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PREFACE

Engineering ceramics are the class of materials which steadily occupy a larger portion of the industrial applications. The reason for this positive development is that engineering ceramics found applications which are not only mechanistic. The development of engineering ceramic materials moved during the last two-three decades from the pure engineering applications to the more sophisticated functional applications. The lectures presented at the advanced research workshop Engineering Ceramics 2023 held in the Smolenice castle, Slovak Republic from 7th to 11th May 2023 with the subtitle Ceramics for circular economy fully confirmed this development. The workshop showed new trends in ceramics research as well as in their usage in the society. Orientation of the research to the nano-ceramics, high entropy ceramics, bio-ceramics, ceramics for energy conversion and storage, ceramic sensors and high temperature materials was supported not only by lectures from academia but also by the lectures from industry. In many cases advanced manufacturing was applied for the preparation of ceramic materials and showed a great potential of this processing method. There were also the lectures on the recycling of batteries.

This book of abstracts has an ambition to cover the current trends in ceramic materials research and open these themes to a wider research community. The main intention was to bring together the engineering and functional ceramics community and discuss both the resent achievements in the materials research and their implementation to real applications. The main focus was devoted on materials for improvement of the living standards of population, healthcare, environment, energy conversion and storage, recycling, ultrahigh temperature ceramics, and engineering ceramics armed with their functional properties applied in various fields of development. Book of abstracts should motivate industry for taking an intention to this exciting area of research. The principal aim was to build bridges between academic knowledge and industrial demands in the field of high-tech ceramics and looking together for completely new areas of application for the functional engineering ceramics.

Pavol Šajgalík and Zoltán Lenčéš

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Synthesis and sintering of multi-phase phosphate ceramics

Ľ. Bača[1,2*], T. Sivčáková[1], M. Matejdes[3], M. Horváth Orlovská[1], K. Tomanová[1], Z. Hajdúchová[1], P. Veteška[1], M. Janek[1,4]

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Keywords: phosphate ceramics, synthesis, multiphase ceramics, sintering

Excellent biocompatibility and bioactivity of hydroxyapatite and other phosphates for medical bone reconstruction application is known, however, current trends include also the acceleration of a healing process which should be reflected in the development of designed bioactive materials and material science itself. Material design improvement plays a crucial role in body interactions and successful patient treatment. The application of various doping ions in the hydroxyapatite-based grafts, significantly affects their biological response. In this study three different kinds of phosphate materials were synthesized. Calcium, strontium and barium salts were used for preparation of pure phosphate powders. The phase evolution in the synthesized powders was studied. Moreover, from these individual powders multi-phase phosphate ceramics were prepared to selectively enhance the material properties, its biological response, and bioactivity. The microstructure of sintered phosphate ceramics was studied by scanning electron microscopy and energy dispersive X-Ray analysis.

Acknowledgements

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Extrusion-based 3D printing of polymer-derived silicon (boro)carbide

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Keywords: polycarbosilane, robocasting, fused deposition modeling, silicon carbide, spark plasma sintering

There is a trend toward more performant or competitive materials with the objective to improve the efficiency of actual systems and to repel technological boundaries. Silicon carbide (SiC) can be considered as such a strategic material. It attracted strong interests due to its properties targeted for future materials and technologies especially in aerospace. Inherent difficulties to the traditional techniques for manufacturing such dense materials with a complex geometry can be overcome by the development of new manufacturing approaches on the first hand, and the deployment of synthetic paths where chemistry of materials and ceramic science are combined rationally to process multi-scale complex solid state architectures. This second part can be investigated by the polymer-derived ceramics (PDCs) route, which offers new opportunities in ceramic sciences. The molecular origin of preformed preceramic polymers such as polycarbosilanes plays indeed a major role in the elaboration of 3D SiC-based objects endowed with properties that reach far beyond those of existing materials. Here, the aim of this talk is to introduce two strategies to design 3D SiC-based objects:

1 - Modification of polycarbosilanes with boron molecules in order to produce boron-doped SiC powders that can form robocasting inks to deliver porous 3D SiC-based components then dense 3D SiC-based structures at relatively low temperature through the implementation of an original SPS process.

2 - Tailor the extrusion ability of polycarbosilanes to fit with a pellet-based fused deposition modeling process and form after a two-step heat-treatment process 3D stoechiometric SiC and derived composites parts.

New perspectives of glass recycling: weak alkali activation and cold consolidation of structural and functional components

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Keywords: waste glass, alkali activation, gelation, inorganic polymers, additive manufacturing

The development of valuable new products ('up-cycling') is fundamental for avoiding any landfilling of the glass fractions ('waste glasses') which are normally unemployed, e.g. due to polymer and metal contaminations [1]. The balance between inputs and outputs of supplementary materials, energy and emissions, however, remains challenging. This presentation aims at defining new structural and functional materials by alkali activation treatments at nearly room temperature, triggered by the same chemical composition of waste glasses, possibly mixed with other inorganic (and mainly glassy) residues, with limited external inputs.

Alkali activation corresponds to the extensive dissolution of silicate and alumino-silicate powders, suspended in concentrated aqueous solutions of alkali hydroxides, silicates and aluminates. With a proper balance among constituent oxides (SiO_2, Al_2O_3, alkali oxides), condensation reactions of the dissolution products determine, at nearly room temperature, stable gels, featuring a three-dimensional 'zeolite-like' network structure (resulting from the bridging of SiO_4 and AlO_4 units, the latter being stabilized by alkali ions in the surroundings). In this framework, waste glasses have been widely considered, as providers of SiO_2 and alkali oxides, after dissolution operated by highly concentrated attacking solutions [2]. Very recent findings [3] support the development of far more sustainable alkali-activated materials, operating with diluted alkali hydroxide solutions (molarity not exceeding 3M, configuring a 'weak alkali activation'). Zeolite-gels may result from the surface activation of fine powders of relatively Al_2O_3-rich waste glasses, such as glasses from dismantled pharmaceutical containers, or blends of waste glass with other Al_2O_3-rich residues, such as volcanic materials [4, 5]. Suspensions in alkaline solution undergo consolidation, upon drying at 40-80 °C ('cold consolidation'), simply from the binding of adjacent glass particles operated by the newly developed gels.

Full circularity cannot be achieved without a clear identification of useful target products [1]. Dense and porous structural components are intended to replace building products, such as clay bricks, lightweight concrete, glass and ceramic foams, already obtained by energy- and material-demanding processes. Dense products imply the adoption of glass cullet or other inorganic residues also in form of coarse powders, bound by thin layers of a matrix resulting from fine powders. On the contrary, cellular products rely on the gas incorporation in matrices at the early stages of consolidation, by intensive mechanical stirring and/or decomposition of foaming agents (such as peroxides), possibly supported by surfactants. Finally, cellular materials, not only resulting from foaming, but also from the application of modern additive manufacturing technologies, are considered for their potential in water remediation, in analogy with several alkali-activated systems [6, 7]. In particular, pharmaceutical glass easily leads to 3D scaffolds by direct ink writing of activated powder suspensions, also comprising TiO_2 powders, as photocatalytic secondary phase.

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Machine-learning based processing-microstructure-property relationships for ceramics – Challenges and opportunities

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Keywords: sintered microstructures, ultrafast sintering, machine learning, microstructure sensitive properties

Machine learning approaches are being extensively used in a variety of research fields in material science. Notable success has been demonstrated in using machine learning for the design of chemical composition of both soft and hard materials. However, success has been limited in using machine learning to design microstructures especially for ceramics. We will review the status of machine learning for the design of microstructures and highlight an important limitation for ceramics – lack of high throughput experiments and the lack of large datasets.

We will then focus on laser sintering of alumina, and a machine learning approach to predict the microstructure. Laser sintering allows ultra-fast sintering close to full density within a few tens of seconds. The microstructure and density-grain-size trajectory of laser–sintered alumina is different from those of the furnace–sintered alumina. Therefore, we developed a machine learning (ML) algorithm to predict the microstructure under arbitrary laser power. This algorithm realistically regenerates the SEM micrographs under the trained laser powers. Further, it also accurately predicts the alumina's microstructure under unexplored laser power. Using ultra-fast laser sintering, we fabricated an alumina sample array that contains hundreds of individual sample units, in one laser scan. Due to laser power distribution and the sample location, the individual units in this sample array have different but controllable microstructure. A microstructure-sensitive property, hardness, of the units in the large sample array was measured using micro-indentation. The microstructure of selected units was characterized. Using the results of microstructure and hardness we developed an ML algorithm to not only accurately predict the expected microstructure of alumina of arbitrary hardness, but also predict the hardness based on the observed microstructure with less than 5% error.

High temperature liquid silicates in the processing of ceramics

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Keywords: liquid silicate, high temperature viscosity, vitrification, liquid phase sintering, silicon nitride

This presentation will illustrate the role of liquid phase on the microstructural and mechanical properties of oxide and nitride ceramics.

The appearance of liquids is well known in the processing of traditional ceramics, the densification occurs by vitrification (viscous flow) of a liquid silicate filling all the pore of the green ceramics, followed by the crystallization of secondary phases (e.g. mullite).

The pseudo-structure of glasses at temperatures largely above the T_g will be discussed.

The role of different types of ions (both cations and anions) and of water will be highlighted to show the influence on the physical properties of the liquid.

A good example is the formation of mullite-zirconia composites by reaction sintering. The characteristics of the high temperature liquid formed depend strongly on the nature and amount of sintering additives which on return will influence the microstructure and the mechanical properties.

Another illustrative example in which the presence of liquid is decisive for the material densification is silicon nitride. In that case, the lower amount of liquid phase is insufficient to fill in all the pores but it acts as a path for the species moving during sintering. The necessary high temperature liquid phase to sinter silicon nitride arises from addition of different oxides which forms with the surface silicon oxide a liquid oxynitride silicate. The characteristics of this liquid will depend of a series of parameters: the level of silicon nitride powder oxidation, the type and amount of additives, the presence of different silicon nitride crystal phases, etc. Some examples of silicon nitride (bulk and composite) materials processing and properties will be also shown.

Fracture toughness and strength of (Hf-Ta-Zr-Nb-Ti)C high-entropy carbide microcantilevers

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Keywords: fracture toughness, fracture strength, microcantilever bending, high-entropy carbide, fracture mechanics

High-entropy carbides, as a vast new group of ceramic materials, are novel ultra-high temperature ceramics (UHTCs) of promising mechanical performance that could go beyond the monocarbide systems. In order to develop novel high-entropy carbides with improved fracture resistance, what is the main drawback of UHTCs, it is important to understand the fracture behaviour of their grains and grain boundaries using direct micromechanical testing, which is quite scarce in the literature.

Thus, in the present work, the fracture behaviour of high-entropy ceramic grains in a recently developed (Hf-Ta-Zr-Nb-Ti)C system was investigated during microcantilever bending experiments. The sample was fabricated by ball milling of the component monocarbide powders followed by spark plasma sintering. Microstructure characterization using X-ray diffraction, and scanning electron microscopy with energy dispersive X-ray spectroscopy revealed the formation of a single-phase (Hf-Ta-Zr-Nb-Ti)C system in which the transition metals were practically equiatomic proportions distributed homogenously within the grains, forming a high-entropy material. Microcantilevers were milled out of grains of random orientations using focused ion beam technique, including beams with and without notches. Microcantilever bending experiments, performed in a nanoindenter using a sphero-conical tip, were evaluated using a linear elastic fracture mechanics approach based on the analytical Euler-Bernoulli model and finite element method simulations. It was concluded that beams with no discernible defect on their fracture surface exhibited a fracture strength of 5.5±0.7 GPa and a fracture toughness of 2.44±0.11 MPa·m$^{0.5}$. Although the grain orientation was found to have a negligible effect on fracture strength, the presence of defects, mainly nanopores, significantly decreased the strength down to about 1.5 GPa.

Laser-modified Ti-45Nb alloy's response to bio-environment

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Keywords: Ti-45Nb alloy, high-pressure torsion, laser surface scanning, corrosion resistance, biocompatible properties

Modern hard tissue replacements, used in orthopedic and dental surgery, are most commonly produced using commercially pure titanium (CP-Ti) and the (α+β) Ti-based alloys since their biomechanical compatibility is superior in comparison to other metallic biomaterials. However, these materials are still unable to meet all implantation requirements primarily due to their somewhat limited resistance to degradation in harsh bio-environment and/or presence of cytotoxic elements in their composition that can cause adverse health effects. Therefore, the potential biomedical application of the β-type Ti alloys, which contain non-toxic elements, is considered since these alloys can exhibit lower elastic modulus and improved biocompatibility compared with other Ti-based materials.

The β-type Ti-45Nb (wt%) alloy shows significant potential for application as hard tissue implant material. Nevertheless, an additional improvement of its response in the bio-environment is necessary to maximize its medical applicability. Modification of the alloy's microstructural and surface characteristics through the careful selection of the appropriate processing parameters can ensure the obtainment of favorable alloy biocompatible properties. High-pressure torsion (HPT), as a processing method for the obtainment of ultra-fine grained (UFG) microstructure with higher compatibility with biological systems, and laser surface scanning, as an easy-to-apply surface modification technique for the obtainment of developed bio-active surface, are singled-out as potential methods for the attainment of more durable orthopedic and dental implants.

Having all this in mind, the present research aimed to attain improved corrosive and biocompatible response of the Ti-45Nb alloy in simulated physiological conditions through the alloy grain refinement and the formation of protective surface scales by the alloy combined HPT and laser irradiation processing. For that purpose, the alloy microstructural, electrochemical, and *in vitro* testing were conducted before and after its additional processing. Attained results indicated that the achieved grain size reduction from 2.76 μm to ~200 nm during HPT processing and the appearance of laser-induced morphologically altered and highly oxidized surface led to the significant improvement of the alloy corrosion resistance and the cells-implant interaction. Moreover, an additional increase of the laser pulse energy from 5 mJ to 15 mJ during the alloy irradiation in air led to an increase in oxygen content at the alloy surface from 13.64% to 23.89% accompanied by an increase of cell viability from excellent 127.18% to superior 134.42%. Furthermore, as a result of the controlled alloy microstructural and surface morphological and chemical modifications, the formation of a thick, compact and protective bi-modal external scale, composed of mixed Ti- and Nb-oxides, was enabled in the simulated body conditions. Presence of this surface oxide scale, which consists of inner barrier and outer porous layer, enhanced the alloy's resistance to corrosion deterioration and simultaneously boosted the cell viability and proliferation. Results of the present study showed that the additional HPT and laser surface processing can be successfully utilized to improve the biometallic's response to a bio-environment.

Hierarchically porous 3D printed Sr/Mg-doped hardystonite solid solution by lithography-based ceramic additive manufacturing

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Keywords: additive manufacturing, stereolithography, bioceramics, hardystonite, sinter-crystallization

The advent of lithography-based ceramic additive manufacturing (LCM) technology has enabled new possibilities to produce high-structural resolution ceramic components directly from customized digital models. The present study comprehensively demonstrated the design and manufacturing of triply periodic minimal surface (TPMS; cell dimension: 3 mm × 3 mm × 3 mm, sample dimension: 15 mm × 15 mm × 15 mm, shell thickness: 330 µm, theoretical relative density (TRD): 85%) Sr/Mg-doped hardystonite bioceramic scaffolds using two different slurry formulations. In one strategy, melt-derived Sr/Mg-doped hardystonite ($Ca_{1.7}Sr_{0.3}Mg_{0.3}Zn_{0.7}Si_2O_7$) precursor glass powders (<25µm) mixed with photocurable resin was used for the shaping of high resolution (layer thickness: 25 µm) green bodies followed by controlled sinter-crystallization at 1000°C, in air, to obtain targeted bioceramic phase. Another strategy for achieving the same phase assemblage involves a photocurable engineered silicone suspension consisting of a mixture of silicone resin (SiO_2 yield: 52 wt%) with a photocurable organic resin and active oxide fillers ($CaCO_3$, $SrCO_3$, $Mg(OH)_2$, and ZnO). Both fired scaffolds showed crack-free, sub-micron-sized hierarchically porous, like biomembrane, architecture in addition to macroporosity (designed by digital models) as documented by scanning electron microscopy analysis (Fig. 1). The obtained multiscale porous 3D scaffolds can be useful for bone tissue engineering applications.

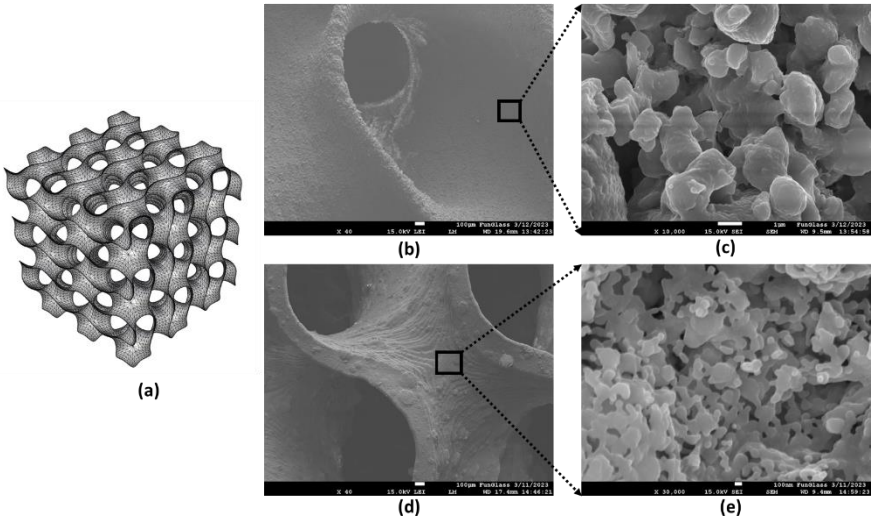

Fig. 1: (a) TPMS CAD model anndd low and high magnification SEM images of fired scaffolds; (b) and (c) from glass powders; (d) a (e) from engineered silicone mixtures

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Deformation and fracture of dual phase high entropy carbide/boride ceramics at nano and micro level

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Keywords: high entropy ceramics, nanoindentation, micropillar/cantilever tests

The deformation and fracture characteristics of recently developed dual phase high entropy carbide/boride ceramics were investigated connected with the processing routes and nano/micro mechanical testing of these systems. The microstructure and fracture characteristics were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) in combination with electron back scattered diffraction (EBSD) and transmission electron microscopy (TEM). Atomic structure and local chemical disorder was determined by means of scanning transmission electron microscopy (STEM) in conjunction with energy dispersive X-ray spectroscopy (EDS). Depth-sensing nano-indentation of individual grains of bulk systems has been applied to study the nano/micro hardness and deformation characteristics. During micro-cantilever tests in bending deformation and fracture characteristics of individual grains and grain boundaries have been investigated. The active slip systems for individual systems have been recognized. The bending strength of micro-cantilevers was strongly dependent on the character/size of the present fracture origins which were in all cases in nano-metric range. The fracture toughness of the individual grains and grain boundaries were investigated, too.

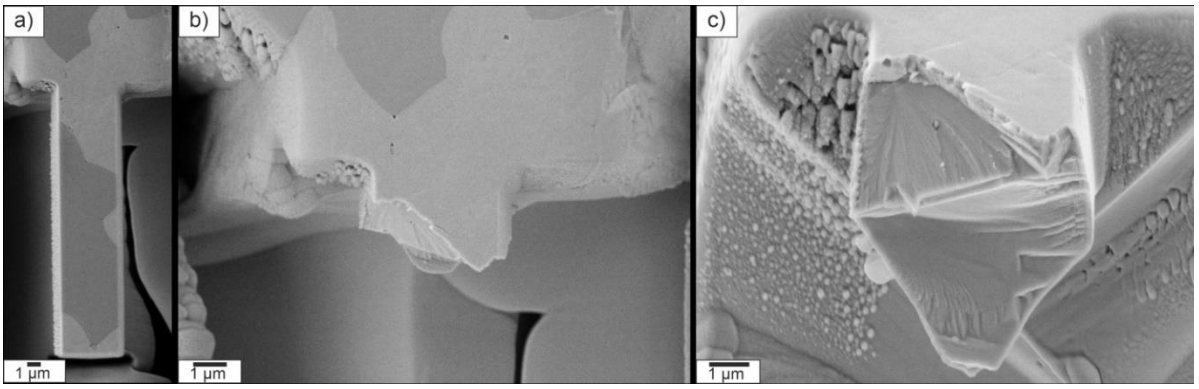

Fig. 1: Fracture of dual phase high entropy system with a fracture origin in carbide grain in the form of nano-pore, SEM

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Silicon nitride ceramics with improved dielectric breakdown strength and AI - determination of the engineering properties

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Keywords: silicon nitride, dielectric breakdown strength, microstructure, deep learning

Silicon nitride (Si_3N_4) was prepared through a reaction-bonding technique using yttria and magnesia as sintering additives, followed by post-sintering of the nitrided compacts at 1850 °C under a pressurized nitrogen atmosphere. Effect of various holding time on microstructures and dielectric breakdown strength (DBS) was investigated. The porosity of the resultant Si_3N_4 clearly decreased with increased holding time, and the full densification could be achieved at the holding time over 6 h. The maximum grain size of rod-like β-Si_3N_4 increased from 45.1 to 154.7 μm with increased holding time from 6 to 48 h. The DBS values were clearly varied by thicknesses (0.30, 0.20, 0.10, and 0.05 mm) of the Si_3N_4 substrate, in which the DBS of the thick substrates (0.30 mm) showed little variation from 35.4 to 47.0 kV/mm, regardless of the holding time, while that of the thin ones (0.05 mm) substantially decreased from 99.5 to 9.8 kV/mm with increased holding time from 6 to 48 h. Those phenomena were significantly correlated with rod-like grains varied by the holding time, because some large-elongated grains could span the substrate thickness-wise throughout.

In a separate work, we conducted artificial intelligence (AI) determination of the fracture toughness of Si_3N_4 evaluated directly from their microstructural images via convolutional neural network (CNN) models. Totally 156 data sets containing microstructural images and relative densities as input feature quantities (IFQs) were used for the AI-determination, in which the data sets were divided into two groups: One was used for training, resulting in the creation of regression models, and the other group was used for testing the validity of the created models. The determination coefficient showed approximately 0.8 even when using only the microstructures as the IFQs and was further improved when combining with the relative densities. It was revealed that the fracture toughness of Si_3N_4 ceramics was well evaluated from their microstructures.

Ultra-high temperature ceramic matrix composites for reusable hot components in aerospace field

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Keywords: ultra-high temperature ceramic composite (UHTCMC), pitch-derived carbon fibres, high-temperature tensile strength, residual thermal stress (RTS), nanoindentation

UHTCMCs represent a novel class of materials that couples the high oxidation resistance of UHTCs to the damage tolerance of CMCs. The coupling of these properties has the potential to enable the development of hot components that can withstand repeated reentry and propulsion stages in support of Net Zero ambitions. Recently, hot-pressed UHTCMCs have demonstrated fracture toughness above 14 $MPa \cdot m^{1/2}$, which is a significant improvement compared to conventional bulk UHTCs (typically 3.5 $MPa \cdot m^{1/2}$), and excellent resistance to ablation and erosion at temperatures up to 2500-3000 °C. In this talk, we will explore the correlations between process, microstructure, and structural properties of ZrB_2-based UHTCMCs produced via slurry infiltration followed by pressure assisted sintering. Starting with a detailed microstructure analysis, we will focus on mechanical behaviour observed through tensile and flexural tests up to 1800 °C, as well as indentation tests ranging from the micro-hardness (Vickers, 10 kg) to the nano-hardness (Berkovich, 10 g). Finally, the presented microstructure features and mechanical properties allow us to highlight the unknown behaviours and the novel findings on these newly developed materials.

Aluminate glasses as precursors for a low-temperature preparation of oxide ceramics and ceramic composites

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Keywords: aluminate glass, translucent ceramics, hot pressing, spark plasma sintering, eutectic microstructure

Aluminate glasses represent a specific group of materials which, in terms of the conventional rules of glass forming and structure, contain no typical glass former. Their structure is also specific, comprising AlO_x polyhedral structural units, which can be four-, five-, or six-coordinated, and connected not only through their vortices, but also through their edges and faces. Such structure favours their fast crystallization at temperatures < 1000 ºC yielding crystalline aluminates, such as YAG, by simple rearrangement of the glass structural units. This, in turn, leads to difficulties with their preparation, which requires fast cooling rates to avoid crystallization. One of the methods of their preparation is flame synthesis: the glasses are prepared in the form of microspheres, which can be sintered by viscous flow to obtain bulk glasses, glass-ceramic or ceramic materials.

The lecture gives an overview of our recent research activities in the processing and characterization of aluminate glasses in the system Y_2O_3-Al_2O_3, also with the addition of small amounts of various additives, which modify their optical and mechanical properties. Viscous flow pressure assisted sintering (hot pressing or spark plasma sintering) under controlled conditions offers an interesting opportunity to prepare aluminate glasses in bulk. This is demonstrated by the preparation of a translucent bulk glass of the YAG composition at the temperature as low as 900 ºC, translucent YAG polycrystalline ceramics at the temperature of 930 ºC, and by the preparation of Al_2O_3-$Y_3Al_5O_{12}$ and Al_2O_3-$Y_3Al_5O_{12}$-ZrO_2 composites with eutectic microstructures at the temperatures < 1600 ºC, and with interesting mechanical properties (Vickers hardness (*HV*), 18.1 ± 0.7 GPa and indentation fracture resistance of 4.9 ± 0.3 MPa·$m^{1/2}$).

Acknowledgements

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Characterisation of tantalum nitride coatings produced by a novel high target utilization sputtering (HiTUS) method under different nitrogen flow rates

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Keywords: tantalum nitride coatings, Mg-Zn-Y-Al alloy, LPSO phases, corrosion, electrochemical method

This work aims to characterise tantalum nitride (Ta-N) coatings deposited on Mg-LPSO alloy using a novel method called high target utilisation sputtering (HiTUS). The coatings were deposited on the Mg-Zn0.9-Y2.05-Al0.25 (at%) alloy extruded at 350 °C at the extrusion ratio R=10 and extrusion rate of 2.5 mm·s^{-1}. Coatings were deposited under different values of nitrogen flow rates: 0, 2, 4, 6, and 8 sccm (standard cubic centimetres per minute). As a reference, the uncoated extruded Mg-Zn0.9-Y2.05-Al0.25 (at%) alloy was used.

The main scope of this work was to analyse the coatings' structure and how the coatings produced under various parameters might change the corrosion resistance and mechanical properties of the extruded Mg-LPSO alloy.

To achieve the goal of the research, optical microscopy observations (Zeiss AxioVision) of the coatings followed by the analysis of the coatings' structure and thickness measurements were done using scanning electron microscopy and focused ion beam (SEM/FIB, Hitachi DualBeam NB5000). The surface roughness of the coatings was measured using an optical profilometer (Sensofar S Lynx). The corrosion behaviour of the extruded alloy and coated samples were investigated in a water-based sodium chloride solution (0.1 M NaCl) at room temperature. The electrochemical testing consisted of open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation measurements. The corrosion rate was calculated using the hydrogen release method, and the surface observations were performed after 1 hour of immersion tests in 0.1 M NaCl. Mechanical properties were examined using a scratch tester (CSM instruments Revetest).

The results of this study show that:

- Nitrogen-free tantalum coating as a complete metallic coating undergoes accelerated corrosion at a higher level than the reference sample (Mg-Zn-Y-Al);
- Localised corrosion was observed on the ceramic coatings produced under various values of nitrogen;
- The best corrosion resistance and the highest mechanical properties exhibited the coating with a nitrogen flow of 6 sccm.

Acknowledgements

This research was financed by the National Centre for Research and Development in Poland under the project "Development of Advanced Magnesium Alloys for Multifunctional Applications in Extreme Environments" (V4-JAPAN/2/15MagMAX).

Improved decay performance of Si/Gr anodes using water-soluble functionalized alginate binders

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Alloying-type Si-based anodes have higher capacity than intercalation-type commercial graphite anodes. However, dramatic capacity decay during the first cycles due to the huge expansion of silicon particles ($\Delta V > 300$ %) is the main problem for the commercialization of silicon-based anodes. Binders play important role to provide better integrity for a longer lifetime. Mechanical properties of binders should meet requirement to allow expansion and shrinkage during repeating cycles. In this study, water-soluble functionalized alginate binders were synthesized to stabilize the structure and improve the capacity decay performance. Binders were characterized by mechanical testing, electrolyte uptake test, and FTIR analysis. Anode slurries were prepared in deionized water by addition of silicon-graphite powders (20:80 wt%) as active material, synthesized binders, and carbon as a conductive agent. Galvanostatic charge-discharge tests were carried out between 0.01-1.5 V vs. Li/Li^+ potential window at different current densities from 0.1 to 2 C-rate. Cycling voltammetry was performed at 0.1 mV/s. It was found that the newly-synthesized binders (s-Alg and d-Alg) have lower electrolyte interaction and swelling values compared to commonly used CMC/SBR binder. Moreover, positive correlation was established between the electrolyte uptake, the mechanical properties and the discharging capacities.

Acknowledgements

The work was supported by APVV-19-0461 and VEGA 2/0167/22 grants.

Effect of sintering additives on thermal conductivity of silicon carbide - graphene composites

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Keywords: silicon carbide, graphene, thermal conductivity, sintering additives, annealing

Almost fully dense (RD ≥ 98%) silicon carbide - graphene composites with two different type of sintering additives (Y_2O_3–Sc_2O_3 or Y_2O_3–Al_2O_3) and with amount of graphene (graphene nanoplatelets and graphene oxide) in the range from 1 to 5 wt. % were sintered in rapid hot press (RHP). Thermal conductivity as a function of amount of graphene, its orientation in SiC matrix and also effect of sintering additives and effect of annealing were investigated.

The highest thermal conductivities were obtained at room temperature in parallel direction to GNPs for annealed SiC-Y_2O_3–Sc_2O_3 material with 1% GO (λ = 238 W/m.K) and 5% GNPs (λ= 233 W/m.K).

The obtained results show that homogeneous distribution of GNPs in SiC matrix, appropriate choice of sintering additives, preferential orientation of graphene, rapid hot-pressing and annealing of samples at 1800°C for 6 h in N_2 atmosphere allows to obtain SiC ceramics with very high thermal conductivity.

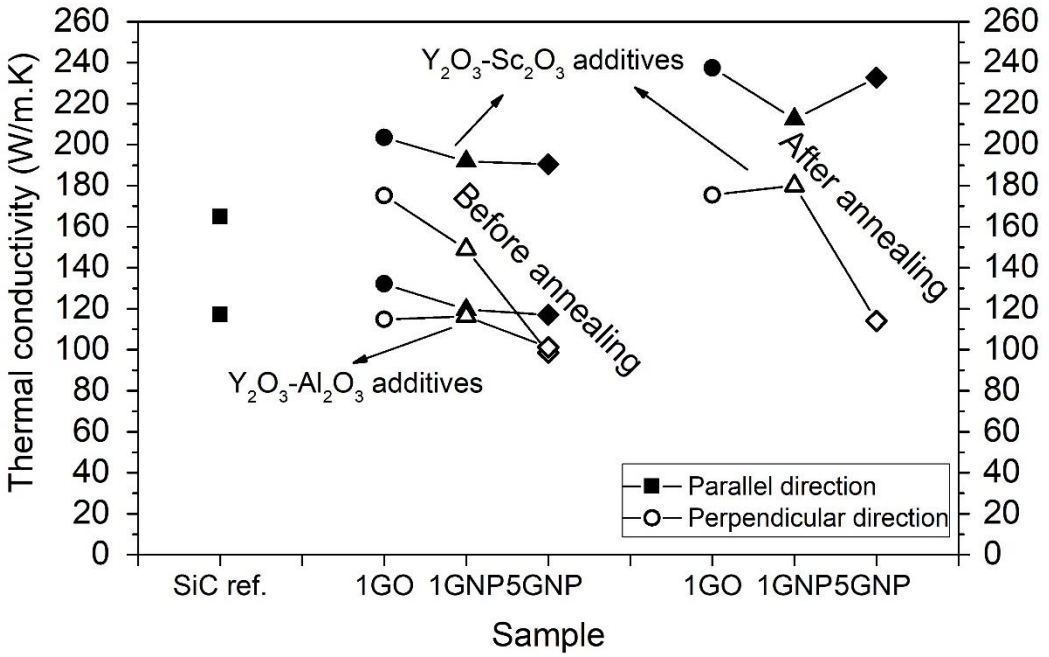

Fig. 1: Thermal conductivity of SiC-Y_2O_3-Al_2O_3 composites and SiC-Y_2O_3-Sc_2O_3 composites before and after annealing with different amount of graphene

Acknowledgements

This work was supported by the Slovak grant VEGA 2/0007/21.

Optimisation of oxyacetylene torch conditions on the surface of $Si_3N_4 – Y_2O_3$ composites

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Keywords: silicon nitride, rare earths oxides, oxyacetylene flame

Dense Si_3N_4 ceramics were prepared by rapid hot pressing (FAST – field assisted sintering technique) at 1700 °C and 50 MPa pressure for 7 min. Yttria as sintering additive was chosen because of the good oxidation resistance of Si_3N_4-Y_2O_3 at high temperatures. Surface of the ceramic substrate was modified by oxyacetylene torch by means of formation of protective layer on the surface based on yttrium silicate. The character of damaged area and surface morphology was studied in dependence from the reached temperature on the surface of substrate, the dwell time on the annealing temperature, gas flow rate and the ratio of oxygen /acetylene gases. Finally, the influence of the mentioned parameters on the degree of oxidation of surface layer, its thickness, porosity and phase composition will be evaluated.

Acknowledgements

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An eco-friendly fabrication of TiO_2 micro- and nanoarrays on 3D printed titanium alloy of contribution

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Keywords: Ti-6Al-4V alloy, surface modification, deep eutectic solvent

Ti-6Al-4V alloy is recognized as the most common and frequently used α + β titanium alloy due to the unique combination of properties such as high strength, low density, high fracture toughness, excellent corrosion resistance and good biocompatibility. It should be noted that creation of micro and nano heterogeneous topographies on Ti-6Al-4V alloy surfaces by the mentioned methods is of particular interest and significance. It is widely accepted that hierarchically interconnected micro and nano structures determine the superior catalytic properties of titanium and its alloys and provide excellent biocompatibility and osseointegration of Ti based materials for prostheses and implants. In the matter of creating micro and nano rough surfaces, the method of electrochemical treatment can be considered as one of the most promising and advantageous due to the numerous benefits: high efficiency, low coast, simplicity of application, short time of procedure, absence of contamination and possibility to be used for parts with complex geometry. The electrochemical surface treatment of pure titanium and Ti-based alloys generally performs in acidic based electrolytes containing H_2SO_4, HCl, HNO_3, H_3PO_4, HF or NH_4F, $HClO_3$, ethylene glycol, n-butanol, methanol, hydrogen peroxide. Such aggressive chemical compositions are justified by the need to dissolve a stable protective oxide layer on the surface of titanium and its alloys. It is obvious that the search for more environmentally friendly alternatives does not lose its relevance.

In this work a novel eco-friendly fluoride-free method of TiO_2 nanotube fabrication was proposed. It was demonstrated that TiO_2 micro- and nano-array can be created on 3D printed Ti-alloy substrates by anodic galvanostatic and potentiostatic treatment in ethylene glycol containing deep eutectic solvent (DES) without fluoride containing additives. It was shown that electrochemical dissolution process of Ti-6Al-4V in DES is creating organized arrays of amorphous non-uniformly growing tubular units based on Ti and O, Fig. 1. The mean outer diameter of tubes was evaluated to be ~ 75 nm and the inner diameter corresponds to ~ 20 nm. The micro-sized pattern looks like micropits ~ 25 μm in diameter and ~ 5 μm in depth, uniformly distributed over the entire surface of the treated samples. Such surface design can be successfully used to significantly increase the surface area of Ti samples and improve its catalytic properties. Fluoride-free electrolyte can be proposed as environmentally friendly alternative to the toxic and aggressive common electrolytes.

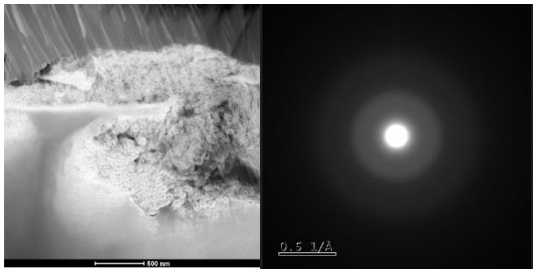

Fig. 1: HAADF STEM micrograph, corresponding diffraction pattern on Ti-6Al-4V alloy after electrochemical surface treatment in DES

Acknowledgements

This work was financially supported by the Slovak Grant Agency (project APVV-20-0322), Slovak Republic and by Research & Innovation Operational Programme funded by the ERDF (ITMS project code 313021T081).

Band-gap engineering of perovskites for photovoltaics

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Keywords: methylammonium lead halide (MAPI), semiconducting oxides, band-gap engineering, novel perovskite oxides

Methylammonium lead halide perovskites are one of the emerging photovoltaic materials with very high efficiencies in thin film solar cells. While prospective cheap and easy processing could be advantageous, fundamental problems like their use of toxic materials and degradation issues motivate to seek for new efficient, non-toxic and stable absorbers for solar cells.

Solar cells based on perovskite oxide absorbers achieved recently up to 8 % power conversion efficiency and promise at the same time intrinsic long-term stability. Current studies deal with very few suitable transition metal oxides even though the field offers a wide range of material combinations, but it is challenging to find narrow band-gap semiconductors among metal oxides.

The present study investigates the influence of substituting the B-site cation on the properties of ABO_3-perovskites. We will show that fundamental requirements for absorbers such as band gap in the visible light, higher absorption coefficient and sufficient charge carrier mobility can be achieved. It is demonstrated that the band-gap can be modified systematically by introducing Cu^{2+} as well as penta- or hexavalent transition metals on the B-site. Semiconducting properties due to these substitutions are analysed by preparing materials via solid state reactions to process thin films grown with several hundred nanometres thickness onto transparent conductive oxides by pulsed laser deposition.

Study of structural & optical properties of high entropy oxide ceramics with fluorite structure

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Keywords: configurational entropy, functional ceramics, high-entropy ceramic, solid state sintering, optical properties

A new class of ceramics, known as high-entropy oxides (HEOs), has generated considerable research interest since the first report was published in 2015. The HEO concept provides access to unexplored regions in the multi-element phase diagram. It has been shown that oxide ceramics containing rare earth in equimolar ratios have a strong tendency to crystallize in single-phase structures stabilized by high configurational entropy. Due to their wider bandgap, rare earth oxides with high entropy are considered potential materials for various applications such as laser hosts, scintillating devices, multi-wavelength phosphors, and luminescence applications. This work describes the single-phase synthesis of a multicomponent rare earth system mixed in an equimolar ratio containing combinations of CeO_2, La_2O_3, Sm_2O_3, Pr_2O_3, Y_2O_3, Dy_2O_3, Gd_2O_3, and Nd_2O_3. For preparing the proposed HEOs, a novel, flame synthesis method was used, combined with high-energy ball milling. This approach facilitates the preparation of single-phase HEOs by controlled crystallization of the microspheres produced by flame synthesis at temperatures below the sintering temperature. The results suggest that the stabilization of the structure depends not only on the entropy effect but also on the type of cations, the synthesis method, the heating and cooling rates, and the crystallite size. The effects of composition, sintering atmosphere and cooling rate on phase formation were studied. The system shows simple cubic or monoclinic structures obtained by slow cooling. This confirms that the rare earth oxides follow a different process of structure stabilization than the highly entropic transition metal oxides. The microstructure of the material was investigated by SEM, EDS, and XRD methods. Photoluminescence results suggested the potential application of high-entropy ceramics as multi-wavelength emission phosphor ceramics.

3D printing of hydroxyapatite augments from composite filaments

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Keywords: 3D printing, hydroxyapatite, ceramic scaffolds, fused filament fabrication, composite filaments

Synthetic hydroxyapatite is known for its osteoconductivity but has the lowest water solubility among the calcium phosphate substances. At the same time, sintered hydroxyapatite has relatively low mechanical strength and poor fracture toughness, that strongly limit its application for direct bone reconstruction applications. Therefore, its modification to improve the mechanical properties while preserving stimulation of cell activity behavior is needed. The continuous research motivation is driven by a growing number of patients having bone defects with critical size e.g. in alveolar areas, demanding novel clinical scenarios. Combined with personalised 3D scans, suitably designed material may enhance the operation success rates and/or minimizes the post operation complications. Fused filament fabrication as low-cost material forming technology is promising for onsite production of desired augments or bone scaffolds, requiring market-established printable composite materials.

In the present study, composites with a solid content of hydroxyapatite at the level of 50 wt% were modified with sintering additives to improve the mechanical properties of the final augment parts. In the first step, the workability of various composite filaments has been tested. Filament printability has been then verified using a commercial 3D printer. We have found that the addition of some specific sintering additives can in lead to remarkable reduction of mixture workability or even making it impossible to prepare filaments. The selected properties of successfully manufactured filaments and 3D printed testing scaffolds are further compared.

Acknowledgements

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Improved optical and laser properties of Nd:Y_2O_3 ceramics by controlling hot - pressing schedule

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Keywords: transparent, laser, ceramics, defects, absorption

The highly transparent and high-performance Nd:Y_2O_3 laser ceramics was successfully fabricated by controlling the hot-pressing schedule. It is the very first time to evidently establish the correlations of optical properties, laser performance and characterizations of laser medium. The important conclusions are as follows:

- The absorption caused by the point defects in polycrystalline transparent Nd:Y_2O_3 ceramics was a more dominant factor of optical extinction than the pore scattering at a short range wavelength of 200 to 400 nm and this was firstly demonstrated obviously with an experimental corroboration. Finally, the higher transmittance level and laser performance of Nd:Y_2O_3 ceramics compared to those of the commercial one were revealed.

- The laser performance of transparent Nd:Y_2O_3 ceramics was highly dependent not only on the transmittance level with emission wavelength at about 1 μm but at a short wavelength, resulting from the energy levels of point defects in band gap.

Origin of resistivity anomaly in La-doped $BaTiO_3$ synthesized with one-pot hydrothermal synthesis

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Keywords: $BaTiO_3$, La doping, dielectric properties, electrical conductivity, thermal conductivity

$BaTiO_3$ ceramics are known to exhibit insulating or semiconducting behaviour depending on the presence or absence of impurities. However, the behaviour of lightly doped $BaTiO_3$ with trivalent rare-earth elements on the A-site is still not fully understood due to the occurrence of a room-temperature resistivity minimum, which is a longstanding problem. Understanding the behaviour of $BaTiO_3$ ceramics is important for the development of new $BaTiO_3$-based materials for a variety of applications, including electronic devices, capacitors, and sensors. Therefore, further research is necessary to elucidate the underlying mechanisms of the room-temperature resistivity minimum in lightly doped $BaTiO_3$ with trivalent rare-earth elements. Here, we have synthesized a set of La-doped $BaTiO_3$ samples with varying La dopant content (0.1 ~ 0.5 at.%) via a one-pot hydrothermal synthesis. La is chosen as it is a well-known A-site doping element in $BaTiO_3$. La doping effects on electrical, thermal, and dielectric properties of $BaTiO_3$ are investigated. Abrupt changes in electrical, thermal, and dielectric properties of La-$BaTiO_3$ are observed near La dopant content of 0.36 at.%. The change in the doping mechanism near La doping content of 0.36 at.% is also analyzed with X-ray photoelectron spectroscopy (XPS). Formation of Ti vacancies for La-doped $BaTiO_3$ with a dopant content greater than 0.36 at.% is found responsible for the resistivity anomaly in $BaTiO_3$ which was also manifested in thermal and dielectric properties.

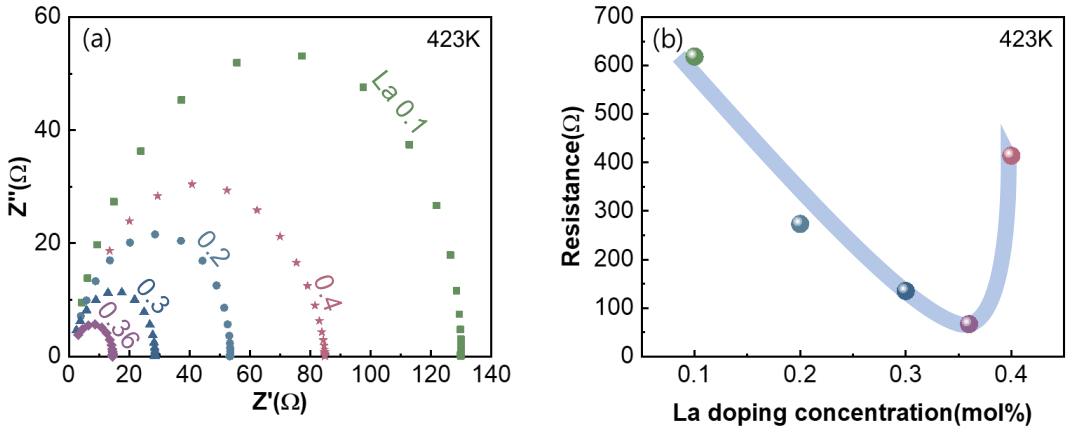

Fig. 1: (a) Complex impedance plot of La-doped $BaTiO_3$ samples ($0.1 \leq$ La doping content in at. % ≤ 0.4) at 423 K and (b) electrical resistance of $(La_xBa_{1-x})TiO_3$ samples ($0.1 \leq x \leq 0.4$) at 423 K estimated from the complex impedance measurement in (a)

Effect of boron source on mechanical, thermal and electrical properties of pressureless solid-state sintered silicon carbide ceramics

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Keywords: silicon carbide, pressureless solid-state sintering, electrical properties, thermal conductivity

The effects of boron source (B, BN, and B_4C) on thermal, electrical, and mechanical properties of pressureless solid-state sintered silicon carbide ceramics were investigated. A high relative density of 99.9% was successfully achieved for all specimens using an appropriate additive composition and optimum sintering conditions. As revealed in this study, the boron source greatly influenced the properties of SiC ceramics. The SiC ceramics sintered with B and B_4C additives showed higher electrical and thermal conductivities and flexural strength compared to those with BN additive at the same density level. The presence of intrinsically weak BN grains in the grain boundaries increased the fracture toughness slightly while the electrical and thermal conductivities of the ceramics were decreased. The electrical resistivity, thermal conductivity, and flexural strength of prepared SiC ceramics varied in the ranges of 3.2×10^4–1.6×10^6 Ω·cm, 72.4–147.5 $W\cdot m^{-1}K^{-1}$, and 386–545 MPa, depending on the boron source.

Graphene-platelet reinforced titanium diboride ceramics: structure, mechanical properties and wear resistance

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Keywords: titanium diboride, graphene platelets, structure, mechanical properties, wear resistance

TiB_2 – SiC, TiB_2 – SiC - GNPs, and TiB_2 –GNPs composites were prepared using field assisted sintering technology at 2100°C in the argon atmosphere. The influence of the silicon carbide and/or graphene platelets addition on microstructure development, basic mechanical properties (hardness, flexural strength, Young´s modulus, fracture toughness), and tribological properties (coefficient of friction μ, specific wear rate) has been investigated.

Two types of graphene platelets with different size (nanosized and microsized) were used. The addition of GNPs has a positive effect on fracture toughness and flexural strength but negative on the hardness. According to the results for optimal strength and fracture toughness the amount of GNPs additive should be 2 wt.% for both types of additives. The highest strength was measured for the system TiB_2 with 2 wt.% GNPs and the highest fracture toughness for the system TiB_2 with 10 wt.% GNPs. Increasing amount of both GNPs has a positive influence on wear characteristics of the composites due to the described wear mechanisms like mechanical wear and tribochemical reaction. The low coefficient of friction ($\mu < 0.5$) at GNPs content above 5 wt.% and the very low specific wear rate 10^{-7} $mm^3/N{\cdot}m$ at 5 N and 10^{-6} $mm^3/N{\cdot}m$ at 50 N are probably due to the formation of zones of tribochemical layer (SiO_2 -TiO_2-C based tribofilm) on the worn surfaces.

Acknowledgements

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UHTCs composities based on the boron carbide with intermetallic additives from Ti-Si system

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Keywords: boron carbide (B_4C), intermetallics, SPS, UHTCs, high pressure high temperature (HPHT)

Composites based on boron carbide (B_4C) have attracted considerable attention because of their outstanding physical and chemical properties. As part of this research, by using appropriate reagents, including boron carbide, carbon, and selected intermetallic compounds mixed in appropriate molar proportions, it was possible to obtain a composite consisting of 99% reacted starting materials. TiB_2-TiC-SiC-intermetallic (TiSi, $TiSi_2$, or Ti_5Si_3) composites were prepared by three different methods: pressureless sintering, hot pressing, and spark plasma sintering (SPS).

Different sintering temperatures are used for each consolidation process. For free sintering, the synthesis was conducted at 1650°C-1750°C, for hot-pressing and SPS it was possible to lower the synthesis temperature to 1500-1550°C and 1400-1450°C, respectively.

The mechanism of potential chemical reactions is related to the type of intermetallic phase used; surprisingly, the simple and lower-temperature method according to the invention [1] is possible only because of the use of a phase in the form of intermetallic (TiSi, $TiSi_2$, Ti_5Si_3) [2] in combination with the appropriate molar proportions of the reactants used. This process eliminated the carbon from the final composition of the material. This was an unexpected effect, particularly when using a commercial B_4C substrate, which typically contains carbon in the form of graphite. The obtained high-temperature refractory TiB_2-TiC-SiC composite showed high mechanical strength and fracture toughness [2]. The chemical reactions that occur during sintering are highly effective. Almost 99% of the initial phases decomposed and allowed the formation of new TiB_2 and SiC phases, which were well-densified at relatively low temperatures. The TiC phase was formed only when no boron was present in the system during sintering. Hence, with the addition of Ti_5Si_3, when there is a significant amount of Ti in the system and a lack of boron, a small amount of TiC is formed [3]. When assessing the sinterability of materials in the case of the free sintering method, it can be concluded that the amount and type of additive added have an impact on lowering the sintering temperature.

Acknowledgements

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Room temperature curable ZrB_2-SiC based ultra-high temperature ceramic coatings for C/C composites for extreme environments

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Keywords: UHTCs, extreme environments, composites, coatings

Advancements in high temperature oxidation and ablation resistant coating technologies for ceramic matrix composites (CMCs) will enable aerospace agencies and commercial entities to develop competitive civil space transport and communication systems. Among CMCs, carbon/carbon (C/C) composites are considered as one of the most promising materials in structural applications owing to their excellent thermo-mechanical properties at high temperature at a relatively low cost. However, C/C composite offer restricted applications owing to its high susceptibility to oxidation at temperature > 400 °C. High temperature oxidation and ablation resistant coating technologies with ultra-high temperature ceramic (UHTC) have exemplified remarkable oxidation and ablation resistance as compared to uncoated C/C composites. UHTC coatings for C/C are commonly prepared through chemical vapor deposition, plasma spray and thermal spray techniques. These state-of-art fabrication techniques besides very complex and laborious are also cost-intensive limiting the wide scale applications.

In this work, we present precursor derived novel ZrB_2-SiC based UHTC coatings as thermal protection system (TPS) for C/C composites. The ZrB_2-SiC based UHTC coating was cured at room temperature and negate the requirement of any additional pyrolysis step as in the case of polymer infiltration and pyrolysis technique. Preliminary high temperature oxidation test on ZrB_2-SiC based UHTC TPS coatings on C/C composite at 1600 °C for 1 h demonstrated remarkable oxidation resistance capability with intact TPS coating. Furthermore, the C/C substrate was also protected by the formation of self-healing $ZrO_x.SiO_y$ glassy ceramic. The ablation behaviour of UHTC coated C/C composite using oxy-acetylene flame at 1800 °C for various time durations have shown promising potential. The phase evolution, stability and morphology have been investigated via diffraction, microscopy and spectro-chemical techniques. The study exemplifies a novel way of new cost effective UHTC coating that can survive in extreme environments.

Thermal conductivity: a tool to assess neck formation and follow up of densification of hydroxyapatite

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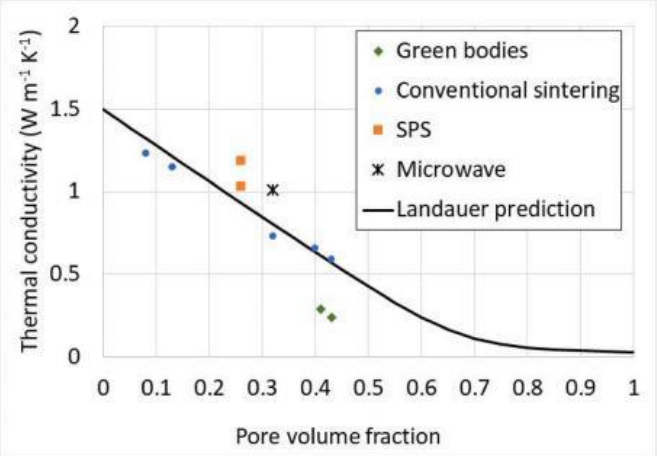
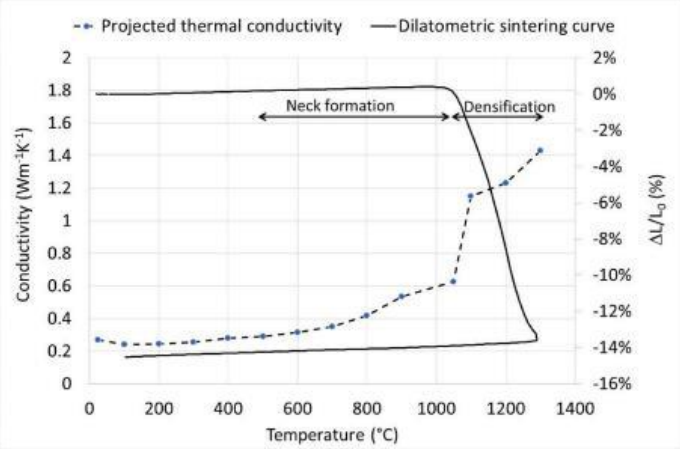
Keywords: thermal conductivity, porous hydroxyapatite, neck formation, initial stage, final stage

Neck formation and densification during sintering have strong effects on the thermal conductivity of a porous ceramic body. This has been described by an analytical model using grain conductivity, grain size, pore fraction and particle – particle contact area as input parameters. It has been tested on hydroxyapatite ceramics sintered with conventional, microwave and spark plasma techniques. The green bodies containing at least 40% porosity yield conductivity values in the range 0.24–0.29 $W \cdot m^{-1} K^{-1}$. Neck formation in the initial stage of sintering increases the values to above 0.5 $W \cdot m^{-1} K^{-1}$. Further increase is achieved by densification, well described by Landauer's relation as part of the model with close agreement to experiment for hydroxyapatite ceramics containing 40 to 5% porosity. An evaluation of thermal conductivity for 100% dense hydroxyapatite gives a value of 1.5 $W \cdot m^{-1} K^{-1}$ which is almost constant between room temperature and 900 °C.





Reactive sputtering of multicomponent transition metal nitride coatings: structure formation and mechanical properties

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Keywords: transition metal nitrides, reactive sputtering, DC magnetron sputtering, HiTUS, nanoindentation, DFT

High entropy metal sub-lattice stabilized nitride coatings based on multicomponent refractory transition metals (TM = Ti, Nb, V, Ta, Zr, Hf**)** are promising candidates for extreme conditions due to their high thermal, mechanical and corrosion properties. The aim of the current work was to compare the processes of reactive sputtering of multicomponent TiNbVTaZrHf–*x*N coatings (*x* = nitrogen flow in sccm) in the case of DC magnetron sputtering and High Target Utilization Sputtering (HiTUS).

Target observations after reactive sputtering in DCMS and HiTUS showed that its poisoning occurred in different extent in the racetrack and in the rims outside of the zone of active sputtering. Despite that, hysteresis was negligible both in techniques. Based on nitrogen consumption indirectly determined from pressure changes during nitrogen flow increase/decrease cycle in HiTUS and DCMS, a unified model of reactive sputtering with continuous poisoning was proposed.

DCMS deposited TiNbVTaZrHf metallic coatings exhibited textured bcc structure; despite significant local variations of the concentrations of individual TM coatings, they formed solid solution attributed to high entropy alloys. Analogous coatings in HiTUS were amorphous. Structure and composition of TiNbVTaZrHf–*x*N coatings were practically identical both in DCMS and HiTUS and depended on the nitrogen flow, *x*. At low *x*, nitrogen concentrations were almost linearly proportional to *x*. At and above critical flow, x_c, nitrogen saturation and stoichiometry around 1.0 were achieved. Coatings exhibited textured fcc structure Despite local deviations of TM and nitrogen concentrations from ideal theoretical amounts, the structure corresponded to single phase solid solution. Thus, these coatings were also classified as the nitrides with the metallic sub-lattice stabilized by high configurational entropy. These observations were corroborated by DFT calculations which justified a transition from bcc toward fcc structure at nitrogen concentrations exceeding 9 at%.

Mechanical properties were closely related to nitrogen stoichiometry. DCMS coating exhibited hardness ~ 40 GPa while that in HiTUS coatings was ~ 33 GPa. The corresponding indentation moduli were ~ 490 GPa vs ~ 400 GPa. They were achieved at optimized x resulting in nitrogen stoichiometry of 48 at % and 45 at%, respectively. However, the ratio H_{IT}/E_{IT} and limited number pillar split tests indicated very low ductility and fracture toughness only in the range of 1 $MPa{\cdot}m^{1/2}$.

The work confirmed that not only reactive DCMS but also reactive HiTUS can produce multicomponent high entropy alloy and analogous TM-nitride coatings with high level of mechanical properties without a need for target poisoning control during deposition.

Rapid pressure-less sintering - how does it work

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Keywords: structural ceramics, lead-free piezoceramics, rapid sintering, heat transfer, core-shell structure

Rapid pressure-less sintering (RPLS), sometimes denoted as fast firing, was first published in the late 1970s and since that time it has been tested on many ceramic materials with the aim either to improve the microstructure of the products, to demonstrate the possibility of saving time and/or energy or to explain the mechanisms of fast densification. The ability to sinter zirconia ceramics at high heating rates was first tested in our laboratories using pressure-less Spark Plasma Sintering (PL-SPS), which uses pulsed direct current for rapid heating. Extremely rapid densification and grain growth were achieved at heating rates of up to 500 °C min^{-1}, so that a centimeter-sized sample was fully densified without cracks within minutes.

The possibility of fast sintering with conventional resistive heating was then verified in a specially designed elevator furnace at controlled heating rates up to 1500 °C min^{-1}. The RPLS has been found as a possible way for preparing defect-free and nearly dense (> 95%TD) alumina and zirconia ceramics of a relatively large size (approximately 1 cm^3) without formation of cracks or other structural defects. The capability of rapid rate sintering was demonstrated also on sintering of lead-free piezoceramic materials, when BCZT powder compacts were for the first time sintered by rapid heating rates within one hour of sintering, while achieving good piezoelectric properties. These findings represent a crucial benefit for the big-scale sintering process in the ceramic industry.

To reveal the major heat transfer mechanism during RPLS, zirconia sample with volume over 30 cm^3 was rapidly sintered to relative density of 86% without crack formation. Experimental data were used for numerical calculations of conduction/convection heat transfer. Obtained results reveal that the maximum temperature in the sample does not exceed 1200 °C if only heating by conduction and convection is considered. Our results therefore indicate that during RPLS of low thermally conductive materials radiation heat transfer is dominant.

We also demonstrated that densification kinetic of RPLS applied from two different onset temperatures (1100 °C, 700 °C) is not notably affected by surface diffusion which took place during conventional pre-heating at higher onset temperature. This result questions the hitherto accepted hypothesis that elimination of surface diffusion at early stage of sintering plays the key role in densification mechanism of fast sintering.

RPLS of nanoparticle yttria-stabilized zirconia often results in the formation of a gradient structure characterized by an airtight layer at the surface and interconnected porosity inside the sintered compact. This structure constrains a sample from further shrinkage and limits its final density. In our work, the origin of the so-called core-shell structure formed during RPLS of zirconia ceramics was discovered and possible ways of its elimination were shown.

Effect of acidic environment on glass-ceramic-metal composite materials

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Keywords: composite materials, basalt, stainless steel 316, artificial acid rain

Ceramic materials are often used in very aggressive and corrosive environments due to their high chemical inertness and corrosion resistance. However, even if corrosion progresses slowly, it still occurs. Corrosion usually depends on the structural properties of the materials. For example, more compact or tightly bonded materials corrode less, whether glass or crystalline materials. With the dramatic increase in nitrogen and sulphide oxide emissions, acid rain pollution has become one of the world's biggest environmental problems.

One of the methods used to measure the corrosion resistance of ceramic materials and ceramic matrix composites (CMCs) is the immersion method, which studies their behaviour by immersing them in corrosive media and measuring the concentration of ions released. Adding different particles to basalt before sintering to obtain CMCs can increase fracture toughness.

The aim of this work was to investigate the effects of the content of 316L stainless steel powder in sintered basalt on its structural properties and resistance to the release of metal ions in acidic environments. The andesite-basalt-based samples were prepared by adding 5, 10, 15, and 20 wt.% of steel powder, respectively, before sintering. The basalt aggregate and the pure sintered basalt served as reference materials. The metal concentrations in the solution were studied for 15 weeks at room temperature and a pH of 3.13±0.01. The major elements Fe, Cr, Mn, and Ni were monitored, while the others were below the limit of quantification. We found that the concentration of metal ions released from the basalt aggregate increases exponentially, implying that the release rate is constant over time. However, the concentration of metal ions released from the sintered samples follows the Weibull cumulative distribution function (CDF), which means that the release rate changes over time and allows us to calculate the characteristic times of ion release. The presence of 5 wt.% steel powder in the sintered basalt accelerates the release of metal ions by about six times. If the steel powder content increases, the metal release rate does not change further. These findings are positive since the highest toughness of sintered basalt is expressed at 20 wt.% of steel powder.

The corrosion stability of glass-ceramic-metal-based composites was found to be satisfactory compared to natural andesite-basalt aggregate. These composites can be used in conditions of acid rain exposure where higher fracture toughness is required.

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Synthesis and characterization of alumina composites reinforced with alumina/mullite fibers

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Keywords: alumina, composite, fibers, mechanical properties

Alumina composite was prepared via simple route. Alumina/mullite fibers are added to improve mechanical properties of composite. The evolution of the phase composition during thermal treatment was investigated by X-ray powder diffraction (XRPD) and thermal analyses. Effect of sintering temperature on mechanical properties, due to the increase of sintering temperature that can produce a higher strength and higher density, was also investigated. SEM observation of composite was also included. Ceramics composites such as the alumina/alumina/mullite, are good candidates for high temperature oxidation atmosphere applications, as they have excellent mechanical and other performance requirements.

Densification of additive-free B_4C-SiC composites by spark plasma sintering

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Keywords: B_4C, SiC, composite, SPS, densification

Boron carbide (B_4C) - silicon carbide (SiC) ceramic composites were obtained through the densification of B_4C and β-SiC powders with different ratios using the spark plasma sintering (SPS) technique. The thermal treatment was carried out for 5 min in Ar atmosphere in a temperature range from 1850 °C to 2000 °C under a pressure of 70 MPa. The effect of starting powders ratio on the sintering behavior, relative density, microstructural development, and mechanical properties of the obtained composites was investigated. The obtained results showed that only starting compounds, *i.e.* B_4C and SiC phase, are observed in the sintered ceramic materials. SEM micrographs revealed that the sintered composites are composed of densely compacted B_4C and SiC grains with a uniform distribution of both phases. The maximal relative density value (100 %) was achieved for the sample densified at 2000 °C with 25% of B_4C and 75% of SiC. The microhardness of obtained composites ranges from 33 GPa to 43 GPa, depending on the constituents' content and the densification temperature. The maximal microhardness value was achieved for the composite densified at 2000 °C which contains a maximal amount of B_4C (75%). In order to examine the behavior of composites in extreme conditions, the surface changes induced through the interaction of obtained composite materials and CO_2 pulse laser were also studied. During the irradiation, the laser pulse duration was ~2 μs with average pulse energy of 120 mJ. The results of this study show that the SPS technique can be a very effective densification method for the obtainment of additive-free B_4C - β-SiC ceramic composites with promising properties for application in radiation at extremes.

Colorless borosilicate medical waste glass-based dispersions shaped via additive manufacturing for water treatment applications

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Keywords: upcycling, 3D printing, TiO_2, photocatalysis treatment, degradation of dyes.

The work is focused on the open-loop recycling of end-of-life borosilicate glasses for the development and shaping of 3D glass substrate constructs for wastewater treatment. The rise of additive manufacturing demonstrates stereolithography as a promising technique for fabricating glass-based materials due to the scalability of the process and access to a larger design space through higher tunability of geometries and thereby material properties. Inspired by natural membrane-like cellular architectures, triply periodic minimal surfaces (TPMS) are of particular interest in our intended applications. The present study was dedicated to manufacturing of highly porous TPMS constructs, using masked stereolithography, starting from a simple blend of photocurable resin with glass powder (<38 μm). The gyroid model was selected with varying porosity from 75-90%. Additionally, some prototypes related to thermal treatment were also designed to improve the translucency of the 3D scaffolds. Furthermore, the obtained 3D printed scaffolds were coated with TiO_2 by dip coating technique and further utilized for the photocatalytic degradation of dyes. In comparison to TiO_2 coating, 3D scaffolds were capable to degrade 50% more methylene blue in 75 min. With the 3D scaffolds immobilized with TiO_2 degrade 95% of methylene blue dye in 75 min under UV irradiation. In addition, the efficiency of the scaffolds was assessed for five consecutive cycles and the degradation efficiency was 75% after fifth cycle, which confirms the stability of the system.

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Various ceramic fibers types based on tailored silazanes

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Keywords: ceramic fibers, polysilazane, fiber spinning, functional fibers

Non-oxide ceramic fibers are very attractive and essential for the fabrication of lightweight thermostructural materials like metal matrix (MMCs) and ceramic matrix composites (CMCs), due to their superior mechanical properties, such as high tensile strength > 2 GPa and stiffness, combined with excellent thermal stability and oxidation resistance to temperatures above 1000 °C. The disadvantages are the high price, the limited commercial availability and the restricted number of fiber types which are mostly based on carbosilanes leading to ceramic SiC fibers. As an alternative we have been developing ceramic SiCN fibers for about 20 years based on inexpensive silazanes that are commercially available in large quantities from industry using relatively simple processing strategies.

In this contribution an overview will be given on the processing, characterization, and potential of very different types of ceramic fibers based on polysilazanes. Beside thin ceramic SiCN fibers we developed thick fibers with diameter up to more than 100 µm, very interesting for MMC applications. The combination of the silazane with acrylonitrile led to a C/SiCN fiber type with outstanding oxidation stability and flame resistance in comparison with carbon fibers. Furthermore, the chemical modification of silazanes with iron complexes resulted in a superparamagnetic ceramic FeSiCN fiber after pyrolysis suitable for structural and functional applications like shielding, defect detection in CMCs and their separation from used ceramic components using magnets. In order to expand the manufacturing options and thus also the fiber properties, the silazane precursors were tailored for the use for electrospinning, which enables the manufacturing of ceramic fibers in the sub-micrometer diameter range. Such ceramic nonwovens are very attractive for filtration or as catalyst supports.

Tribological characteristics of dual-phase high-entropy ceramics

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Keywords: dual phase high entropy carbide, wear, hardness, wear mechanisms

Wear characteristics of a fine-grained dual-phase high-entropy boride/carbide (HEB/HEC) ceramics were studied using ball-on-flat technique/dry sliding in air with SiC ball as tribological partner at applied loads of 5, 25 and 50 N with a sliding speed of 0.1 m/s and a sliding distance of 500 m. The experimental material showed very high relative density, relatively homogeneous chemical composition of HEB and HEC grains and high Vickers hardness (*HV1* = 29.4±2.0 GPa). The microstructure, deformation and damage characteristics were studied using scanning electron microscopy equipped with EDAX and confocal electron microscopy. The friction coefficient value during the test with 5 N was approximately 0.55 and during the test with 25 and 50 N approximately 0.5. The specific wear rates during the test with 5 and 25 N were very similar with values 7.93×10^{-7} mm^3/Nm and 6.63×10^{-7} mm^3/Nm and at 50 N significantly higher with value 9.11×10^{-6} mm^3/Nm. The dominant wear mechanisms in all cases were mechanical wear, tribochemical reactions and tribo-layer formation.

Alumina toughened zirconia composites with enhanced mechanical reliability and lifetime

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Keywords: alumina toughened zirconia, fracture toughness, strength, subcritical cracking, lifetime prediction

Preparation of alumina toughened zirconia composites (ATZ) is a relatively well recognized method for the improvement of properties of tetragonal zirconia. These materials are well commercialised due to their very good mechanical properties, but still open for the further improvement. The weakest point of tetragonal zirconia materials is the lack of resistance for subcritical cracking and stress corrosion. Long-term loading of tetragonal zirconia components in humid environment (in air or water) leads to the decrease of strength. ATZ composites could eliminate this weakness in very effective way.

In the presented work an attempt was made to create composite in order to reduce the effect of stress corrosion cracking. The ATZ type composites were prepared using reactive sintering process utilizing different zirconia powders. Materials obtained by means of such procedure revealed very fine microstructure and had extremely high fracture toughness, even higher than 12 MPa·m$^{0.5}$. Bending strength of these materials was also very high and exceeded 1 GPa. The subcritical crack propagation phenomenon in the mentioned materials were tested using constant stress rate test performed in the form of biaxial bending. Calculations of strength-probability-time (SPT) diagrams were performed using the data collected during these tests in order to estimate the survival time of the material working under loads for materials where change of strength for different stress rates was observed. Some of the tested ATZ materials were definitely resistant for slow crack propagation phenomenon.

Acknowledgements

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Improvement of the density and roughness of alumina parts processed by binder jetting

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Keywords: binder jetting, laser refinement, hybrid process

Binder jetting (BJ) is an additive manufacturing process in which powder materials are selectively joined by a binder. The main drawbacks of this technology are the low green density implying insufficient density after sintering and the poor finished surface of the parts. This talk will present some advances to solve these problems.

Alumina powder was used as a model material processed using different routes to obtain granules with various characteristics. The first part of this research was devoted to the improvement of the granule properties (particle size, morphology, flowability), the characteristics of powder bed (roughness, packing density) and the process parameters (binder saturation, layer thickness) in order to achieve the highest printed parts quality in terms of compressive strength and volume density. Optimized values reach 102.2 ± 11.1 MPa and 64.2 ± 1.9% T.D. The second part focused on the infiltration of printed bodies with a ceramic suspension to enhance density and properties of the porous binder-jetted parts. The density raised up to 87.9 ± 0.5% after infiltration of a pre-consolidated body followed by sintering. The last part was devoted to the improvement of the finished surface by considering an additive/subtractive hybridization method using a ns pulsed laser. By this way, the typical average roughness *Ra* was reduced from approx. 30 µm (original printed surface) to approx. 10 µm (laser-ablated surface).

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Reuse and recycling of lithium-ion batteries (Re_2LiB) – different strategies for the recovery of critical raw materials

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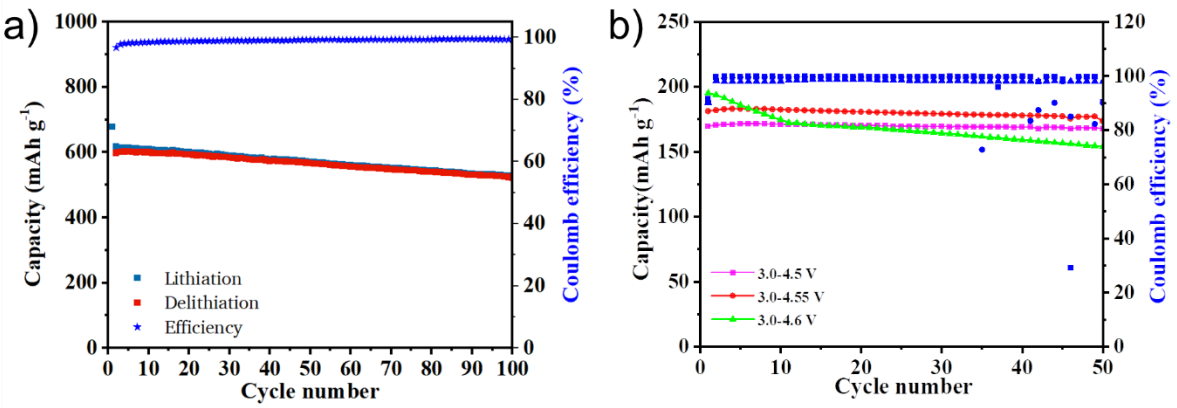
Keywords: hydrometallurgy, direct-recycling, lithium-ion battery, graphite, cobalt

Lithium-ion batteries (LIBs) recycling sector is driven by the tight availability of raw materials utilized in LIBs manufacturing, the unequal distribution of natural resources, and the increasing demand of the end-consumer market. Graphite negative electrodes are unbeaten hitherto in LIBs due to their unique chemical and physical properties. The proven global reserves of natural graphite were around 71 million tons in 2014, but the demand is steadily growing at a rate of 250ktpa, with approximately 72 % of graphite going into LIBs between 2016 and 2025 [1]. As concerns the cathode technologies, Co and Ni play a determinant role both in terms of price and geographical availability, as well as the Li contained in the cathode and in the electrolyte. This scenario clarifies that smart recycling or repurposing of spent LIBs is becoming strategically important together with the urgent need to improve the current reclaiming technologies [2].

Herein we present a facile and up-scalable recovery of spent graphite (SG) from end-of-life LIBs by hydrometallurgical process [3]. We also correlate the electrochemical performance of the regenerated graphite, comparable to the benchmark commercial pristine graphite, with the state-of-health (SOH) of the spent battery. The recycled graphite is also studied as stabilizing matrix for Si nanoparticles, which are notoriously suffering the drawback of pulverization due to the huge volume expansion (> 300%) with lithium alloying reactions [3,4]. We synthesized carbon coated Si:regenerated graphite composites with various energy densities and successfully mitigated the severe capacity fading caused by Si pulverization by tuning the Si:regenerated graphite ratio and the thickness of the carbon layer. Finally, spent $LiCoO_2$ (LCO) is recovered by direct recycling, restoring the correct Li amount in the crystal structure.



{1: a) GCPL of a Si:regenerated graphite composite (9 % of Si) cycled between 3-0.005 V and b) GCPLs of LCO obtained by direct recycling method and cycled in different voltage windows

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Densification and microstructure evolution of ZnO in the cold sintering process

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Keywords: cold sintering, zinc oxide, densification, mechanical strength

The cold sintering process (CSP) is a novel technique that utilizes a transient sintering aid and externally applied pressure to activate a dissolution–precipitation densification process below 300°C. Compared to conventional sintering methods, this process is energy-saving and allows unique combinations of thermally metastable materials. However, the effect of the transient phase on microstructure and final properties of the cold sintered parts still needs to be investigated.

In this work, the effect of different transient liquid phases (water, acetic, citric and formic acid) on the CSP of ZnO was investigated. This was carried out by a comparative study with respect to densification, microstructure evolution, and mechanical properties of cold sintered samples. The results are discussed in light of the pressure solution creep mechanism involved in the process.

It was found that densification, microstructure and mechanical strength are significantly controlled by the chemistry of the liquid phase. The experimental setting also influences the cold sintering process, and the presence of transient liquid at higher temperatures also changes the optical apperance of the sintered zinc oxide, associated with the choice of transient phase. Finally, enhanced densification and mechanical strength were observed for samples cold sintered using formic acid, showing the potential of scaling up the CSP for ceramics.

Additive manufacturing and mechanical testing of non-oxide ceramic matrix composites

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Keywords: ceramic matrix composites, fused filament fabrication, size effect, additive manufacturing, ceramic fibers

Non-oxide ceramic matrix composites (CMC) combine a high creep resistance with a low density. Their fiber reinforcement results in an excellent damage tolerance and thermal shock resistance, overcoming typical shortcomings of monolithic ceramics. C/C-SiC is one of the main CMC materials, which is often used for friction and aerospace applications. C/C-SiC is produced by liquid silicon infiltration of a previously pyrolyzed carbon fiber reinforced plastic (CFRP) preform. This CFRP contains either thermosetting or thermoplastic polymeric precursors with a high carbon yield after pyrolysis.

For the processing and later resulting properties, the cross-linking and pyrolysis of the used polymers is essential. We will show that for regularly applied phenolic resins, the amount of hardener not only affects the resulting carbon yield, but also the temperature range for cross-linking. Secondly, the fiber preforms constrain the shrinkage during pyrolysis forming a crack pattern. The crack pattern, not only influences the silicon infiltration, but also the resulting properties. As part of the talk, we will discuss, how these crack patterns can be categorized. In another part of our talk we will report on additive manufacturing of C/C-SiC using fused filament fabrication (FFF) of fiber-filled polyetheretherketone (PEEK). As a thermoplastic polymer, PEEK has to be crosslinked before pyrolysis. Furthermore, FFF also offers the possibility to tailor the porosity to optimize the following pyrolysis. We explain factors and processing strategies to cross-link PEEK without impairing shape stability of the preforms and how a high density with improved pyrolysis can be achieved. Finally, we will report on the mechanical tensile and bending testing of C/C-SiC. It will be shown for tensile testing that although the volume under load was increased significantly, the strength was not affected. For bending testing, the Weibull modulus was not a material constant, either. The results are discussed regarding the Weibull weakest link and energetic size effect approaches.

(Thermo)mechanical and microstructural properties of different high-performance ceramics fabricated by vat photopolymerization

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Keywords: additive manufacturing, vat photopolymerization, alumina, zirconia, silicon nitride

In recent years, additive manufacturing (AM) techniques have started to become increasingly relevant fabrication methods in the field of high-performance ceramics. The growing importance of these components in this field also necessitates the availability of testing and characterization protocols to ensure the high levels of quality and homogeneity of parts made through AM can be demonstrated, and to allow for a thorough understanding of the relevant structure-property relationships.

One of the most prominent advantages is the exceptional level of strength and isotropy in additively manufactured components. In this contribution the mechanical and microstructural properties of specimens made from additively manufactured alumina, zirconia, aluminum nitride, and silicon nitride components, and which were fabricated using vat photopolymerization (VPP) techniques, are presented. The influence of different testing orientations with respect to the building direction was investigated. It is shown that proper choice of the materials system, as well as the printing and post-processing parameters, are crucial in the realization of a homogeneous and isotropic microstructure, and thus also in manufacturing ceramic components with isotropic material properties and no artifacts from the layer-by-layer build-up. In terms of strength, the obtained values for the AM parts are already equal to those of isostatically pressed or injection molded components.

It is also shown that lithographic AM can be used to fabricate highly translucent parts from alumina and zirconia, while still possessing a high density and extremely fine microstructure, therefore highlighting the exceptional quality of the printed components using the VPP approach.

Mesoscale strength of ceramic and glass surfaces measured using microcantilever beam specimens: Changes due to chemical reactions

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Keywords: strength, mesoscale, chemical reactions, microcantilever beam specimens

Knowledge of the mechanical properties of glass and ceramic surfaces is important in terms of friction, wear, strength, etc. In particular, understanding and controlling the mechanical properties of the mesoscale near the surface is essential to improve the mechanical reliability of glasses and ceramics as a result of chemical changes caused by the external environment. Bending tests using microcantilever specimens are an excellent method for pinpointing any point in a material. The objective of this study was to investigate the effects of chemical reactions on glass and ceramic surfaces and their influence on the mechanical properties of the near-surface region. Strength of Si_3N_4 ceramic surface which was contacted with molten Al or sulfuric acid was lower than that of as-received surface because of degradation of the grain boundaries. Such mechanical degradation was also found to occur in soda-lime glass produced by the float method when SO_2 gas is blown onto its surface due to changing its composition by several tens of nm. The fracture toughness near the surface was improved by removing this region by etching. On the other hand, in aluminosilicate glass, replacing Na^+ with K^+ resulted in a significant increase in strength, although the fracture toughness remained unchanged. Since the specimen height was smaller than the compressive stress layer in this test, it was concluded that the mechanical properties were evaluated only in the chemically altered region, and the higher strength was attributed to the increase in Young's modulus resulting from ion exchange. In addition, when microcantilever specimens fabricated on quartz glass were subjected to bending tests in water, their strength was higher than that measured in air. This may be attributed to the volumetric expansion due to the diffusion of water near the surface of the quartz glass as a result of the high tensile stress. In conclusion, the proper use of chemical reactions in glass and ceramics can contribute significantly to improving their mechanical properties and mechanical reliability.

Novel diboride-based high entropy ceramics

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Keywords: high entropy ceramics, diboride ceramics, mechanical properties, spark plasma sintering

Highly pure high-entropy diboride ceramics (HEBs) were produced by two-step spark plasma sintering, consisting of boro/carbothermal reduction of oxides mixtures at 1800°C and pressure-assisted sintering at 1900°C. The aim of this work was to improve the mechanical properties of (Ti-Zr-Hf-Nb-Ta)B_2 diboride system by the addition of different amounts of SiC (5 – 25 vol.%) and formation of new non-equimolar diboride structures in this diboride system.

The addition of SiC significantly improved densification of HEB materials. The room temperature mechanical properties, such as hardness, flexural strength and fracture toughness continuously increased with the increasing amount of SiC up to 20 vol.%. A significant drop in the mechanical properties observed for the composite with 25 vol.% was caused by the significant coarsening of the microstructure. On the other hand, the dynamic oxidation rate of the materials significantly decreased with the addition of SiC up to 25 vol.%. It was concluded that the $(Ti_{0.2}Zr_{0.2}Hf_{0.2}Nb_{0.2}Ta_{0.2})B_2$ composite sintered with 20 vol.% SiC showed the best combination of room and high temperature mechanical properties.

Based on the $(Ti_{0.2}Zr_{0.2}\ Hf_{0.2}Nb_{0.2}Ta_{0.2})B_2$ structure, a group of high-entropy diborides with non-equimolar transition metal ratios were theoretically predicted using Density Function Theory implemented in VASP and experimentally investigated. Three most promising non-equimolar diboride structures were selected, considering the formation energy, cohesive energy and mechanical properties of the structures: $(Ta_{0.6}Hf_{0.1}Zr_{0.1}Ti_{0.1}\ Nb_{0.1})B_2$, $(Ta_{0.6}Hf_{0.25}Zr_{0.05}Ti_{0.05}\ Nb_{0.05})B_2$, $(Ta_{0.6}Hf_{0.2}Zr_{0.1}Ti_{0.05}\ Nb_{0.05})B_2$. All of these non-equimolar structures were succesfully synthesized to a single phase and sintered to a relative density higher than 96 %. The nanohardness of the individual grains of non-equimolar structures was significantly higher when compared to the equimolar composition. Similarly, the Young's modulus of non-equimolar compsoitions was slightly higher than that of equimolar one. It was shown that by optimization of the molar ratio of the individual transition metals, the mechanical properties of HEBs can be improved.

Acknowledgements

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Joining of SiC and SiC_f/SiC using various techniques

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Keywords: joining, SiC, SiC_f/SiC, microstructure, strength

The sintering of SiC is inherently difficult because of the high degree of covalent bonding in SiC and the low self-diffusivity, requiring very high temperature and pressure for densification. Therefore, the challenges with sintering SiC mean that only simple shapes like plates or tubes are typically fabricated. However, SiC-based materials, such as monolithic SiC and SiC fiber-reinforced SiC matrix composites (SiC_f/SiC), with complex shapes expand their application area continuously due to the strong demand for high temperature materials. This is why the development for reliable joining techniques for SiC-based materials is essential.

In this talk, the properties of monolithic SiC or SiC_f/SiC joints made with various joining techniques, including preceramic polymer joining, MAX phase joining, transient eutectic phase joining, Si-C reaction bonding, and direct joining without adding a filler, will be presented in terms of their basic mechanisms, microstructures, strengths, and advantages and disadvantages. Especially, the possible elimination of joining interface will be highlighted for both monolithic SiC and SiC_f/SiC joints made with Ti_3AlC_2 filler at 1900 °C under 3.5 MPa. Thermal decomposition of Ti_3AlC_2 filler and subsequent solid-state diffusion into the base SiC enables the elimination of joining interface, showing the high joint strength of 300 MPa. This can be an ideal joining technique for practical applications because the absence of joining interface leads to the preservation of excellent mechanical properties of the base SiC at the entire joint. Finally, comments are provided for the use of various joining techniques in advanced nuclear reactors where stringent irradiation stability under neutron irradiation as well as hermeticity and joint strength are required.

AUTHOR INDEX

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