly at laboratory conditions at 900-1000-1050-

1150 ºC in an oxidizing atmosphere and after that industrial fast firings were conducted at a peak temperature of 1150 ºC at Altın Çini and Seramik Co. Inc. A possible aventurine effect was proposed to show the variation of glaze colour patterns with the increasing of firing temperature. All of the glaze surfaces were smooth and glossy after laboratory firings. Moreover, dark brown colour with yellowish transition effect on the glaze surface was obtained under industrial fast firings. L*a*b values were measured by a spectrophotometer. Final surfaces of the aventurine glazes were characterized by a X-ray difractometer (XRD). Glaze samples were visualized by scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) techniques.

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Transform from industrial ceramic product to artistic form

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Keywords: industrial ceramic, raw waste, ceramic art, sculpture, imitation granite

Natural granites can be quite estethic materials for making sculptor. Not only natural granite materials but also imitation granite tiles can be quite estethic materials. From this viewpoint, in this study's aimed to create art objects using wastes of raw ceramic tiles which are imitated from natural granites. Industrial raw ceramic tile wastes are provided by Oua Granite Ceramic Factory. Raw wastes collect from dimentions is 60 × 60 × 2 cm which bodies colourized with different colours. Forementioned raw tiles are formed as sculptures by hand. Formed some of the sculpture pieces fired in Qua Granite manufacturing roller kiln and other the sculpture pieces fired in laboratory chamber kiln. Forms finished by, combined with fired sculptor pieces and using different sort of material (like glass, metal and wood, etc.)

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Portuguese blue-on-blue 16th–17th c. pottery

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Keywords: Portuguese ancient ceramics, Lisbon blue on blue pottery, XRD, XRF, micro-Raman

Blue on blue (berettino) sherds appeared in numerous production and consumption archaeological excavations in Lisbon and other archaeological sites in Portugal (mid 16th–beg 17th c.). The abundance of this interesting faience lead us to compare it with similar pottery from other well-known production centres in Italy, namely Liguria (Savona and Albisola), Spain (Triana kilns) and Low Countries.

Differences in the diffraction patterns of the sherds' pastes from the four countries were observed. In most samples cobalt blue silicate was identified in the dark blue or light blue glazes by the use of micro-Raman spectroscopy and diffuse reflectance spectra.

A comparison was also made for all blue on blue sherds studied here with many others 16th–17th c. sherds from Lisbon using bivariate plots of K/Si vs. Ca/Si. Lisbon and Seville pottery behave very differently, whereas Italian and Low Countries sherds occupy intermediate positions.

By combining the use of the mineralogical composition for the pastes obtained with the use of XRD diffractograms – and also of the spectroscopic characterization (XRF, Raman and GSDR spectroscopies) for pastes and glazes – we conclude that the blue on blue pottery found at the Lisbon dated from the 16th/17th c. was produced in Lisbon workshops, using Miocene raw materials collected locally[1]. The Pliocene kaolinites' sands, common in the south shore of the Tagus River in the production of pottery and tiles, were not used for the blue on blue pottery productions in Lisbon.

All this information points to a conclusion that archaeologists believed for quite some time, that blue on blue berettino found in Portugal and its colonies was not exclusively made in Italy and Seville. The large amount of plates and bowls using such decorative technique suggested that production was in fact internal and made in the same workshops where Portuguese faience was manufactured. One has to reinforce the importance of this discovery for Post-Medieval Portuguese archaeological studies. This paper demonstrates that Lisbon was not only producing a different type of pottery but supplying the internal market and possibly sending large amounts of this ware to Portuguese overseas colonies and even to North European countries and their colonies.

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Student speech contest

Austria

Mechanical characterization of $LiTaO_3$ and $LiNbO_3$ single crystals for smartphone applications

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Keywords: lithium tantalate, lithium niobate, biaxial strength, toughness, fractography

Lithium tantalate ($LiTaO_3$) and lithium niobate ($LiNbO_3$) single crystals possess various attractive properties such as piezo-electricity, pyro-electricity, non-linear optical behaviour, making them interesting for many electronic devices (e.g. modulators, transducers or detectors). In the smartphone market, for instance, these ceramic materials have found important application as surface acoustic wave (SAW) filter substrates for high frequency data transfer.

For this application, the single crystals are grown under specific “cuts” and the surfaces are conditioned (polished and metallized) to tailor the material’s anisotropy and meet the required functionality. Finally, components are solder joined to a functional ceramic (or polymer) substrate. Due to the different thermal expansion coefficients and Young’s moduli between the combined materials (e.g. ceramics, metals, polymers), significant internal (residual) stresses can be generated during the fabrication process. If the tensile stresses overcome the strength of the brittle single crystals, cracks initiate and propagate, leading to reduction of the functionality or complete failure of the microelectronic module. Although appropriate functional characterization of these materials can be found in literature, a lack of knowledge exists regarding their mechanical properties.

In this work, a throughout understanding of $LiTaO_3$ and $LiNbO_3$ single crystals was assessed in terms of strength and fracture resistance with respect to the cutting direction and surface quality of the wafer. The biaxial strength was evaluated on plate-like specimens, using the ball-on-three-balls test, and results were interpreted using Weibull statistics. Additionally, *in-situ* tests of FIB-notched micro cantilevers were conducted to quantify the fracture toughness of the most critical cleavage planes. The materials response to contact damage was also analysed using nanoindentation. Experimental findings showed a significant difference in strength between $LiTaO_3$ and $LiNbO_3$ for the same surface finishing. In addition, deviation from Weibull statistics was observed in $LiNbO_3$. Fractography of the tested samples helped identifying cleavage planes, showing differences in the fracture patterns for both materials. This may be explained by the different fracture toughness and cutting orientation with respect to the loading plane.

The results of this work provide fundamental knowledge on the mechanical performance limits of functional ceramic single crystal materials with regard to the crystal orientation and surface conditioning.

Belgium

Sol-gel synthesis and low-temperature deposition of thin SiO_2 layers as scratch resistant coatings for functional films

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Keywords: roll-to-roll coating, scratch resistance, low temperature, low emissivity, SIMS

In recent years, functional window films have gained much interest. These windows films can be used for a wide variety of applications. Some common examples of these applications are UV-blocking, window tinting, insulation and shatter resistance. Most of the window films are functionalized by thin layers on a flexible substrate. It is also known that these thin layers are not stable in air and prone to deterioration caused by moisture and abrasion. This drawback can be overcome by the deposition of an additional scratch resistant coating.

A thin silica coating was deposited on a polyethylene terephthalate (PET) film with a thickness of 60 μm, functionalized with a thin metal oxide layer. This oxide layer was deposited by sputtering and is often used for functional window films. It is shown by contact angle measurements that the silica precursor and the metal oxide have a good chemical compatibility. The precursor composition was modified to be applicable in industrial settings by keeping chlorides out of the reaction mixture. The effect of organic acids compared to the effect of hydrochloric acid on the sol-gel chemistry[1,2] was inquired by studying the kinetics of the condensation reactions.

Secondly, the drying behavior of the precursor solution was optimized for coating. This was done by introduction of a precondensation step and a final quenching step. These additional steps were monitored by ^{29}Si-NMR[3,4]. It is shown that these steps lead to a better condensation of the precursor after deposition and a decrease in drying time. Subsequently, the shelf life of the precursor was looked into. It was shown that the precursor solution was sufficiently stable to assure continuous deposition during at least one working shift of eight hours.

The precursor solution was deposited onto the substrate by reverse gravure roll-coating[5]. The ratio between web speed and application speed was optimized to obtain sufficient wetting of the film. A temperature program for in-line drying of the coating is set up. The temperature program is important to transfer the results to industrial setups where the time available for drying is limited. One must keep in mind that the temperature should be high enough to obtain complete drying of the precursor solution while it should be low enough to avoid melting or breakdown of the organic substrate.

The deposited coatings were subject to application tests, which consisted of cross hatch (ASTM D3359), Pencil hardness (ASTM D3363) and visual light transmittance tests. The results showed that the deposited coatings had a good adhesion to the substrate. The pencil hardness turned out to be 3H and a drop in visual light transmittance of maximal 3% was recorded.

The determination of the thickness of a transparent coating on a transparent substrate is very difficult. Secondary ion mass spectrometry (SIMS) combined with optical profilometry has shown to be an ideal approach to tackle this problem. These methods have been used to correlate coating thickness with pencil hardness and adhesion onto the substrate.

Patent pending.

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Czech Republic

Mechanical properties of hybrid ceramic composites prepared by ice-templating

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Keywords: ice-templating, alumina, epoxide, hybrid composites, strength

Ice-templating, also known as freeze-casting, is a relatively simple, inexpensive, and very versatile technique to fabricate bulk porous scaffolds with controlled microstructure. The basic idea of ice-templating is to obtain porosity that is replica of ice crystals, by freezing suspension and subsequently removing the ice crystals by sublimation of the solvent. Typical processing steps of the ice-templating process are shown in the Fig. 1.

Promising application of ice templating is preparation of hybrid ceramic materials. Effort in designing and manufacturing hybrid ceramic composites is to emulate nature's toughening mechanisms by infiltration of polymers into ceramic structures. Such biomimetic materials have significantly better mechanical properties (tensile strength, fracture toughness) than the individual compounds that they are made of. However, for future applications is necessary to scale up ice-templating process. The main challenge linked with large scaffolds prepared by ice-templating method is achieving of controlled ice crystals growth throughout the whole sample volume. This phenomenon is caused by loss of sufficient temperature gradient in the ceramic suspension as the solidification front moves away from the cooling plate. Thus it is necessary to precisely control the ice-templating process.

Ceramic suspension containing alumina (Al_2O_3) in water was used in this work. An influence of suspensions solid loading and additives on formation of lamellar roughness and inter-lamellar bridges was investigated during ice-templating of large ceramics scaffolds. Effects of these microstructural ceramic parts of hybrid composites on mechanical properties were studied and discussed.

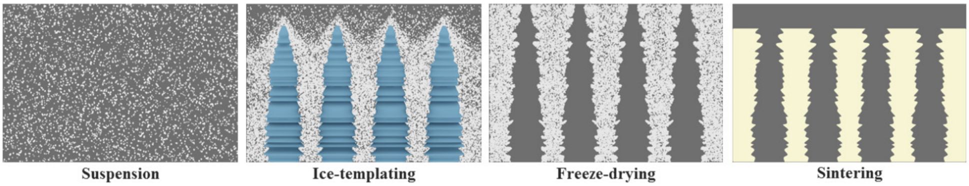

Fig. 1. Typical processing steps of the ice-templating process

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Finland

Pulsed laser ablation in supercritical carbon dioxide to synthesize photocatalytically active nanoparticles

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Keywords: nanoparticles, pulsed laser ablation in pressurized fluids, supercritical carbon dioxide, Raman, ablation in controlled atmosphere

In the past decade, nanotechnology and nanoscience have expanded rapidly in almost all advanced fields in the industry[1]. More specifically, the ubiquitous influence of nanomaterials in almost every field of industry has led to a sudden and urgent global demand of nanoparticles. In this regard, pulsed laser ablation in liquids (PLAL) technique has sought to revolutionize the production of nanoparticles since the list of potential materials for PLAL is immense, which means nanoparticles can be synthesized from this limitless list of potential materials by using PLAL[2,3]. The productivity of PLAL technique has been questioned in the past and concluded as a shortcoming of the method, but with latest demonstrations of productivities higher than 4 g/h, PLAL easily competes against other colloidal synthesis techniques. The next revolutionary step in the domain of PLAL synthesis is pulsed laser ablation in pressurized fluids. Kuwahara et al., reported that the ablation efficiency of copper in CO_2 was several tens of times more at higher pressure compared to lower pressure[4]. In the field of pressurized fluids, a fluid is said to be in its supercritical state when its temperature and pressure exceed its respective critical point values. When combined with PLAL, supercritical fluids, such as, supercritical carbon dioxide ($ScCO_2$), have been reported to support formation of interesting reaction fields for plasma technology and nanotechnology[5]. In this study, we demonstrate pulsed laser ablation (PLA) in $ScCO_2$ to synthesize photocatalytically active nanoparticles by ablation of a titanium target. $ScCO_2$ is an interesting fluid, which allows high reaction rates compared to liquids due to higher diffusivity in supercritical fluids. Moreover, it is possible to change the solvent power just by changing the temperature and pressure, which will cause change in the solubility[5].

In our study, a titanium target in $ScCO_2$ was ablated at 20 MPa and 40 °C using a 1062 nm fiber laser. The ablated target and the synthesized nanoparticles were studied by TEM, XRD, Raman spectroscopy, and methylene blue (MB) discoloration tests. TEM showed presence of networks of almost perfectly round nanoparticles with diameters varying from 5 nm to 36 nm. The network structure was comprised of chains of nanospheres with a mean diameter around 13 nm. The electron diffraction pattern showed the particles were highly crystalline which was substantiated with the high peaks in XRD pattern. The MB discoloration tests indicated the photocatalytic activity of the synthesized nanoparticles. By discussing the key results from XRD and Raman for the phases formed from titanium, this study demonstrates the potential of PLA in $ScCO_2$ to create novel nanomaterials.

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France

In situ HT-ESEM study of MO_2 (M = Ce, Th) first stage of sintering: from neck elaboration to microstructure design

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Keywords: sintering, ceramics materials, *in situ* microscopy

As a key-step in the elaboration of ceramics materials, such as nuclear fuels (UO_2), the sintering has been studied for years. If grain growth processes were investigated thanks to experimental works and calculations, the elaboration of necks during the first step of sintering was generally assessed only through numerical models, frequently based on simple configurations (two spherical single crystals in contact).

In order to complement such numerical approaches, the elaboration of necks during the sintering of CeO_2 and ThO_2 microspheres, herein used as model compounds, was experimentally observed by HT-ESEM[1]. The study of the morphological modifications in a single grain first led to determine the variation of the number of crystallites included in the sphere and the attached mechanisms, i.e. oriented attachment then diffusion. Also, the time required to reach a spherical single crystal grain was evaluated for each temperature[2].

The kinetics associated to the evolution of neck, contact angles and centers displacement during the sintering of two microspheres were then evaluated. In this case, the evolution of polycrystalline assemblies and of single crystals was studied in parallel (Fig. 1). The comparison of these results with that supplied by the SALAMMBO model then allowed us to estimate the bias associated to the polycristallinity of the powders[3,4].

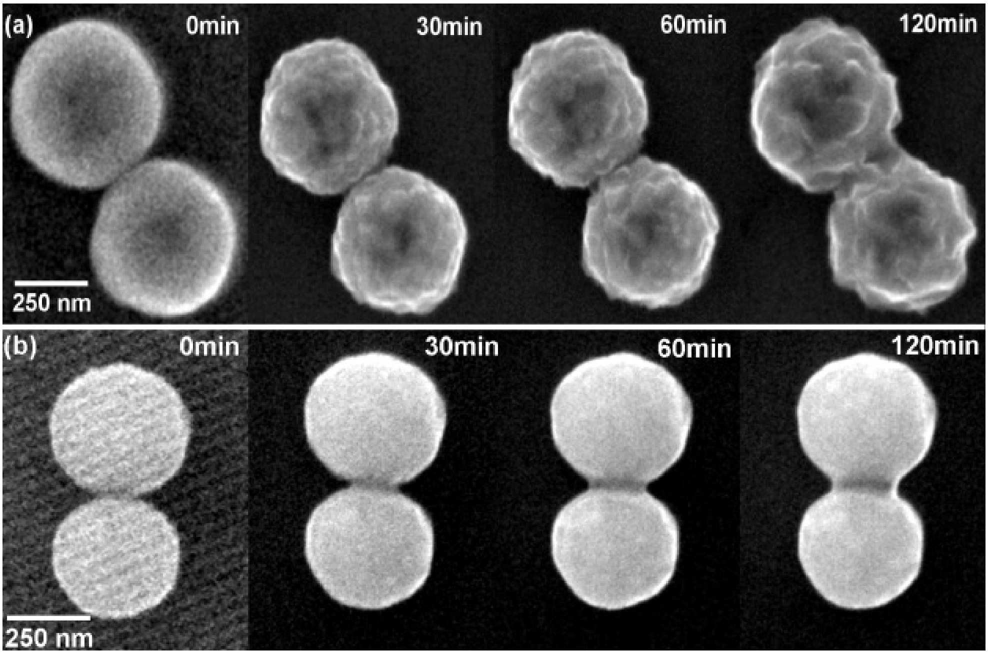

Fig. 1. *In situ* HT-ESEM observation of CeO_2 microspheres sintering at 1050°C: (a) poly- and (b) single-crystal particles

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Germany

Fabrication of crack healing ZrO_2 composites containing Nb_2AlC repair fillers

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Keywords: MAX phase, repair filler, crack healing

The lifetime of ZrO_2 advanced engineering ceramics is limited due to flaws like microcracks and micropores formed during manufacturing process or service, leading to catastrophic failures of ceramic devices under high load. Ternary carbides with nanolaminar crystal structure, also called $M_{n+1}AX_n$ phases, gained recent interest for their unique combination of metallic and ceramic properties. Further studies explored the oxidation abilities of $M_{n+1}AX_n$, demonstrating multiple crack healing capability at high temperatures[1–3]. In this work, the possibility of utilizing $M_{n+1}AX_n$ phases as repair fillers in a ZrO_2 matrix is presented, whereby fracture toughness can be enhanced and high temperature crack healing behavior of the composites enables an improved reliability of these engineering ceramics.

Single-phase Nb_2AlC powder was synthesized by pressureless annealing of NbC/Nb/Al raw powder mixtures. The successful synthesis and phase purity was verified by XRD measurements. ZrO_2-Nb_2AlC composites loaded with 0–20 Vol% Nb_2AlC repair filler were fabricated by pressureless sintering and Spark Plasma Sintering (SPS) methods, examining the influence of applying extremely high heating rates during sintering on the composite stability and density. With XRD measurements it was shown that only with SPS completely dense and phase pure samples could be manufactured, due to the thermal controlled decomposition of Nb_2AlC in ZrO_2.

Mechanical properties (hardness, Young's Modulus) and porosities of the resulting ZrO_2-Nb_2AlC composites were determined, revealing an independence of the examined Nb_2AlC content, which is required for structural applications of these composites as for example thermal barrier coatings. To investigate the high temperature behavior and possible crack healing abilites, oxidation kinetics of the composites were studied up to 1400 °C by the determination of the oxide layer thickness and morphology. Artificial cracks were introduced in the ZrO_2-Nb_2AlC composites by Vickers indentation and the effect on bending strength and fracture toughness was measured. In 3-point-bending tests the composites with 20 Vol% repair filler showed full strength recovery after annealing in air at 1200 °C.

Acknowledgment
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Hungary

Silicon nitride-based composites reinforced with zirconia nanofibres

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Keywords: spark plasma sintering, Si_3N_4, ZrO_2 nanofibre, electrospinning, mechanical properties

Silicon nitride (Si_3N_4) ceramics exhibit remarkable combinations of mechanical, chemical and thermal properties; however, the main concern for its widespread application is their low fracture toughness. In order to enhance the fracture behaviour we present an alternative route to improve the fracture toughness of Si_3N_4 and we prepared ZrO_2 nanofibres to combine two types of toughening effects such as fibre–toughening and phase transformation toughening. For comparison, besides the ZrO_2 nanofibres reinforced composites (ZrO_{2f}/Si_3N_4) we also studied the reinforcing effect of ZrO_2 particles (ZrO_{2p}/Si_3N_4). Si_3N_4-based ceramics mixed with various fractions of ZrO_2 additions are fabricated by liquid phase spark plasma sintering (SPS) at 1600 °C. We studied the microstructure and mechanical properties of ZrO_{2f}/Si_3N_4 and ZrO_{2p}/Si_3N_4 composites. It was found that fracture toughness and flexural strengths show significant improvements in the case of ZrO_2 fibre reinforced Si_3N_4 composites. The sample loaded by 15 wt% ZrO_2 fibres had 10.05 ± 0.7 MPa·$m^{1/2}$ fracture toughness and 543 ± 19 MPa flexural strength, which means 105% and 115% improvements respectively, regarding to the reference sample. The incorporation of fibre into the Si_3N_4 composite can be an effective way to increase the fracture resistance and avoided the catastrophic fracture behaviour since ZrO_2 fibre is able to improve mechanical properties of the composites in a complex way, such as phase transformation toughening and fibre-toughening mechanisms.

Iran

Processing of Si_3N_4 for EDM-able bodies

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Keywords: silicon nitride, titanium nitride, electrical discharge machining, electrical conductivity

Silicon nitride (Si_3N_4) as a structural ceramic has been studied intensively, thanks to its exceptional profile of properties such as high strength and hardness, chemical stability, and good wear as well as remarkable corrosive resistance at high temperatures. In spite of its impressive properties, owing to its high hardness and difficult machining, the wide usage of the silicon nitride has been limited, especially in applications that require reproducible 3D bodies with precise dimensions. A successful approach is to incorporate electrically conductive reinforcements into silicon nitride matrix. This incorporation makes the composite electrically conductive, so that electrical discharge machining (EDM) can be employed. EDM is an attractive machining method, which is only applied to the electrically conductive bodies. Moreover, it is a precision machining method, using that the shaping process is possible in relatively concise period of time.

In the present research, titanium nitride (TiN), as an electrically conductive phase, ranging from 20 to 40 vol. % was added to silicon nitride. Sintering of the composite bodies was done with pressureless sintering (PS) and direct hot pressing (HP). In order to reach the maximum relative density, pressureless sintering of the composites was carried on by two-step sintering cycle at maximum temperature of 1650, 1700, and 1750 °C. Relative density of 97.9% was achieved for the sample with 40 vol. % TiN sintered at 1750 °C. This sample has the highest fracture toughness (7.1 ± 0.3 MPa.m$^{1/2}$) and the lowest electrical resistivity ($2.16\times10^{-6}\Omega$m) among the other samples.

Due to the decrease in thermal gradient between coil and graphite die, direct hot pressing was used. To do so, the graphite die was connected to electrical power directly. The relative density of 99.8% was achieved for the sample with 40 vol. % TiN, sintered at 1700 °C. This composite also showed remarkable mechanical properties such as bending strength and fracture toughness. Bending strength (904 ± 81 MPa) and fracture toughness (7.3 ± 0.7 MPa.m$^{1/2}$) increased by increasing the amount of TiN. The electrical resistivity of the sample with 40 vol. % TiN was measured $1.9\times10^{-5}\Omega$m. Machining of the composites, sintered by both pressureless sintering and hot pressing was successfully done by electrical discharge machining, as well. Investigation of the surface roughness of the samples, EDM-ed under two different electrical currents was done by a profilometer.

Italy

Fabrication and properties of hybrid, liquid-repellent coatings

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Keywords: nanostructured coatings, superhydrophobic surfaces, sol-gel

The control of the wetting properties of solid surfaces is extremely relevant for a wide spectrum of industrial applications, i.e. building industry, electronics and renewable energies. Thus, huge efforts have been devoted to the fabrication of surfaces with tailored wetting properties. More specifically, many scientists focused on the mimicry of the so-called Lotus Effect, which can be observed on the surface of lotus leaves: water drops do not stick, rather they remain spherical and roll off very easily. Such behavior is due to the combination of a dual-scale, hierarchical surface structure (i.e. on the micro- and the nano-scale) with a chemical composition that leads to low surface energy. A surface with such characteristics will be able to trap air within its features and will not let water drops penetrate, thus hindering sticking and allowing removal. Therefore, in our studies we followed a biomimetic approach for the design of liquid-repellent surfaces.

First, we developed a hybrid coating mimicking the Lotus Effect. The inorganic component of the coating was obtained via dip-coating the surface with a suspension of alumina nanoparticles; the resultant gel film was first heat-treated, then transformed into a boehmite AlOOH layer with a peculiar flower-like nanostructure by immersion in boiling water. We investigated the formation of a properly structured coating on different materials, adjusting process parameters (e.g. dispersant, treatment temperature) to achieve the best results in terms of wetting properties. In fact, after chemical modification with a fluoroalkylsilane (FAS) to decrease surface energy, the coating was superhydrophobic (SH), with a water contact angle (WCA) well above 150° and contact angle hysteresis (CAH) lower than 10°. XPS analyses confirmed the grafting of FAS chains to the surface, while DFT calculations provided a deeper insight into the formation of the FAS monolayer. We also extended the repellence to other liquids, causing great increase in contact angles with low surface tension liquids (e.g. alkanes and oils), thus the coating could also be defined as oleophobic. Furthermore, this coating showed excellent resistance to chemically aggressive environments, maintaining superhydrophobicity even after prolonged testing.

We also pursued an alternative approach to liquid repellence. Once again we followed a biomimetic approach, taking the slippery surface of pitcher plant as a model. We started from the aforementioned hybrid coatings and added a fluorinated lubricant to fill the pores in the coating and to create a continuous liquid film. In such situation, a liquid drop is in contact with the liquid phase rather than with the solid surface. These innovative materials are called Slippery Liquid-Infused Porous Surfaces (SLIPSs). Even though they displayed much lower WCA than regular SH surfaces, they still had exceptionally low CAH (about 2°) and water drops showed no sign of adhesion. These surfaces have potential self-healing properties, as the infused oil should be able to repair damaged areas where the liquid film is depleted. Moreover, SLIPSs might show liquid repellence even in adverse conditions, e.g. under high pressures at which SH surfaces usually fail. The properties of these surfaces still have to be fully explored, but the first observations are extremely appealing.

In summary, we fabricated and optimized two biomimetic coatings with notable liquid repellence. Their application in many industrial fields is yet to be achieved, but the huge potential advantages foster further research and investigations to improve their performance and properties.

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Latvia

Phase transition of $Ba_4Gd_3F_{17}$ nanocrystals in Er^{3+} doped transparent glass ceramics

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Keywords: glass ceramics, upconversion luminescence, oxyfluoride, site-selective spectroscopy

Transparent oxyfluoride glass ceramics are suitable hosts for rare earth ions. The low phonon energy of the crystalline phase combined with transparency, good chemical and mechanical properties of oxide glass matrix are desirable for optical applications.[1] Among other rare earth ions, erbium is a widely investigated candidate for infrared to visible upconversion luminescence (UCL) processes, however the efficiency of UCL depends on the properties of the host material. Previously highly efficient UCL has been detected in Ba^{2+} containing glass ceramics with fluorite and distorted fluorite type nanocrystals,[2] nevertheless there is limited information about UCL in fluorite derived phases.

In this research we report novel transparent Er^{3+} doped oxyfluoride glass-ceramics containing $Ba_4Gd_3F_{17}$ nanocrystals, prepared from melt quenched glasses with general composition of $17Na_2O$-$9BaF_2$-$(8-x)GdF_3$-$xErF_3$-$6Al_2O_3$-$60SiO_2$ (x = 0.1–4) in mol%. Intense UCL resulting from energy transfer between Er^{3+} ions was detected under near-infrared excitation in these glass ceramics (see Fig. 1). Longer characteristic decay times, higher UCL intensity and splitting of the luminescence bands compared to the precursor glass indicated the incorporation of erbium ions in the crystalline phase. The thermal treatment of the precursor glasses promoted the growth of nanocrystals. The formation of fluorite type nanocrystals was detected using X-ray diffraction, however changes in the morphology and deviations in the luminescence and luminescence excitation spectra suggested ordering of the fluorite phase. For comparison, single-phase Er^{3+} doped cubic and rhombohedral $Ba_4Gd_3F_{17}$ were prepared and the local environment of Er^{3+} in both polycrystalline ceramics and glass ceramics was analysed using site-selective spectroscopy. A phase transition in glass ceramics in the temperature range 650–700 °C was detected and associated with the ordering of cubic phase resulting in the formation of rhombohedrally distorted fluorite type $Ba_4Gd_3F_{17}$.

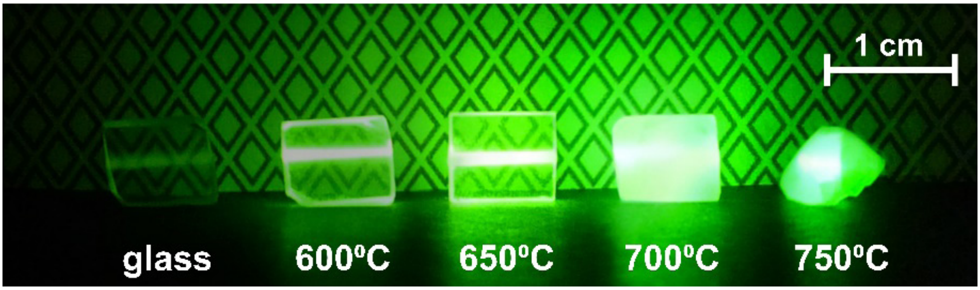

Fig. 1. Photograph of the glass and glass ceramics doped with 1 mol% ErF_3 obtained by the heat treatment at different temperatures, excited with 975 nm

Acknowledgments

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The Netherlands

Transport through grafted ceramic membranes

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Keywords: organic solvent nanofiltation, grafting, gamma aluminum oxide, PDMS, Spiegler Kedem model

Unlike their polymeric counterparts, ceramic membranes benefit from a rigid architecture which does not swell in the presence of organic solvents. However, their hydrophilic surfaces makes them ill-suited to organic solvent nanofiltration. Grafting short chains of PDMS not only shrinks the pore to the desired size but also renders them suitable for organic solvent nanofiltration (OSN). These membranes exhibit particular transport phenomena due to the localized swelling of the PDMS. The degree of swelling is solvent-dependent, which impacts both the permeability and retention of the membrane.[1]

We have examined how solvent mixtures permeate and solutes are retained across PDMS-grafted gamma-alumina selective layers supported on alpha-alumina. Four types of membranes were fabricated: two initial pore sizes of alumina, 5 nm and 9 nm, each grafted with two sizes of PDMS, either a degree of polymerization $n = 10$ or $n = 20$. A range of solvents and their mixtures were tested, from ethanol to toluene, in a cross-flow setup from pressures 10 to 40 bar. Characterization by permporometry and contact angle, as well as retention and permeability measurements indicated a membrane well suited to OSN applications. Parameters such as the size of the initial pore, swollen pore and solute are inputs to a version of the Spiegler Kedem, modified to predict the performance of these grafted ceramic membranes. By allowing the diffusion (but not convection) of solutes through the swollen graft, we find that predictions obtained through this Spiegler Kedem model agree with the experimental data.[1]

Acknowledgments

Both the Netherlands Organisation for Scientific Research (NWO) and the Institute for Sustainable Process Technology (ISPT) are thanked for their financial support.

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Norway

Development of all-oxide thermoelectric stacking device

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Keywords: processing, oxides, thermoelectric device

Due to high stability, environmental friendly impact and reasonable cost, oxides are interesting for thermoelectric devices for energy conversion at high temperature. Besides the advantages, oxides have challenges due to efficiency and processing. The efficiency of a single TE material is described by the ZT or figure of merit, which includes Seebeck coefficient, electrical and thermal conductivity. An all-oxide thermoelectric device (Fig. 1) contains an n- and a p-type conductor separated by an insulator. The direct p-n junction is the crucial part of the device having the same function as the metal current-collector being the limitation for high temperature applications for conventional devices.

Development of this new device design requires improved efficiency of the oxide materials through designed microstructure followed by an advanced ceramics processing approach. For our all-oxide device, we have selected $Ca_{0.932}MnO_3$ (CMO), $Ca_3Co_4O_9$ (CCO) and $LaAlO_3$ (LAO) as n-type, p-type and insulator materials respectively, based on coefficients of thermal expansions. Each of these three oxides were synthetized and sintered using spray pyrolysis and spark plasma sintering (SPS). The all-oxide thermoelectric device was developed using aqueous tape casting followed by co-sintering using SPS. Power output and efficiency of the device were recorded from 700 to 800 °C in air. We observed reaction layer at the p-n junction. Chemical stability and compatibility of the three materials are discussed. The work will report on the fabrication of the TE materials and device with their TE properties.

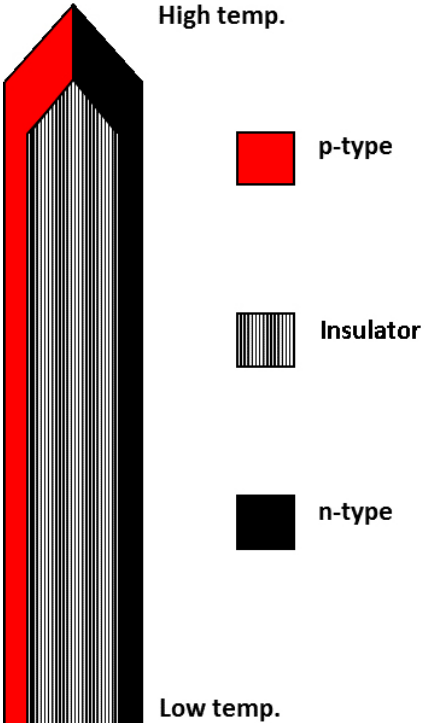

Fig. 1. A single pair of thermoelectric device

Acknowledgement

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Poland

Strontium oxynitride phosphor doped with Eu^{2+} ions: phase purity/optical properties relationship

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Keywords: oxonitridosilicate, flux, phosphor, photoluminescence characterization, solid state synthesis, gas pressure synthesis

Eu^{2+}-doped $SrSi_2O_2N_2$ was prepared via a gas pressure method or a solid state reaction method with various amount of Na_2CO_3 fluxing agent. The phase composition of obtained materials was studied using X-ray diffraction. The local environment of the activator ions in the structure was examined using X-ray absorption near-edge spectroscopy (XANES). The photoluminescent properties were investigated by emission, excitation and quantum efficiency measurements. Decay times and thermal stability of the powders were determined as well.

Obtained results show that nitrogen and CO partial pressure during the process of synthesis influence the phosphor crystallization. It has been found that usage of Na_2CO_3 flux improves crystallization of the desired phase, enhancement of optical properties was also visible. An optimum concentration of the flux was 5 wt% since exceeding this value resulted in formation of an excessive amount of glassy phase, as well as some evidence of the secondary phase formation.

Romania

Multiferroic properties of Eu-substituted $BiFeO_3$ ceramics

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Keywords: bismuth ferrite, multiferroics, spark plasma sintering

$BiFeO_3$ ceramics exhibit a number of interesting functional properties, however, it presents difficulties when it comes to processing in terms of thermodynamic instability during heat-treatments and reaction kinetics.

The focus of the study was to investigate the influence of Eu substitution in $BiFeO_3$ ceramics upon structural modification and its implications on functional properties. In this work, $Bi_{1-x}Eu_xFeO_3$ (x = 0; 0.05; 0.10; 0.15; 0.20) powders were prepared by sol-gel method. Powder densification was obtained through spark plasma sintering method at 650 °C at an applied pressure of 50 MPa.

The powders and ceramics were characterised in by means of X-ray diffraction, scanning electron microscopy coupled with energy-dispersive X-ray spectrometry. Electrical and magnetic properties were investigated by impedance spectroscopy and, respectively, vibrating sample magnetometry.

Acknowledgments
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Serbia

Spider silk-ceramics composites

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Keywords: spider silk, composite, calcite, ceria, europium, maghemite

Spider silk (SS) has been well known by its extraordinary mechanical properties paired with biocompatibility and possibility of transformation into a various material forms. In this work SS was used as a template for synthesis of three novel biomaterials: SS-calcite composite, SS coated with europium doped ceria nanoparticles, and SS coated with superparamagnetic

γ-Fe_2O_3 nanoparticles. SS-calcite composite was synthesized by simple method using biomineralization approach. The biomineralization process was observed during five days and it was found that two days of treatment were sufficient to obtain pure rhombic-shaped calcite crystals homogeneously dispersed trough 3D spider mesh. With increasing the incubation time, the number and size of crystals increased. SS coated with Eu doped nanoceria was easily obtained by time and cost effective precipitation synthesis procedure. The SS fibers were homogeneously coated with Eu doped CeO_2 nanoparticles with average nanoparticle size of 3 nm due to a great affinity of ceria to oxygen rich functional groups of SS proteins. Eu^{3+} was introduced as an activator ion in ceria crystal lattice and luminescent properties of the obtained composite were investigated by excitation spectra. SS coated with superparamagnetic γ-Fe_2O_3 nanoparticles was obtained with similar precipitation technique. Maghemite nanoparticles were uniformly distributed on the surface of SS fibers and magnetic properties of obtained composite were described. These three novel composites open new possibilities for spider silk based materials in various fields, especially for biomedical application.

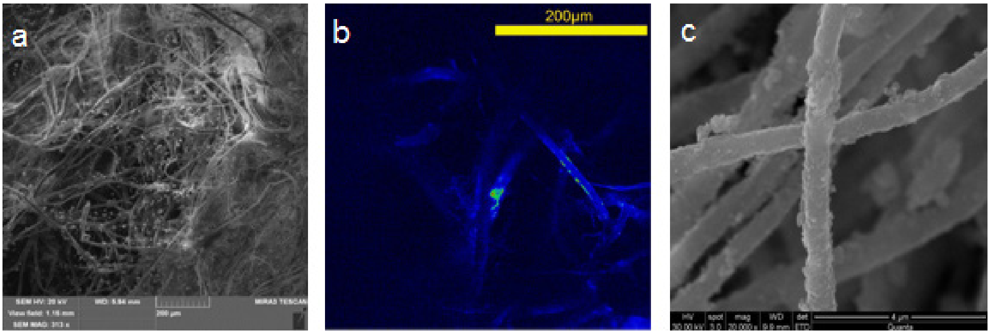

Fig. 1. (a) SEM micrograph of SS-calcite composite; (b) NLM image of SS coated with Eu-doped ceria nanoparticles; (c) SEM image of SS coated with maghemite nanoparticles

Acknowledgment

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Slovakia

The effects of tip sharpness and coating thickness on nanoindentation measurements in hard ceramic coatings on softer substrates by FEM

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Keywords: nanoindentation, tip radius, W-C coating, hardness

The FEM modeling combined with the experimental nanoindentation hardness and indentation modulus depth profiles with the indenter tips with different radii on hard W-C coating/ softer steel substrate with different coating thicknesses revealed strong influence of the tip radius and coating thickness on the shape of hardness and indentation modulus depth profiles and subsequent underestimation of coating property values extracted from the profiles. The effects of tip radius and coating thickness on hardness profiles have the same physical reason - faster penetration of the zone of plasticity into substrate at the same relative indentation depths when indenter tip radius increases and/or coating thickness is reduced. Thus, the validity of the "10% rule" is limited also by the indenter radius. The main parameters critical for proper nanoindentation measurements in the studied W-C coating/steel substrate system include indenter tip radius $\leq$500 nm, coating thickness $\geq$0.5 μm and the ratio of the tip radius to coating thickness $\leq$0.1.

Acknowledgments
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Slovenia

Formation mechanism of PLD-derived $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ thin films

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Keywords: pulsed-laser deposition, PMN-PT epitaxial thin films, Pb-excess, cation stoichiometry

Pb-based materials with $PbZr_{1-x}Ti_xO_3$ (PZT) at the forefront remain to dominate the field of piezoelectrics, as lead-free alternatives are still facing some fundamental and processing issues.[1] Epitaxial thin films of $Pb[Mg_{1/3}Nb_{2/3}]O_3$-$PbTiO_3$ (PMN-PT) exhibit piezoelectric properties superior to PZT.[3] Notably, the preparation of lead-based materials is also not obstacle-free, the main one being the volatility of Pb. In order to realize the full potential of the materials, formation of Pb-deficient pyrochlore inclusions needs to be circumvented. We have shown that, in addition to meticulous control of the growth parameters and compensating for the lead-loss by using targets with an optimal amount of Pb-excess, it is also very important to select the right underlying material, not only in terms of lattice matching, but also to consider the sticking coefficients for the deposited materials. Despite a smaller lattice mismatch with $SrTiO_3$, $LaNiO_3$ was more successful in stabilizing the perovskite phase.

In PMN-PT with three diverse B-site cations it is also imperative to control the ratio of the cations, which is largely affected by the dynamics of the laser plasma plume. In order to understand the material transfer, we examined the composition of the films by means of EDXS analysis using a single-crystal standard. As the process pressure plays a key role in the transfer, films prepared at different pressures were further analyzed with transmission electron microscopy (TEM). We found that increasing the pressure resulted in a substantial improvement of the electrical properties, beyond of what can be achieved by simply avoiding pyrochlore formation. Experiments with oxygen/argon mixtures showed that this effect is not related to oxygen vacancies in the films prepared at lower pressures.

While the formation of ferroelectric PZT has been thoroughly studied and exploited for domain engineering, few studies on relaxor-PT systems can be found in the literature. Understanding the mechanism of the PMN-PT growth process is a powerful tool for improving the quality of the layers, and could furthermore be used to construct guidelines for other multicomponent systems with volatile constituents, including lead-free materials.

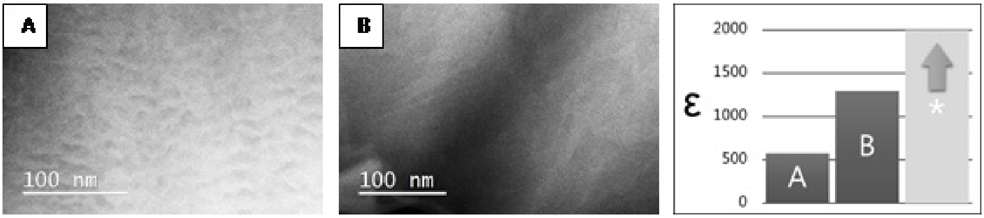

Fig. 1. TEM images (left), revealing the domain structure, and measured permittivity (right) of samples prepared at 0.13 mbar (A) and 0.27 mbar (B). The last column (*) implies the potential for shifting the boarder even further

Acknowledgment

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Spain

Nd^{3+} doped transparent oxyfluoride glass-ceramics

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Keywords: glass-ceramics, crystallisation, laser, optical fibres, neodymium

The growing field of photonics demands the design of new rare-earth (RE)-based optical materials for their use in optical telecommunications, solid-state lasers and other applications. Oxyfluoride glass-ceramics (GCs) are promising RE-hosting candidates due to their good processing and optical properties. They combine the good chemical and mechanical stability of oxide glass matrices with the excellent optical properties of low phonon energy fluoride nano-crystals (NCs).[1]

Among the rare-earth ions, Nd^{3+} has been recognized as one of the most efficient for solid-state lasers in crystals and glasses due to its intense $^4F_{3/2}$-$^4I_{11/2}$ emission at around 1.06 µm. In literature only few works about optical GCs fibres are encountered, making this field of research really attractive.

In this work transparent glass-ceramics bulk and fibres containing LaF_3 NCs and doped with Nd^{3+} ions with concentrations of 0.1–2 mol% have been prepared by melt-quenching followed by a controlled crystallization process.[2] The crystallization mechanism of fluoride NCs has been studied by DTA and HR-TEM showing that the crystal growth is a diffusion-controlled process and the NCs size is limited to 9–12 nm. Further structural characterization was obtained by means of XRD, SAXS and XANES (ESRF facility). A detailed optical characterisation, also supported by EDXS, shows that Nd^{3+} ions in the GCs are incorporated both in the crystalline and amorphous phases. By a selective excitation it was possible to isolate the emission of Nd^{3+} ions in the NCs obtaining a considerable increase in the luminescence efficiency and to reproduce the spectroscopic properties of pure Nd^{3+} doped LaF_3 crystals prepared with complex crystals grow techniques.

Optical fibres with Nd^{3+} doped glass-ceramics core and SiO_2 cladding have been also prepared and studied in detail. The same structural and optical behaviour as for GCs bulk samples has been obtained. It offers the possibility to reproduce in the optical fibres the properties encountered for bulk samples. The first studies show the light propagation into the Nd^{3+} GC core with attenuation of 16 dB/m, similar to other non-silica fibres.

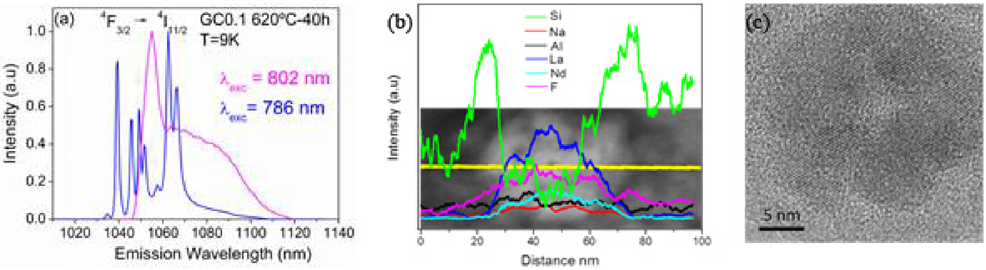

Fig. 1. (a) Selective excitation of GC bulk sample. (b) EDXS analysis in STEM mode and (c) HR-TEM of crystals in a GC fibre

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Turkey

Production of IV-B group boride composite ceramics via SHS

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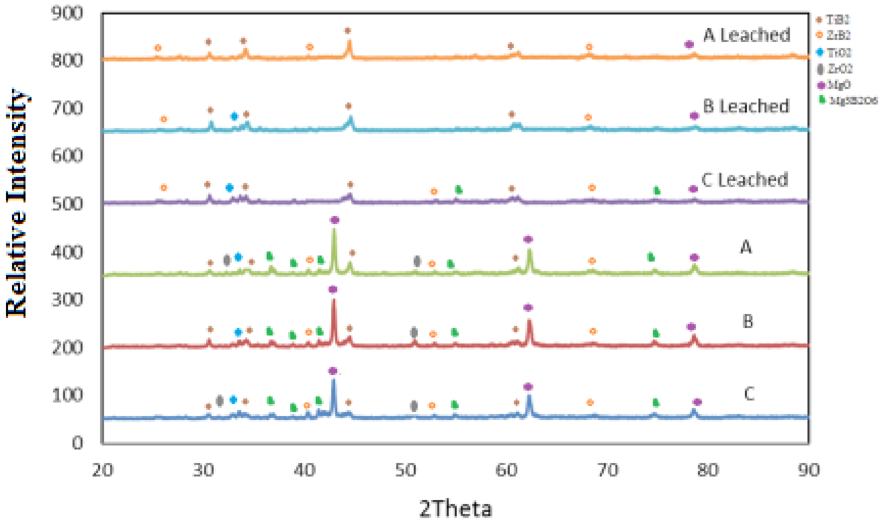
Keywords: SHS, composite ceramics, borides, ZrB_2, TiB_2

TiB_2 and ZrB_2 are important metal borides. They are being used in various industrial areas such as space technology, nuclear industry owing to their unique physical properties such as high thermal/electrical conductivity, high melting point and low density. In the SHS experiments, a mixture of ZrO_2, TiO_2, B_2O_3 and Mg powders were used in order to produce advanced ZrB_2-TiB_2 composite ceramic powders. The metal oxide powders have over 97% purity and 150 µm average grain sizes. In the experimental set, TiB_2-ZrB_2 composite powders were produced by SHS and leaching processes. In this experiment set TiB_2 and ZrB_2 ratios were changed and optimum conditions were determined, initial conditions and results of these series are presented in Table 1.

After the SHS experiments leaching process was carried out, Fig. 1 indicates leached and unleached products of ZrB_2-TiB_2 composite powders.



A%40 ZrB_2 %60 TiB_2 – B%50 ZrB_2 %50 TiB_2 – C%60 ZrB_2 %40 TiB_2

Fig. 1. XRD Graphs of Unleached and leached ZrB_2-TiB_2

Table 1. Initial conditions of ZrB_2- TiB_2 SHS experiments

No	Zr/Ti	$ZrO_{2\ (g)}$	$TiO_{2\ (g)}$	$B_2O_{3\ (g)}$	$Mg_{(g)}$	SHS Product(g)
1	90/10	23.20	2.96	41.90	31.92	90.00
2	80/20	20.64	5.92	40.12	33.33	90.30
3	70/30	18.04	8.89	38.32	34.31	71.90
4	60/40	15.46	11.85	36.53	36.14	71.80
5	50/50	12.89	14.82	34.74	37.54	91.20
6	40/60	10.31	17.78	32.94	38.95	94.90
7	30/70	7.73	20.74	31.20	40.40	57.00
8	20/80	5.15	23.71	29.30	41.72	97.50
9	10/90	2.57	26.67	27.57	43.16	60.30

United Kingdom

A phase diagram study of (Ba,Ca)(Zr,Ti)O_3 piezoceramics from combining structural and functional measurements

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Keywords: lead-free piezoceramics, phase transitions, crystal symmetry, functional properties

Piezoelectric ceramics have been widely used in sensors, actuators and ultrasonic transducers due to their ability to achieve efficient conversion between electric and mechanical vibrations. There is an urgent desire to move to lead-free materials achieving comparable piezoelectric performance to lead-based materials. One of the most promising alternatives is the pseudobinary system $zBa_{0.70}Ca_{0.30}TiO_3$-$(1-z)BaZr_{0.20}Ti_{0.80}O_3$ ((Ba,Ca)(Zr,Ti)O_3) due to the presence of a morphotropic phase boundary (MPB) in the phase diagram, and reports of large piezoelectric coefficients comparable to lead-based systems[1].

However, with the development of the structural study in this lead-free system, there was a debate on the crystal structure of the MPB region: (1) MPB was a single boundary separating the rhombohedral and tetragonal phases[1]; (2) the MPB region was actually a separate orthorhombic (*Amm2*) phase region, bridging the polymorphic transitions between the rhombohedral and tetragonal phases.[2]

In this study, all $zBa_{0.70}Ca_{0.30}TiO_3$-$(1-z)BaZr_{0.20}Ti_{0.80}O_3$ ceramics ($z = 0$-1, with $z = 0.1$ step) were fabricated systematically by conventional solid state method, using pre-calcined $Ba_{0.70}Ca_{0.30}TiO_3$ and $BaZr_{0.20}Ti_{0.80}O_3$ powders as reagents. The phase purity and compositions of sintered ceramics were determined by XRD. The determination of phase transitions was achieved by measuring the temperature dependence of both structural and functional properties on the same batch of ceramics. The temperature dependent dielectric properties and ferroelectric hysteresis loops revealed phase transition points, while the corresponding changes in crystal symmetry were observed by Raman spectroscopy and synchrotron radiation powder X-ray diffraction. A conclusive phase diagram based on *in situ* structural and functional properties measurements is therefore constructed and shown as figure below.

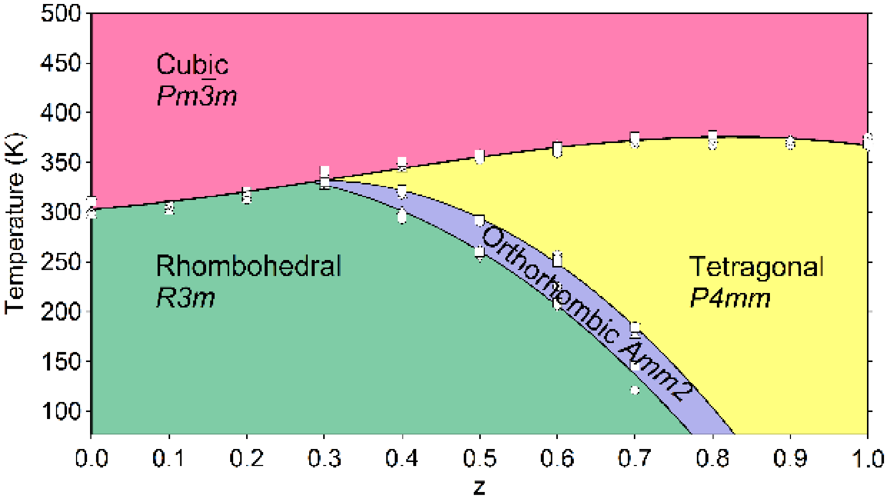

Fig. 1. Combined phase diagram of $zBa_{0.70}Ca_{0.30}TiO_3$-(1-z)$BaZr_{0.20}Ti_{0.80}O_3$ (z = 0-1)

Acknowledgments

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