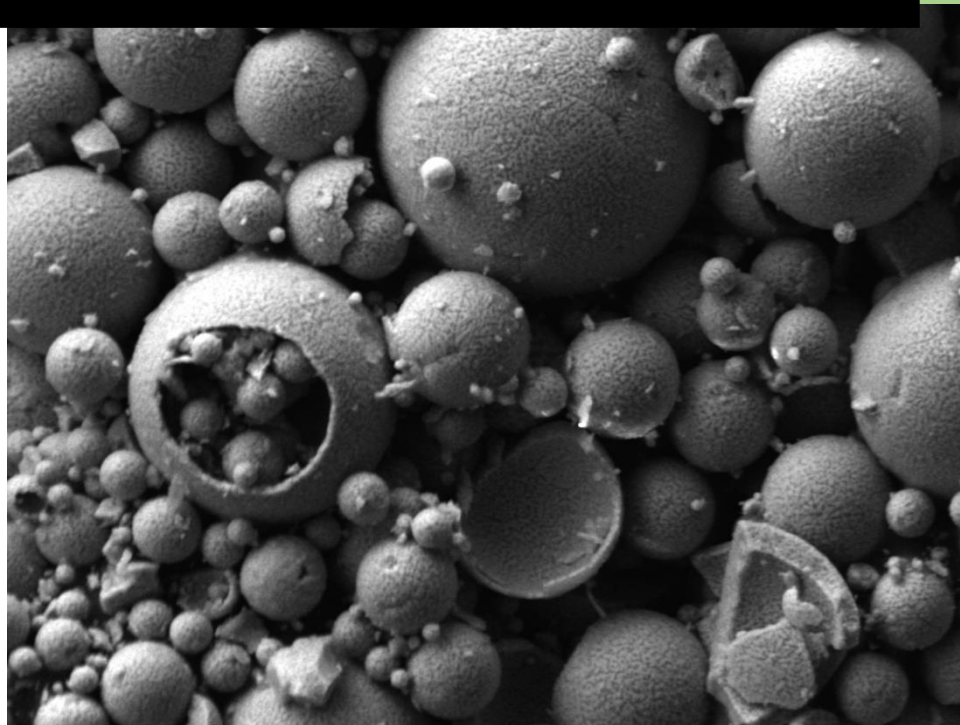


2020

Processing and Properties of Advanced Ceramics and Glasses



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Obsah

A. Dasan / Additive Manufacturing of Optically Transparent Glass Structures for Next-Gen Sensing, Optical and Photonic Applications (FunGlass Symposium)	4
A. Dasan / Massive Production of Glass Microspheres for Advanced Manufacturing Applications: Optimization, Characterization and Challenges	6
M. Mahmoud / Preparation of Porous Glass Microspheres Based On Glass Wastes (FunGlass Symposium)	8
M. Orlovská / Repeatability of an extrusion-based 3D printing technology in ceramic production	10
M. Vozárová / Boron carbide ceramics prepared by additive manufacturing technology	16
N. Afsharimani / Sol-Gel Based Coatings for Corrosion Protection of Mg Alloys (AZ31B) (FunGlass Symposium)	18
I. Parchovianská / Oxidation resistance of PDC glass-ceramic coatings on stainless steel	20
M. Parchovianský / Oxidation behaviour of PDC coatings with glass fillers on AISI441 stainless steel	22
M. Žitňan / Deposition of ceramic precursors on various substrates by using desktop printer (FunGlass Symposium)	24
A. Akusevich / Ce ³⁺ -doped phosphors prepared by sintering of microspheres of yttrium-aluminate glasses (FunGlass Symposium)	26
R. Dagupati / Barium phosphate glasses: structure investigation by SVTD modeling and NMR spectroscopy (FunGlass Symposium)	28
P. Petrisková / Preparation of TiO ₂ nanotube arrays on transparent spinel for photocatalytic applications	30
O. Hanzel / Preparation and properties of functionally graded SiC-graphene composites	32
A. Talimian / Fabrication of Magnesium Aluminosilicate Glass-Ceramics Reinforced by 3Y-ZrO ₂ Addition	34
H. Ünsal / Wetting and reactive melt infiltration of transition metal disilicides during the development of Ultra-High Temperature Ceramic Matrix Composites	36
S. Chen / Porosity evolution of the 45S5 bioactive glass porous microspheres by adjusting the alkali activation conditions (FunGlass Symposium)	38
F. Kurtuldu / Cerium and gallium containing mesoporous bioactive glass nanoparticles for biomedical application (FunGlass Symposium)	40
M. Hujová / Inorganic Waste Upcycling: The lessons learned, and the outlook for the future (FunGlass Symposium)	41

Additive Manufacturing of Optically Transparent Glass Structures for Next-Gen Sensing, Optical and Photonic Applications

A. Dasan¹, J. Kraxner¹, E. Bernardo², D. Galusek^{1,3}

¹*FunGlass, Alexander Dubček University of Trenčín, Trenčín, Slovakia*

(e-mail:arish.dasan@tnuni.sk)

²*Department of Industrial Engineering, Università degli Studi di Padova, Padova, Italy*

³*Joint glass centre of the IIC SAS, TnUAD, and FChFT STU, FunGlass, Alexander Dubček University of Trenčín, Trenčín, Slovakia*

ABSTRACT

Although digitally manufactured polymer, metal and ceramic parts are already successfully used in sectors such as aerospace, automotive and healthcare, fully transparent glass components are still in their infancy. However, the possibilities are exciting and the potential benefits immense since the technology has freedom of design capabilities; being aware of recent developments in this area is going to be crucial for industries specially when thinking about next-gen sensing, optical and photonic components. Since bringing new technology and new products to market, in an efficient and cost-effective method, is a key factor for the success of these industries, the development of innovative strategy for 3D glass systems with better 3D printing materials and technology is essential. In this presentation, we discuss photocurable silicate based glass slurries, yielding transparent glass objects using stereolithography technology. It also covers discussion about the overall manufacturing approach, including viscous flow sintering, challenges, prospect on future directions and possible applications.

Keywords: Additive manufacturing, Transparent glasses, Stereolithography, Optical

INTRODUCTION

3D printing technology, also known as Additive Manufacturing (AM) is one of the most trending areas in manufacturing technique that enables the flexible preparation of highly complex and precise dimensional parts using layer-by-layer process as directed by Computer Aided Design (CAD) file, without going through the traditional mold fabrication and tooling qualification. Recently, the aforementioned technology finds its application in all kinds of niches such as medical, aerospace, automobile, electronic, jewelry, etc., with positive and interesting ways. Although most of the AM technologies have widely studied on polymer, metal and ceramic based objects, AM of glass parts are very limited even though it is very essential for day life applications. Particularly, still there has been minimal research towards the AM of optically transparent glass parts when comparing with opaque structures (e.g. involving bioactive glasses and polymer-derived silicon oxycarbide glasses). However, recent developments on the AM of transparent glass not only showed excellent properties compared to that of commercial glass, but also the complexity never possible before and with customizable optical properties. Here, we presented some preliminary results of a photocurable glass suspension and subsequent thermal treatment steps, based of viscous flow sintering, to achieve the targeted object.

EXPERIMENTAL

Precursor glass powders were prepared by the conventional melt quenching method. Photosensitive glass slurries were prepared by direct mixing of commercial photocurable organic resin with fine glass powders. A desktop SLA 3D printer (Original Prusa SL-1, Prusa Research s.r.o, Czech Republic), light source at a wavelength of 405 nm, was used for printing purpose.

RESULTS

In this study, eutectic composition of yttrium aluminium silicate glass powders (Y_2O_3 , 39.90 wt %; Al_2O_3 , 20.14 wt %; SiO_2 , 39.97 wt %) was selected as it has potential applications in the field of sensing, optics and photonics. Glass transition temperature (T_g), onset crystallization (T_x) and crystallization temperature (T_c) were found to be respectively at 674°C, 1067°C and 1134°C, as evidenced by TG/DTA analysis. The primary challenge is the optimization of sintering temperature without any crystallization or viscous collapse, that enables to obtain nearly full theoretical density of the system and transparency. To better understand the glass powders behaviour with photocurable organic resin, four different commercial photocurable organic resins were utilized for mixing. The thermal treatment was done in two steps; i) debinding of organic resin around 600°C (according to TGA results) and ii) sintering of debound bodies. The preliminary results showed that YAS glass objects sintering starts around 950°C and reaches 1050°C without any crystallization or viscous collapse. However, the parts were not fully transparent due to lack of densification as a result retaining of the porosity. In future, more optimization process such as modifications of the suspension, thermal treatment, sintering techniques etc., will be studied.

CONCLUSION

To continue searching of new materials and new routes to achieve optically transparent glass structures via AM technology, the present study, i.e., photocurable glass suspensions and followed by viscous flow sintering technique could be a significant step toward obtaining the next-Gen 3D transparent glass objects.

ACKNOWLEDGMENT

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Massive Production of Glass Microspheres for Advanced Manufacturing Applications: Optimization, Characterization and Challenges

A. Dasan¹, A. Talimian¹, J. Kraxner¹, E. Bernardo², D. Galusek^{1,3}

¹*FunGlass, Alexander Dubček University of Trenčín, Trenčín, Slovakia
(e-mail:arish.dasan@tnuni.sk)*

²*Department of Industrial Engineering, Università degli Studi di Padova, Padova, Italy*

³*Joint glass centre of the IIC SAS, TnUAD, and FChFT STU, FunGlass, Alexander Dubček University of Trenčín, Trenčín, Slovakia*

ABSTRACT

Flame synthesis is typically used to manufacture glass microspheres, spraying irregular glass powders into an oxygen-methane (O_2/CH_4) torch. The flame melts the powders in spherical droplets, transformed into glass microspheres by quenching in distilled water. This method brings a specific advantage in the processing of some compositions, hardly yielding a fully amorphous material by conventional melt quenching method, due to the high crystallization rate. As an example, achieving a glass with the stoichiometry of åkermanite ($Ca_2MgSi_2O_7$, i.e. $2CaO \cdot MgO \cdot 2SiO_2$), a well known biomaterial, is not normally feasible. The present study will show that a massive production of glass microspheres with åkermanite composition could be established by flame synthesis, starting from partially crystallized powders. Microspheres are destined to advanced manufacturing applications, e.g. involving additive manufacturing technologies, such as selective laser sintering and stereolithography. The obtained microspheres were analyzed by using XRD and SEM. The effect of particle size, feeding rate and other challenges will be addressed.

Keywords: Additive manufacturing, Glass microspheres, Stereolithography, SEM, XRD

INTRODUCTION

Due to their spherical shape, microspheres have always been more attractive than conventional irregular powders. Key advantages are better flow properties, controllable size, and relatively high strength-to-density ratio. These characteristic properties would be beneficial for advanced manufacturing technologies such as additive manufacturing (3D printing), tape casting, etc. For instance, in VAT polymerization technique, microsphere fillers can flow within a liquid photocurable polymer much better than irregular particles. As a result, not only better rheological properties (essential for printing process) but also higher solid loading, favouring the dimensional stability and the surface finish of printed objects, can be proposed. Moreover, tailored topographies (e.g. microporosity) can be produced with high definition. For selective laser sintering/melting technique, the improved flow ability of powder beds is essential, for high geometrical accuracy and homogeneity of heating. For material extrusion techniques, microspheres are supposed to drastically reduce shrinkage and warping. However, for all these techniques, the quantity of microspheres as feedstock materials is crucial (from grams to kilograms per experiment), so it is necessary to optimize the massive production of microspheres. In this presentation, we will address a relatively large-scale production of glass microspheres with åkermanite composition in detail.

EXPERIMENTAL

Semicrystalline powders with åkermanite composition were prepared by melt quenching method. To prepare glass microspheres, sieved irregular particles were introduced through vacuum powder feeder using oxygen as a carrier gas into an oxygen-methane torch, at a temperature of approximately 2200 °C. Subsequently, formed molten spherical droplets were immediately quenched by spraying them with distilled water and collected using a tank containing distilled water, followed by filtration through a ceramic filter with a pore size below 0.3 mm.

RESULTS

In order to study the effect of particle size on the microsphere synthesis, four different ranges of particle size distribution varying from 100-80 µm, 80-63µm, 63-40 µm and 40-25 µm were tested. For scale-up production, up to 40 µm there were no issues to obtain fully amorphous microspheres with varying feeding rates. The main concern, when using below 40 µm size powders, consisted of particle agglomeration, causing the presence of some unmelted particles, as shown in Fig. 2. However, fully melted particles were obtained operating with a low feeding rate (2.0g/min). It should be noted that there are no significant changes in glass compositions before and after spheroidisation as evidenced by EDX analysis.

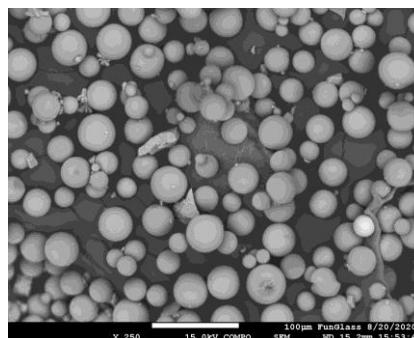
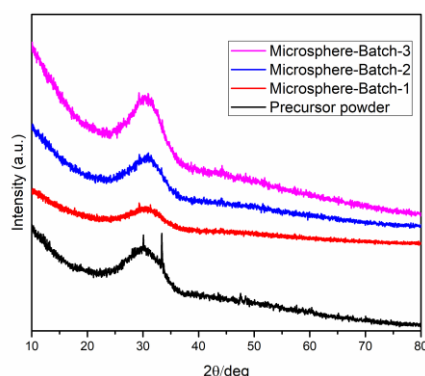


Fig. 2 SEM image of microspheres

Fig.1 XRD of precursor and microspheres

CONCLUSION

Solid glass microspheres with åkermanite composition were successfully produced, in the size range from 100 to 25 µm, by the flame spheroidization process. Scale-up studies clearly showed that the efficiency of spheroidization and feeding rate were affected when the feed particle size decreases, due to agglomeration.

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Preparation of Porous Glass Microspheres Based On Glass Wastes

M. A. Mahmoud¹, J. Kraxner², E. Bernardo³

^{1,2}*Glass Processing Department, FunGlass – Centre for Functional and Surface Functionalized Glass, Trenčín, Slovakia*

³*Department of Industrial Engineering, University of Padova, Italy*

ABSTRACT

Alkali activation of glass waste (Johns Mansville Slovakia) has been done by using 5M and 7M of NaOH. The obtained materials are fed into flame synthesis for producing glass microspheres. SEM showed formation of porous and solid glass microspheres for the activated glass waste by 7M and 5M of NaOH, respectively.

Keywords: Alkali activation, Glass, Microspheres, Porous, Waste

INTRODUCTION

An enormous amount of waste glass is formed through the industrial sectors all over the world. A lot of work has been done to investigate the optimum condition for the best use of the waste glass. However, there are some obstacles, such as the absence of recycling equipment, which prevent a mitigation of negative effects on the environment [1]. Porous glass microsphere (PGM) is ultra-lightweight inorganic nonmetallic material with a hollow structure, and it can be used for many purposes and has excellent properties as a new material produced lately [2]. The main objective of this study is preparation of the porous glass microspheres based on industrial wastes which further can be used for environmental applications.

EXPERIMENTAL

The glass wastes were obtained from Johns Mansville Slovakia and the chemical composition was investigated through XRF technique. The obtained composition was 55.2 SiO₂, 23.0 CaO, 13.6 Al₂O₃, 5.1 B₂O₃, 0.9 MgO, 0.6 K₂O and 0.4 Na₂O in wt. %. The glass waste was crushed below 40 µm in order to be more efficient for alkali activation, NaOH was used with different molarity (5M and 7M) as strong alkaline solutions for alkali activation. The loading weight of glass powder and alkaline solution was 65 % and 35%, respectively. The glass powder was mixed with NaOH for 1 h through a mechanical stirrer at 500 rpm. The produced gel was dried at oven for 24 h, the obtained dry material after alkali activation was crushed and sieved between 40-80 µm and then applied into the flame synthesis for producing glass microspheres. The morphology of the obtained glass microspheres was checked by a scanning electron microscope.

RESULTS

XRD showed that after alkali activation by 5 and 7 M NaOH, the amorphous glass (before applying alkali activation) changed into crystalline phases due to the formation of calcium silicate hydrated compounds (C-S-H) [3]. SEM showed formation of the porous glass

microspheres for only the sample activated by 7 M NaOH, which means 5 M NaOH was not sufficient for the complete attack of Si-O-Si and Al-O-Si bonds in the glass powder. Generally speaking, the results showed that the glass waste activated by 7 M NaOH successfully produced the porous glass microspheres as shown in Fig.1.

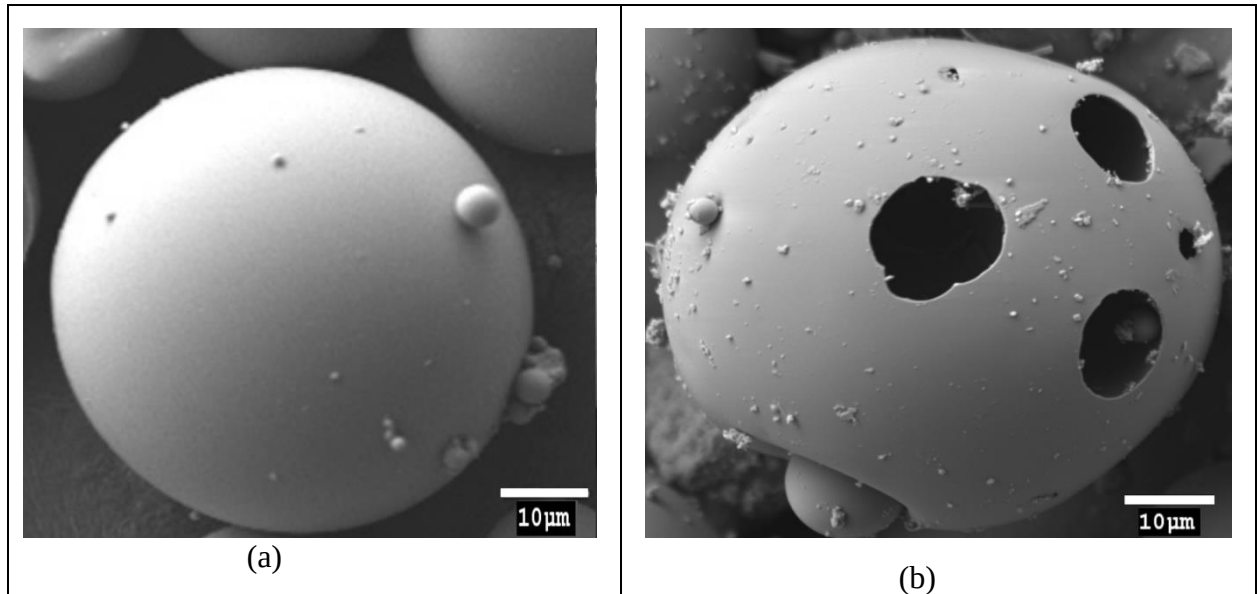


Fig.1 SEM of glass microspheres after alkali activation of (a) 5M NaOH and (b) 7M NaOH

CONCLUSION

Porous glass microspheres were successfully prepared based on the activated glass waste by 7 M NaOH.

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Repeatability of an extrusion-based 3D printing technology in ceramic production

M. Orlovská¹, M. Hain², M. Kitzmantel³, P. Veteška¹, M. Janek¹, Ľ. Bača¹

¹ *Department of Inorganic Materials, Institute of Inorganic Chemistry, Technology and Materials FCHPT STU, Radlinského 9, 812 37 Bratislava, Slovakia*

² *Institute of Measurement Science, Slovak Academy of Sciences, Dúbravská cesta 9, 841 04 Bratislava, Slovakia*

³ *RHP-Technology GmbH, Forschungszentrum, 2444 Seibersdorf, Austria*

ABSTRACT

In recent years additive manufacturing came under the spotlight as a cost-effective and fast preparation technique not only in the plastic industry but also in the ceramic field. Amongst these methods, Fused Filament Fabrication is considered the most accessible and cost-efficient technique with the help of which dense or structured ceramic parts of the various design can be processed. In this work, the FFF technique was implemented for the preparation of high dense alumina parts of different designs using a low-cost desktop 3D printer. For comparison and setting of printing parameters, also pure polylactic acid (PLA) filament, mainly used in filament 3D printing, was applied. The repeatability of the printing process was investigated by non-destructive micro-computed tomography analysis. Results showed that the same printing parameters do not always ensure the same quality of printed parts. Moreover, a change in object design led to various types of defects due to the nonuniformity during the printing process.

Keywords: alumina, Fused Filament Fabrication, 3D printing, PLA, micro-computed tomography

INTRODUCTION

Additive manufacturing, as a novel fabrication method, attracts nowadays an interest in numerous industries (metals, composites, plastics and more) thanks to its fabrication simplicity and cost-effectiveness. Various materials can be prepared through different 3D printing technologies, which were already summarised and categorised [1]. From these methods, Fused Filament Fabrication (FFF) is one of the most approachable techniques. In principle, material in the form of a filament is fed through a nozzle or orifice under controlled conditions on a build platform, creating a three-dimensional object of defined dimensions [2, 3]. Since this technology is being also used in the ceramic field, many research groups are focused on the printing optimisation process [4 - 6], preparation of composite filaments [6 - 9] and on the thermal post-treatment processes [10 - 12]. All these preparation steps and their systematic research are essential for better understanding of connections between each step and to finally achieve desirable and comparable results with those technologies usually used as a standard preparation technique in the ceramic industry, i.e. casting or injection moulding. However, even for plastics, an optimisation of printing process parameters is a significant challenge for dimensional accuracy [13, 14], the strength of the parts [15, 16] or surface roughness [17, 18].

In this work, the preparation of high-density alumina ceramics by FFF method is being studied, where different infill patterns and designs are used to achieve density comparable with bulk samples. Moreover, since no article in ceramic 3D filament printing is focused on repeatability

and reliability of a single 3D printing process, results are, besides standard characterisation methods, also monitored through micro-computed tomography (μ CT).

EXPERIMENTAL

A thermoplastic composite filament of diameter 1.75 mm was prepared to contain 50 vol.% of high purity alumina powder (99.99 %) and a polyolefin-based binder system. Cylinders, bars and pillars were designed in 3D modelling program Tinkercad (Autodesk Inc., USA), and printing was performed in a commercial desktop 3D printer Anet A8 (Shenzhen Anet Technology Co., Ltd., China) with a nozzle of diameter 0.4 mm. For every single design, ten pieces each were printed. Printing speed 10 – 15 mm/s, hotend / bed temperature 240 / 60 °C, overlapping factor 55 %, layer thickness 0.1 mm and extrusion multiplier factor 1.05 were set as an optimised printing parameter for the composite alumina filament. Infill patterns and infill densities during slicing has been changed to obtain the highest possible bulk densities, namely rectilinear of $\pm 45^\circ$ infill orientation, Archimedean chords and concentric with densities of 95 and 100 %, respectively. For comparison, pure PLA samples (Fillamentum, Czech Republic) of the same design were printed using similar printing parameters as previously. Only hotend temperature changed due to the different melting temperature of the plastic system.

A bulk density of cylindrical specimens was measured by an Archimedes method in mercury, and for bars and pillars, density was determined from weight and dimensions. The relative densities were calculated from determined bulk densities. The theoretical density of PLA, and composite alumina filament after printing is set to 1.24 g.cm^{-3} and 2.49 g.cm^{-3} , respectively. Non-destructive visual display of internal structure was performed using Nanotom 180 X-ray computer microtomograph (μ CT) with a submicron resolution of up to $0.5 \text{ }\mu\text{m/voxel}$.

RESULTS

Relative densities, calculated in respect of their theoretical values, of as printed cylindrical PLA and composite Al_2O_3 objects (*Tab. 1*) showed differences between using different infill patterns independently of using various infill densities or extrusion multiplier factors. No matter what type of filament material is used, densities of printed objects are the highest in the case of using a rectilinear infill pattern of 95 % infill density and an extrusion multiplier factor 1.05. Nevertheless, bulk densities did not reach the theoretical value of each printed material, maximum 98 % and 95 % of the theoretical value for PLA and composite Al_2O_3 , respectively. Despite that, the printing setting including 95 % rectilinear infill density achieved the best value in case of preparation of highly solid objects by FFF method using a low-cost desktop 3D printer. However, higher values cannot be achieved by a simple combination of infill patterns and their densities. Even if the layer thickness of 0.1 mm given a higher degree of ovality what could result in better infill path overlapping, bulk densities results indicate that voids or small pores were still located inside the printed objects [19].

Tab. 1 Relative density of as-printed objects (PLA and composite Al₂O₃) of various designs including different infill patterns (rectilinear, concentric, Archimedean chords), infill densities (95 and 100 %) and extrusion multiplier factors (1.00 and 1.05).

Design	Infill pattern	PLA				Al ₂ O ₃	
		95 % infill, mult. 1.00	95 % infill, mult. 1.05	100 % infill, mult. 1.00	100 % infill, mult. 1.05	95 % infill, mult. 1.05	100 % infill, mult. 1.05
Cylinder	Rect.	97.0 ± 0.4 %	98.1 ± 0.4 %	95.4 ± 0.1 %	97.1 ± 0.7 %	94.5 ± 2.1 %	89.5 ± 3.6 %
	Conc.	90.9 ± 3.8 %	95.8 ± 0.8 %	92.9 ± 2.5 %	98.9 ± 0.2 %	90.8 ± 2.7 %	92.7 ± 2.6 %
	Arch. chords	85.4 ± 3.1 %	92.8 ± 0.3 %	92.2 ± 0.7 %	94.2 ± 0.6 %	85.9 ± 2.0 %	86.9 ± 2.5 %
Bar	Rect.	-	91.7 ± 1.2 %	-	-	95.2 ± 1.8 %	-
Pillar	Rect.	-	92.2 ± 3.8 %	-	-	92.8 ± 2.5 %	-

According to bulk density results of cylindrical samples (see *Tab. 1*), the best printing parameters were also selected for further preparation of prismatic samples – bars and pillars. It was observed that the highest values of bulk densities were obtained for rectilinear infill pattern of 95 % density using both, plastic and composite filament. On the other hand, changes in shape led to bulk density decrement together with larger deviations. This trend was not yet clearly explained in the literature. Based on these results, even if the used printing strategy should ensure preparation of relatively solid objects, it can be still presumed the presence of voids and inner pores, mostly for pillar design. This can correlate with changes in the contact area between the printed object and a work platform, and with the structure of sample volume. Cylinders are mostly created with an infill structure in comparison to pillars where perimeters and solid layers (outer shell) formulate larger printed volume than infill path. This change in printing variables (infill contra outer shell) influences mechanical performance and aesthetical quality of final printed part resulting in bulk density differences of various object design. The voids and printing imperfections, as suggested, were situated amongst infill paths (cylinders), and between the outer shell and the internal structure (bars and pillars). The localities were detected by μ CT scanning where the internal structure of 3 randomly chosen objects of each design has been analysed. For example, in *Fig. 1* images of μ CT-scanned cylindrical samples can be seen.

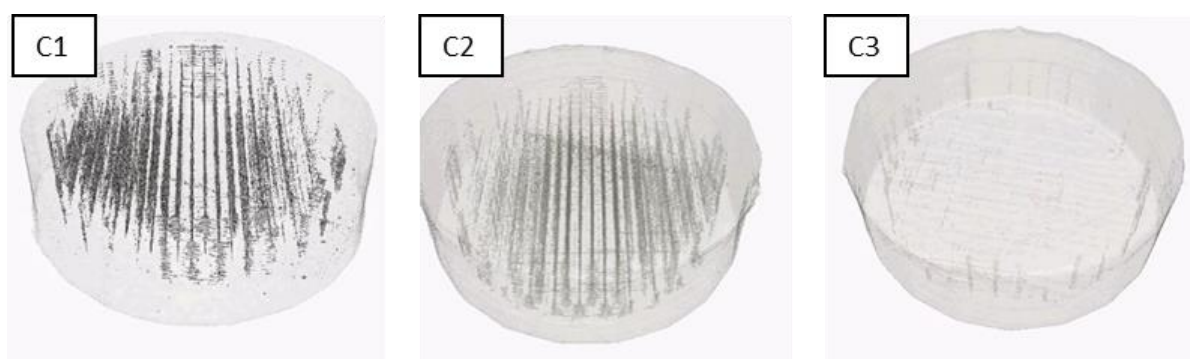


Fig. 1 Images of micro-CT scanned cylindrical objects. The same procedure was used for the preparation of ten cylindrical objects, and three randomly chosen samples from the serie are shown.

A porosity calculation extracted from μ CT-scans revealed 5 times lower value in comparison to porosity calculated from bulk density measurements. In most cases, it is a problem of micropores presence which cannot be observed even with μ CT device as it depends on

penetration depth and the measurement sensitivity. The most probable presence of imperceptible pores was found in the printed filament paths as it is visible from SEM analysis of the filament cross-section (Fig. 2). Those pores could be either created during the preparation of filaments or during the printing process, usually oriented in the printing direction [20].

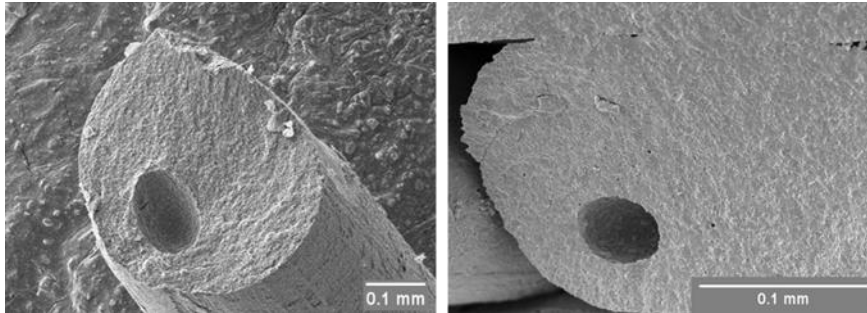


Fig. 2 SEM images of pores situated in the filament after printing (on the left) and in the filament path (on the right)

Looking into differences occurred within each object design, the repeatability of the printing process is the lowest for pillars and the highest for bars. Bars showed almost perfect process repeatability, including highly solid internal structure since pillar had differences in voids place presence. Calculations of sample volume (considering solid structure) showed that pillars have less by half volume space than cylinders or bars used in this work, 0.32 cm^3 compared to 0.65 cm^3 for pillar and bar, respectively. Considering those, if the filament contains small imperfections, such as pores or agglomerates, then they can influence the filament properties and thus the quality of 3D printing.

CONCLUSIONS

In this work, an extrusion-based 3D printing technique, Fused Filament Fabrication, was used to prepare composite ceramic objects using alumina filament of 50 vol.% solid loading. Three different object design (cylinders, bars, pillars) were printed containing various infill patterns, densities, and extrusion factors to obtain the highest possible bulk densities. The best results were obtained using a rectilinear infill pattern of 95 % infill density and extrusion factor 1.05. Nevertheless, bulk densities did not reach the theoretical value of each printed material, maximum 98 % and 95 % of the theoretical value for PLA and composite Al_2O_3 , respectively. Bulk density measurements in combination with μCT results showed that voids and micropores, decreasing bulk density results, are present even if such high infill densities and layer thickness as low as 0.1 mm are used for the printing. Moreover, these imperfections cannot be removed by a simple combination of these parameters. However, bulk densities seem to be dependent also on the printed volume. Small imperfections in the filament affect the quality and repeatability of 3D printed parts in the following order: bars - cylinder - pillar. In the case of bar specimen, almost fully dense deformation-free 3D printed objects were prepared.

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Boron carbide ceramics prepared by additive manufacturing technology

M. Vozárová^{1,2}, E. Neubauer², M. Orlovská¹, V. Trembošová³, J. Feranc⁴, Ľ. Bača¹, M. Janek¹

¹ *Institute of Inorganic Technology and Materials, FCHFT STU, Radlinského 9, Bratislava, Slovakia* ²

² *RHP-Technology GmbH, Austrian Research Center, 2444 Seibersdorf, Austria*

³ *Institute of Materials and Machine Mechanics SAV v. v. i., Dúbravská cesta 9/6319, Bratislava, Slovakia*

⁴ *Institute of Plastic, Rubber and Fibers, FCHFT STU, Radlinského 9, Bratislava, Slovakia*

ABSTRACT

Boron carbide is an industrially interesting material with unique properties, but it is very challenging for shaping and processing. Additive manufacturing of boron carbide offers the possibility of processing this very hard and demanding material in a fast and economic way. This work is focused on the preparation of highly filled B₄C polymer filaments to produce boron carbide ceramics using fused filament fabrication (FFF) technology.

Keywords: Additive manufacturing, boron carbide, fused filament fabrication

INTRODUCTION

Boron carbide is a material with low density (2.52 g cm⁻³), low coefficient of thermal expansion (4.35 10⁻⁶ K⁻¹), and high hardness (up to 49 GPa), which makes it usable as structural material in engineering, space, nuclear and other industries, as well as in the production of materials for ballistic protection [1,2]. However, due to its combination of high hardness, low plasticity, and high cohesivity of fine powders, boron carbide is difficult to process directly using additive manufacturing. So far, the researchers have been able to involve B₄C to the FFF process only via indirect additive manufacturing or as neutron shielding composite filament [3–5]. This paper reports for the first time the successful preparation of highly filled filament containing boron carbide that was used for the production of boron carbide ceramics using FFF technology.

EXPERIMENTAL

The composite filament was prepared from fine and high purity B₄C powder and thermoplastic polymer with a solid loading of 65 wt. %. The binder system consists of the thermoplastic polymer, surfactant, and plasticizer. The prepared feedstock was homogenized and shaped into filament using a double-screw extruder. The extruded filament was subsequently tested for additive manufacturing forming using printer Wanhao Duplicator i3 using 0.6 mm nozzle. The prepared samples were debinded in Argon atmosphere and sintered in a gas pressure furnace at a temperature of 2200°C.

RESULTS

As presented in Fig. 1 A, the fracture surface of an extruded filament shows good homogeneity of the powder in the binder system without any significant defects. After debinding and sintering, a filament with a fine microstructure (Fig. 1 B) and a relative density of 95 % was prepared. No cracks or defects were observed. The complex-shaped samples were successfully prepared during the FFF process and they retained their shape after debinding and sintering with the average value of linear shrinkage of 21 %. The samples before and after sintering are compared in Fig.1 C.

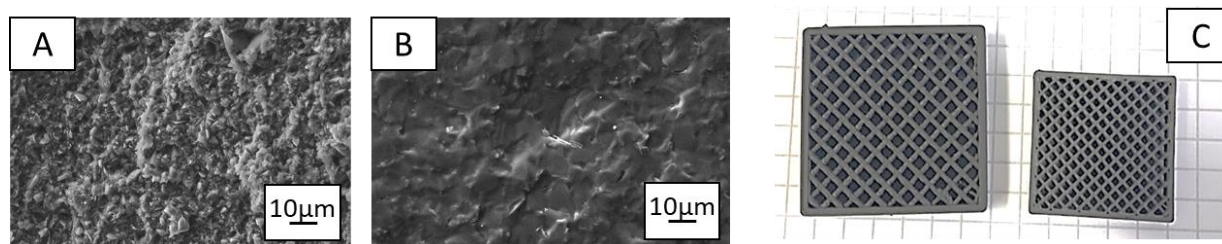


Fig. 1. The SEM images of the fracture surface of as extruded filament (A), sintered filament (B), the comparison of the sample as a green body (left), and after sintering (right) (C).

CONCLUSION

The complex 3D parts were successfully prepared from the highly filled filament with fine boron carbide powders using FFF technology. SEM images of 3D printed, debinded and sintered objects show promising results after further material research and optimization.

ACKNOWLEDGMENT

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Sol-Gel Based Coatings for Corrosion Protection of Mg Alloys (AZ31B)

N. Afsharimani ^{1*}, A. Talimian ¹, A. Durán ², Y. Castro ², D. Galusek ^{1,3}

¹*Centre for Functional and Surface Functionalized Glass, Alexander Dubček University of Trenčín, Študentská 2, 91150, Trenčín, Slovakia*

²*Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, 28049 Madrid, Spain*

³*Joint Glass Centre of the IIC SAS, TnUAD and FChFT STU, Študentská 2, 91150, Trenčín, Slovakia*

* nasima.afsharimani@tnuni.sk

ABSTRACT

In the present work, we report on electrochemical corrosion protection of magnesium alloys (AZ31B) using graphene-modified hybrid silica sol-gel coatings. Potentiodynamic polarization results using 0.05 M NaCl electrolyte solution showed that graphene containing silica coatings significantly improve the corrosion resistance of AZ31B alloys. In addition, a significant passive region was observed for such coatings.

Keywords: Magnesium alloy; Sol–gel coatings; Corrosion protection; Barrier properties; Graphene nanosheets

INTRODUCTION

Magnesium alloys play an important role in modern engineering; however, their application is limited due to the poor corrosion resistance. Several efforts have been made to improve the corrosion resistance of magnesium products; the protection methods are mainly focused on producing an oxide layer on the surface, known as anodization. Although anodization methods improve the corrosion resistance significantly, the layers are susceptible to mechanical damages and lack self-healing properties. Sol-gel methods have emerged as an environmentally friendly alternative to traditional toxic chromate conversion coatings¹. Besides, the application of graphene as filler in protective coatings has been shown to be an effective strategy to improve anticorrosion properties owing to its chemical inertia, impermeability and environmental compatibility². The aim of this work was to use cost-effective large-scale available graphene nanosheets (GN) for incorporation into silica-based sol-gel coatings to improve the corrosion resistance of magnesium alloys (AZ31B).

EXPERIMENTAL

Commercially available AZ31B Mg alloys were used as substrates. The anodization process was performed using an aqueous electrolyte of 1 M NaOH at 30 V for 10 min at room temperature. Graphene nanosheets were chemically modified and denoted as GN-chem³. GPTMS-TEOS (GT) silica sol was prepared by mixing 3-glycidolxypropyl trimethoxysilane (GPTMS), Tetraethoxysilane (TEOS) and absolute ethanol (EtOH) with a molar ratio of 0.05:0.05:0.40, respectively. Acidulated water (1M HCl) was added dropwise to initiate hydrolysis and condensation processes. GT/GN-chem sol was also prepared by adding GN-chem following a similar procedure. The sols were deposited on anodized AZ31B substrates by dip-coating and thermally treated at 180 °C for 1 h.

RESULTS

Fig. 1 shows the polarization curves of the bare and anodized AZ31B alloys, GT and GT/GN-chem coatings. For the polarization curves, the anodic branch is the most important feature related to the metal dissolution and corrosion resistance. For all samples, corrosion potential (E_{corr}) is shifted to more positive values and corrosion current density (J_{corr}) shifted to smaller values compared to the bare AZ31B alloy. When compared to AZ31B alloy, the value of corrosion potential of GT/GN-chem coating increases from -1.40 ± 0.10 to -1.26 ± 0.03 V and the value of corrosion current density decreases one order of magnitude from 5.00 ± 0.50 to $0.10 \pm 0.05 \mu\text{A}\cdot\text{cm}^{-2}$. This indicates the formation of an efficient anodic protection that inhibits the overall corrosion reaction ($\text{Mg} + 2 \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{H}_2$).

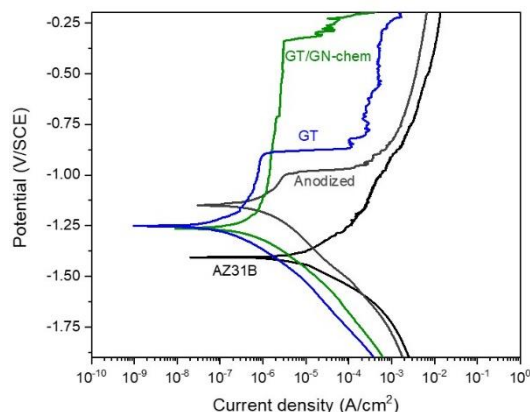


Fig. 1. Potentiodynamic polarization curves of bare AZ31B alloy and substrates coated with anodized layer and hybrid sol-gel GT coatings without and with graphene nanosheets.

CONCLUSION

Hybrid silica sol-gel coatings containing graphene nanosheets were prepared to control the corrosion protection of magnesium alloy AZ31B in 0.05 M NaCl. The study proposes the addition of slightly modified graphene nanosheets to silica sol-gels can provide a promising barrier property.

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Oxidation resistance of PDC glass-ceramic coatings on stainless steel

I. Parchovianská¹, M. Parchovianský¹, P. Švančárek¹, G. Motz², D. Galusek^{1, 3}

¹ *FunGlass, A. Dubček University of Trenčín, Študentská 2, 911 50 Trenčín, Slovakia*

² *University of Bayreuth, Ceramic Materials Engineering, D-95440 Bayreuth, Germany*

³ *Joint Glass Centre of the IIC SAS, TNUAD and FChFT STU, Študentská 2, 911 50 Trenčín, Slovakia*

ABSTRACT

The work describes an oxidation resistant environmental barrier coating system applied to stainless steel substrates. For that purpose, double layer polymer derived ceramic (PDC) coating systems consisting of a bond coat and a top coat were developed and studied with respect to their oxidation resistance at temperatures of up to 1000 °C in synthetic air atmosphere. The prepared coatings provided oxidation resistance up to 900 °C. At higher temperatures the coating delaminated from the substrate.

Keywords: PDC coating, oxidation, synthetic air

INTRODUCTION

The high temperature corrosion and oxidation resistance of stainless steel can be enhanced by polymer derived ceramic (PDC) coatings, which offer a number of advantages in comparison to traditional methods of ceramic processing, especially easy application on substrates of any shape by simple methods like dip-coating, spray-coating or spin-coating [1]. They are also specific by low temperature processing and the potential to tailor the properties via microstructure and composition design. Polymer derived ceramic composite coatings are promising candidates to be used as alternative environmental barrier coatings for corrosion and oxidation protection of metals [2].

EXPERIMENTAL

The perhydropolysilazane-based bond coat was applied on AISI 441 stainless steel via dip-coating and fixed by pyrolysis at 450 °C before the composite top coat was spray-coated and again pyrolysed in air at 850 °C. The top coat was prepared from the commercial polymer - Durazane1800 (Merck KGaA, Germany), passive filler (YSZ – yttria stabilized zirconia, Inframat, USA) and commercial glass (G018-281, Schott AG). In order to evaluate protective properties of the coating, oxidation tests were carried out at the temperatures of 900, 950 and 1000 °C in synthetic air with the isothermal dwell time of 24 and 96 hours.

RESULTS

After oxidation tests, the porosity and cracking in the coating increased with increasing oxidation time and temperature until spalling of the coatings occurred when exposed to 950 °C for more than 24 h (Fig. 1). The dark grey sites were characterized as the coating porosity, filled with embedding resin during the cross section preparation. The high porosity observed after oxidation is caused by the differential sintering mainly of the glass fillers by viscous flow. Exposure to oxidation at 1000°C led to an entire coating delamination, as indicated by abrupt increase in the weight loss.

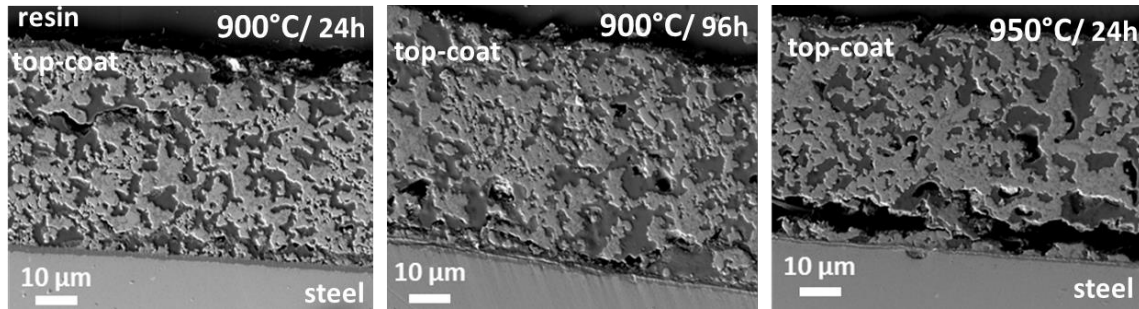


Fig. 1: SEM cross-section of coated samples after oxidation tests in synthetic air

CONCLUSION

The protective effect of the coating was observed at the temperature 900 °C, while at higher temperatures and longer exposure times the delamination and failure of the protective properties was observed.

ACKNOWLEDGMENT



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Oxidation behaviour of PDC coatings with glass fillers on AISI441 stainless steel

M. Parchovianský¹, I. Parchovianská¹, P. Švančárek³, G. Motz², D. Galusek^{1, 3}

¹*Centre for Functional and Surface Functionalized Glass, Študentská 2, 911 50 Trenčín, SK*

²*University of Bayreuth, Ceramic Materials Engineering, D-95440 Bayreuth, Germany*

³*Joint Glass Center of the IIC SAS, TnU AD, and FCHFT STU, Študentská 2, 911 50 Trenčín, Slovakia*

ABSTRACT

The aim of this study is to investigate the oxidation resistance of an AISI441 stainless steel with and without the coating at temperatures of up to 1000 °C in atmosphere of water vapor. The protective effect of the PDC coatings applied to the stainless steel is demonstrated up to 950 °C, while at the temperature 1000 °C the layer of oxidation products was found at the interface bond coat/top coat.

Keywords: PDC coatings, oxidation, water vapor

INTRODUCTION

New materials for high temperature applications are always in demand and are a great challenge in many fields of industry. High-temperature technologies place increased demands on the materials used, as they significantly shorten their service life due to HT corrosion. The development of new types of protective coatings (EBC) prolongs their service life. PDC are promising materials for high temperature applications as they have excellent oxidation, corrosion and thermal shock resistances and are stable at high temperatures [1].

EXPERIMENTAL

The AISI 441 steel was coated with a two layer coating protection system. The bond coat was prepared from the commercial polymer Durazane 2250 (Merck KGaA, Germany) by dip-coating (dip-coater RDC 15, Relamatic, Switzerland). The pyrolysis of the bond-coat was carried out in air (Nabertherm® N41/H, Germany) at a temperature of 450 °C for 1 h. The top coats were prepared from the commercial polymer – Durazane 1800 (Merck KGaA, Germany), passive fillers and commercial glass. The passive fillers used were ZrO₂ stabilized with 8 mol. % Y₂O₃ (8YSZ, Inframat, USA), in house prepared AYZ powder and commercial glass (G018-281, Schott). The oxidation tests were carried out at the temperatures of 900, 950 and 1000 °C in the atmosphere of water vapor with the isothermal dwell time of 24 and 96 hours.

RESULTS

Fig. 1 shows cross-section of coated steel exposed to atmosphere of water vapor at different temperatures and holding times. No oxidation products were observed at 900 °C, and the coating was intact by the corrosion. The layer of oxidation products (Cr₂O₃ and (Mn,Cr)₃O₄ spinel) have been observed at the bond/top coat interface after corrosion at 1000 °C. No delamination at the interfaces steel/bond coat or bond coat/top coat was found.

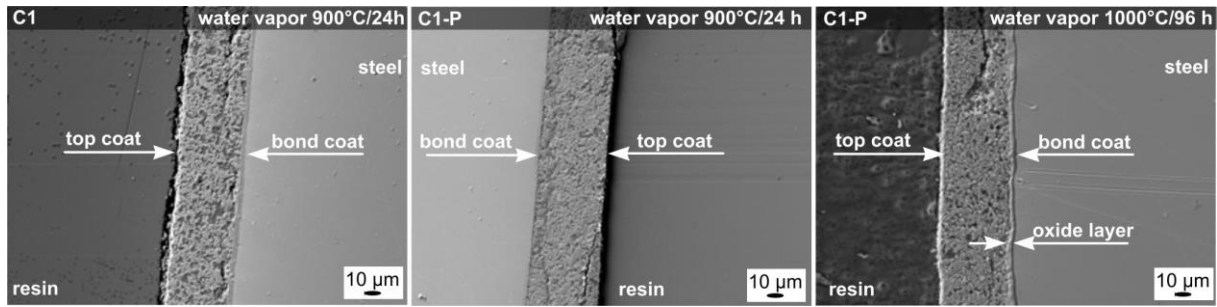


Fig. 1: SEM cross-section of coated samples after oxidation tests in water vapor
CONCLUSIONS

The protective effect of the prepared EBC was observed at the temperature 900 °C, while at higher temperature (1000 °C) and longer exposure times (96 h), the layer of oxidation products was observed at the interface bond coat/top coat.

ACKNOWLEDGMENT

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Deposition of ceramic precursors on various substrates by using desktop printer

M. Zitnan¹, L. Müller², S. Höppener³, U. S. Schubert³, J.J. Velázquez^{1,4}, L. Wondraczek²

¹*FunGlass, Alexander Dubček University of Trenčín, Študentská 2, 91150 Trenčín, Slovakia*

²*Otto Schott Institute of Materials Research, Friedrich-Schiller-University Jena, Fraunhoferstrasse 6, D-07743 Jena, Germany*

³*Jena Center for Soft Matter, Friedrich-Schiller-University Jena, Philosophenweg 7, D-07743 Jena, Germany*

⁴*Joint Glass Centre of the IIC SAS, TnUAD and FChPT STU, Študentská 2, 91150 Trenčín, Slovakia*

ABSTRACT

In this work we have shown the possibility to inkjet a liquid ceramic precursor on glass substrates. We formulated a sol-gel based ink with a suitable mixture of solvents and proved its printability. The geometrical characteristics of the printed lines, like line thickness and cross-section profiles were also studied.

Keywords: inkjet printing, sol-gel, silica, zirconia

INTRODUCTION

Inkjet printing is allowing affordable, precise and contact-less transfer of matter on substrate. It offers the added value of complex patterning compared to the common solution deposition methods such as spin coating or dip coating. However, there are still some drawbacks that should be addressed. For instance, the method is highly sensitive to the physicochemical properties of the ink¹. Between them, important parameters, such as viscosity and surface tension must be precisely adjusted to control the geometrical characteristics of printed structures, like line width and cross-section profile. The variety of synthetic routes providing stable sols enables the adjustment of the properties of prepared sols². The sol-gel method offers the ways to produce sols with the required characteristics³. In this work, we proposed to use sol-gel-based inks synthesized in suitable solvents and studied the effect of the ink's properties on the line width and profiles of printed structures.

EXPERIMENTAL

A desktop printer Hewlett-Packard model Deskjet 3000 with HP300 thermal ink cartridges was modified to allow printing on substrates with thickness up to 1.5 mm. Minimal changes to the hardware preserved the printer's ability to be controlled by conventional software. The use of original cartridges keeps the ink design financially reasonable. Before printing with ceramic precursor, the original black ink was removed. The cartridge was rinsed with a mixture of water and ethanol. Ceramic precursors were synthesized using the sol-gel route to reach the physicochemical properties of the original black ink, such as low viscosity with relatively high surface tension. These properties should ensure good drop formation ability after jetting through the nozzles. Silica and zirconia sols were prepared by conventional route from tetraethyl orthosilicate or zirconium isopropoxide with the addition of absolute ethanol and water acidulated with nitric acid. Low pH < 2 allows us to reach the meta-stable region, where the observed gelling times are sufficiently long. Moreover, the acidic route provides control over the growth rate of SiO₂ or ZrO₂ agglomerates. The precursors were deposited on soda-lime glass slides. To improve wetting, the slides were plasma-treated in Ar atmosphere. After drying

at 90°C, the coatings were characterised by confocal optical microscopy to determine the width and thickness of the structures.

RESULTS

Transparent and yellowish transparent sols were obtained for Silica and Zirconia precursors, respectively. Si-sol with gelation time in order of weeks was prepared. Structures on the glass slides in a form of thin lines were deposited by inkjet printing. The maximal thickness of printed SiO₂ lines was determined to be 1.2 µm: no coffee-ring effect was observed. On the other hand, most of the ZrO₂ sols were not printable due to the strong sensitivity of the sol to the water content. Finally, a printable mixture of solvents with H₂O to EtOH ratio 2:1 was found. However, the printed lines show a strong coffee-ring effect, with the height of the rims exceeding 1.3 µm.

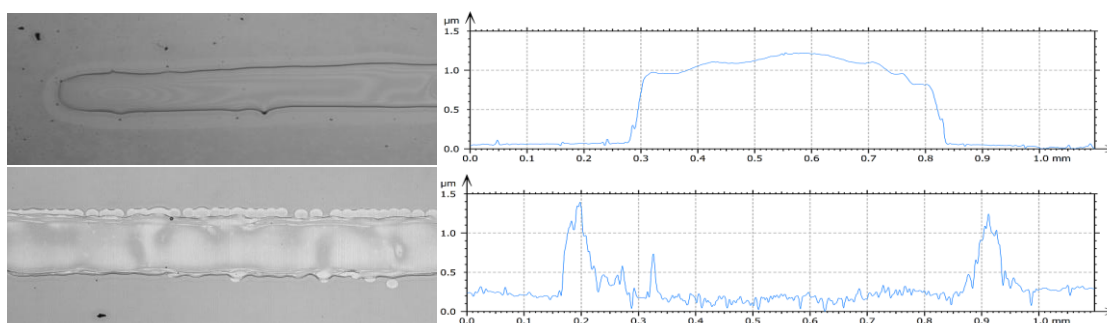


Fig.1. Printed silica (top) and zirconia (bottom) lines on a soda-lime glass substrate on the left, and their cross-sections profiles on the right side.

CONCLUSION

Silica and zirconia sols have been prepared by varying the parameters of the sols to obtain rheological properties suitable for inkjet printing technique using a modified commercial printer. The structures in a form of thin lines were inkjet printed on the substrate. This work opens the way to create 2D structures by using sol-gel method and modified cheap desktop inkjet printer.

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Ce³⁺-doped phosphors prepared by sintering of microspheres of yttrium-aluminate glasses

A. Akusevich^{1*}, R. Klement¹, I. Parchovianská¹, M. Parchovianský¹, A. Prnová²

¹ *FunGlass, Alexander Dubček University of Trenčín, Študentská 2, 911 50 Trenčín, Slovakia*

² *Joint Glass Centre of IIC SAS, TnUAD and FChFT STU, Študentská 2, 911 50 Trenčín, Slovakia*

**Corresponding author e-mail: alena.akusevich@tnuni.sk*

Keywords: Ce³⁺, phosphors, solid state lighting, pc-WLED.

INTRODUCTION

White light-emitting diodes (WLEDs) are nowadays constructed via combination of blue LED chip covered with yellow-emitting Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce) phosphor powder dispersed in organic binder. However, commercial LEDs are currently limited due to the efficiency drop when increasing input current density. As a result, it is difficult to realize high-brightness white light sources using laser diode excitation chips. To survive from high-flux laser irradiation and thermal attack, the thermal performance of the phosphor converter is a principal technical parameter for the laser lighting. The excellent phosphor for white lighting application is YAG:Ce having many favorable properties, such as efficient absorption of blue light (also possibility of excitation in NUV range), broadband emission in the visible spectral range with high quantum yield, good thermal quenching properties up to 200 °C and excellent chemical and thermal stability. The current phosphor converter is made by embedding YAG:Ce powders in organic binders, but the low heat-resistance (polymer resin degradation at higher temperatures/light flux in LEDs) and thermal conductivity (0.1-0.4 Wm⁻¹K⁻¹) of this mixture greatly hinder its application in high-power, high-brightness solid state lighting (SSL). To overcome these problems, composite materials such as Phosphor-in-Glass (PiG), where the phosphor is dispersed in a glass, has been developed [1].

EXPERIMENTAL

In the present work we report on preparation and preliminary characterisation of compact samples prepared by hot pressing of glass microspheres powders in the Ce³⁺ doped Y₂O₃-Al₂O₃ system with different ratio of YAG to Al₂O₃ phase in a composite. The composition of prepared Ce³⁺-doped glasses is derived from the corresponding un-doped system by equimolar substitution of Y₂O₃ by Ce₂O₃.

The bulk glass from microspheres with eutectic composition was prepared at temperature 840 °C with dwell time 0 min, applying the pressure of 40 MPa. The glass-ceramic samples with YAG crystals embedded in residual glass matrix were prepared at temperatures 1000 °C and 1100 °C with the dwell time 30 and 60 min.

RESULTS

The prepared glass microspheres of given compositions were found to be XRD amorphous. The DSC analysis revealed the two exothermic effects (at temperatures around 940 °C and ranging from 965 °C up to 1060 °C). Both effects correspond to the crystallization of the YAG

phase, as documented also by high temperature XRD [2]. The Al_2O_3 phase as corundum start to crystallize over 1300 °C [2]. The T_g temperature was found to be around 890 °C.

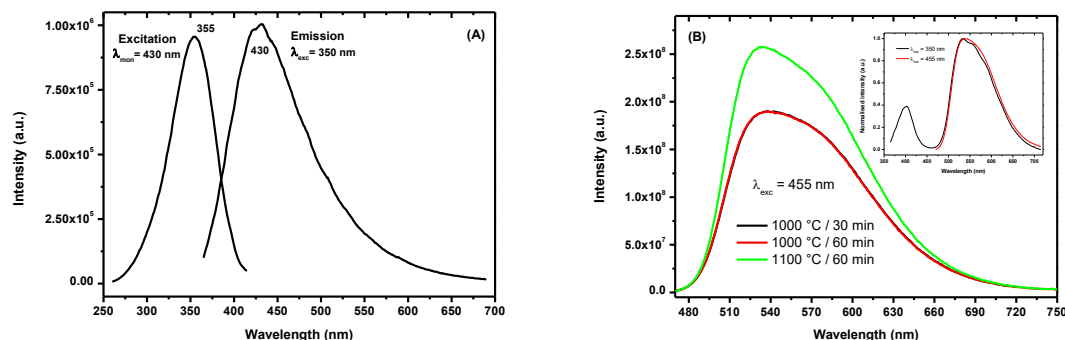


Fig. 1: (A) The excitation and emission spectra of 30%YAG-70% Al_2O_3 (eutectic composition) sample prepared by hot-pressing of glass microspheres at 840°C/0 min. (B) The PL spectra of 30%YAG-70% Al_2O_3 sample prepared by hot-pressing of glass microspheres at different temperatures and dwell time. Inset represents the emission spectra of samples under UV and blue light excitation.

The excitation (PLE) and emission (PL) spectra of the glass bulk sample with eutectic composition is depicted in Fig. 1A. The excitation spectrum was monitored at wavelength 430 nm. The emission spectrum of the glass compact exhibits broad emission band in spectral range of 365–550 nm with the emission maximum at 430 nm. The PL emission spectra ($\lambda_{\text{exc}} = 455 \text{ nm}$) of 30%YAG-70% Al_2O_3 samples hot-pressed at different temperatures and dwell time are shown in Fig. 4B. A typical broad emission bands centred at ~550 nm were observed in the spectra. The PL spectra of compact samples prepared from different compositions of starting glass sintered at 1000°C/60 min were investigated. The emission intensity increases with increasing concentration of Ce^{3+} ions in YAG phase from 1.42 at.% to 2.00 at.%, than the intensity decreased for sample with 3.48 at.% Ce (concentration quenching).

The study of microstructure and testing of mechanical properties of compact bulk phosphors is currently in progress.

ACKNOWLEDGMENT

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Barium phosphate glasses: structure investigation by SVTD modeling and NMR spectroscopy

Rajesh Dagupati^{1*}, Marek Liška^{2*}, Alberto López-Grande³, and Francisco Muñoz^{3*}

¹*FunGlass, Alexander Dubček University of Trenčín, Študentská 2, SK-911 50 Trenčín, Slovakia*

²*VILA-Joint Glass Centre of the IIC SAS, TnUAD, and FChPT STU, Alexander Dubček University of Trenčín, Študentská 2, SK-911 50 Trenčín, Slovakia*

³*Institute of Ceramics and Glass (CSIC), Kelsen 5, 28049 Madrid, Spain*
E-mail: rajesh.dagupati@tnuni.sk, marek.liska@tnuni.sk, fmunoz@icv.csic.es

ABSTRACT

In this work, the Shakhmatkin and Vedishcheva thermodynamic (SVTD) model has been developed for the BaO-P₂O₅ system to derive their short-range structure and predict the volume properties. The model applicability has been examined by comparing the short-range structure obtained from SVTD modeling and by Nuclear Magnetic Resonance spectroscopy. The evaluation of the molar volume of the investigated glasses has been carried out through comparison of the experimental values with the calculated ones by two different approaches: i) with the glass molar volume obtained through a linear combination of the product of the molar fractions of the system components and the volume of respective crystalline phases; and ii) with the molar volumes calculated by a multilinear regression analysis of the experimental molar volume of each composition.

Keywords: BaO-P₂O₅ Glass; SVTD Model; MAS-NMR;

INTRODUCTION

The relationship between phosphate glass structure and its properties has been investigated for 100 years for various applications [1-2] since the arrangement of atoms at the atomic scale level can control the macroscopic properties of the glasses. Therefore, investigating the structure of glasses and its correlation with their properties is an extensive research topic in glass science. Some theoretical models have been developed: among them, the ideal associated solutions model has been proposed by Shakhmatkin, and Vedishcheva (SVTD model) [3]. The model been applied to silicate, phosphate, and chalcogenide glasses to describe their structure.

EXPERIMENTAL

Binary barium phosphate glasses with chemical composition x BaO-(100- x) P₂O₅ (x = 40, 42.5, 45, 47.5, 50, 52.5, 55, and 57.5 mol.%) were prepared by melting and quenching technique and were characterized by X-ray diffraction (XRD), Netzsch Gerätebau dilatometer, X-ray fluorescence (XRF), Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR).

RESULTS

The equilibrium molar amounts of system components against BaO content obtained by the model of associated solutions are plotted in Fig. 1. Three pseudo-regions, such as (i) binary ($0 \leq x \leq 33$), (ii) binary ($33 \leq x \leq 50$), and (iii) ternary ($0.50 \leq x \leq 0.60$) have been observed within the glass-forming region. Fig. 2 shows the distribution of Q^n ($n = 0, 1, 2$, and 3) tetrahedral units, obtained from the model, against the BaO content. The ³¹P MAS-NMR spectra

of all investigated glasses are shown in Fig. 3. The calculated partial molar volumes of the glasses by multi-linear regression analysis and from the SVTD model are shown in Fig. 4a & 4b, respectively. The inset in Fig. 4b represents the molar free volume of the glasses.

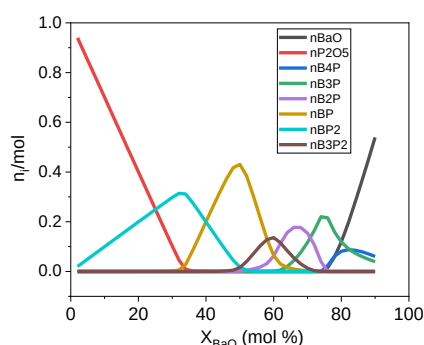


Fig. 1: Equilibrium molar amounts of system components against BaO content.

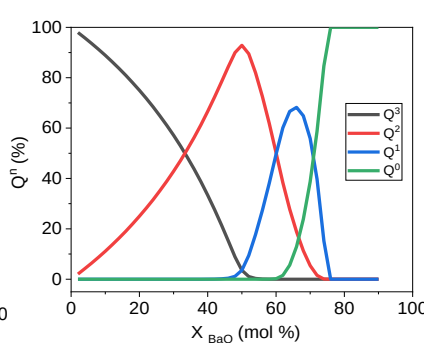


Fig. 2: Distribution of phosphate tetrahedral units against BaO content.

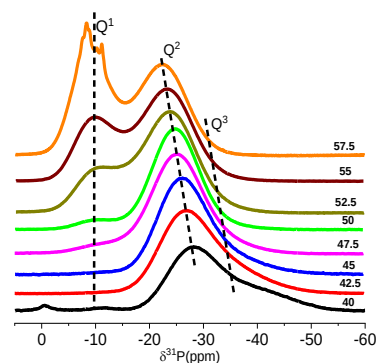


Fig. 3: ^{31}P MAS NMR spectra for BaO- P_2O_5 glasses with different BaO content.

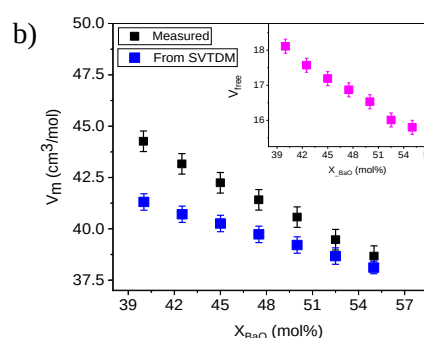
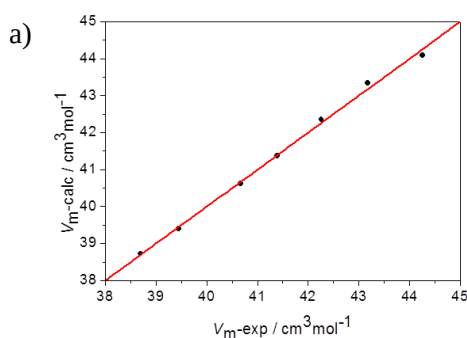


Fig. 4: Experimental and calculated molar volume (V_m) a) Multi-linear regression analysis, and b) SVTD model for BaO- P_2O_5 glasses against BaO content.

CONCLUSION

- A refined Shakhmatkin and Vedishcheva thermodynamic model based on the theory of associated solutions has been developed for BaO- P_2O_5 glasses.
- The quantification of the Q^n tetrahedral units against the analyzed BaO content correlates well with the Q^n tetrahedral units obtained experimentally by MAS-NMR spectroscopy.
- The calculated molar volume of the glasses has been obtained through multilinear regression analysis consistent with the molar volume measured at each glass composition.

ACKNOWLEDGMENT



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Preparation of TiO₂ nanotube arrays on transparent spinel for photocatalytic applications

P. Petrisková¹, O. Monfort², Z. Lenčák¹, L. Satrapinsky³, G. Plesch²

¹*Department of Ceramics, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia*

²*Department of Inorganic Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Ilkovičova 6, Mlynská Dolina, 842 15 Bratislava, Slovakia*

³*Department of Experimental Physics, Faculty of Mathematics Physics and Informatics, Comenius University in Bratislava, Mlynská Dolina, 842 48 Bratislava, Slovakia*

ABSTRACT

TiO₂ nanotubes (TNTs) have been prepared on transparent ceramic spinel (MgAl₂O₄) by anodic oxidation of Ti film deposited by magnetron sputtering. The photocatalytic activity of TNTs was tested by the removal of two model pollutants rhodamine B (RhB) and bisphenol A (BPA). Although the efficiency of TNTs in the degradation of both pollutants was lower compared to TNTs grown on Si or Ti foil substrates, the results are promising, especially for the application of spinel/TNTs composites for air or water purification in harsh environments.

Keywords: TiO₂ nanotubes, photocatalysis, rhodamine B, bisphenol A, pollutant removal

INTRODUCTION

During the last two decades the wastewater purification by UV light driven TiO₂-based photocatalysis gained high attention [1, 2]. Under UV irradiation, the photogenerated electrons (e⁻) and holes (h⁺) react with H₂O and dissolved oxygen to produce reactive oxygen species (ROS) which are able to mineralize organic pollutants [3]. A crucial parameter for the implementation of TiO₂ materials in photocatalytic applications is the specific surface area which is linked to the morphology, crystallite size and crystalline phase composition of the material, anatase polymorph being more effective compared to rutile. For this reason we have prepared a TiO₂ nanotubes on transparent ceramic spinel substrate.

The photocatalytic properties of TNT arrays were assessed by measuring the removal of two model pollutants: an organic dye RhB (10 µM) and an endocrine disruptor compound BPA (50 µM). The samples were exposed from the top to UVA irradiation.

EXPERIMENTAL

The transparent polycrystalline MgAl₂O₄ spinel ceramic substrate was prepared in-lab from MgO (grade EMSURE, Merck) and Al₂O₃ (grade TM-DAR, Taimicron) powders by hot-isostatic pressing of powder compacts at 1550 °C and 200 MPa argon pressure for 5 h. A 1.5 µm thick Ti metal layer was deposited by DC-magnetron sputtering on spinel substrate, which was subsequently anodized in ethylene glycol electrolyte containing 0.5 wt.% NH₄F and 0.2 wt.% H₂O for 30 min at 40 V. The amorphous nanotube-arrays were crystallized to anatase phase annealed at 450 °C for 1 h. The crystalline phase composition was analysed using XRD, the morphology of TNTs was studied by SEM.

RESULTS AND DISCUSSION

The XRD measurements showed that pure anatase TiO₂ crystallized from the amorphous phase. The top view and cross-sections of TNTs grown on different substrates are shown in Fig. 1.

The dimensions of TNT were: inner diameter 60 nm, wall thickness 20 nm, and tube length ~ 1100 nm.

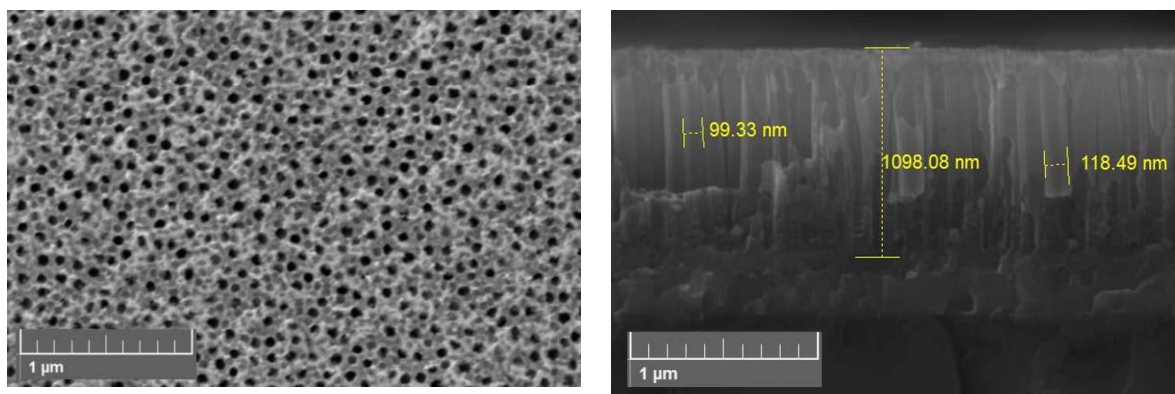


Fig. 1. The top view and cross-section of TNT arrays produced on spinel substrate.

The photocatalytic activity of TNTs grown on ceramic substrate were compared with TNTs grown on polymeric Kapton film, Si wafer and Ti foil. The results are shown in Fig. 2.

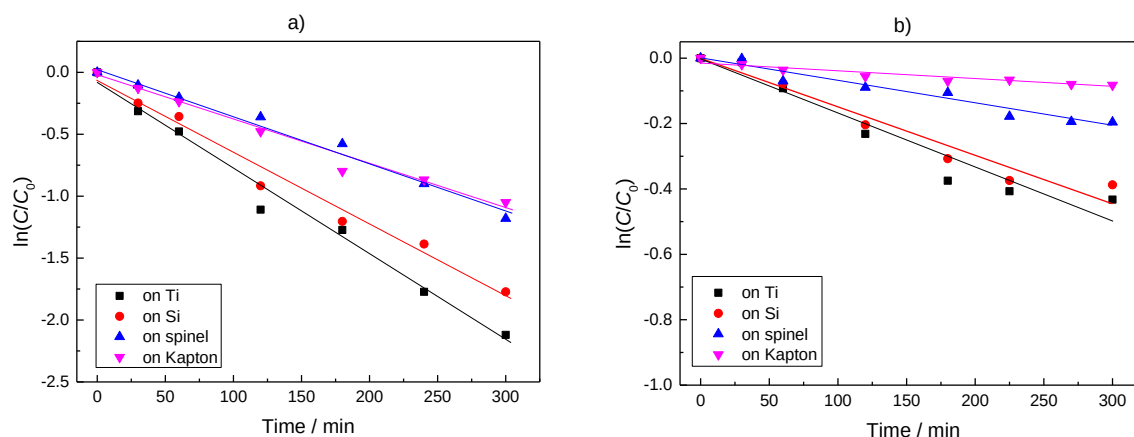


Fig. 2. The degradation rate of RhB (a) and BPA (b) pollutants by UVA excited TNTs.

Although the photocatalytic activity of TNTs grown on spinel is weaker compared to TNTs prepared on Si or Ti substrates, the results are promising, especially for the applications of this spinel/TNTs composites in harsh environments.

CONCLUSION

TiO₂ nanotubes have been successfully prepared on transparent ceramic spinel substrate by anodic oxidation of Ti film deposited by magnetron sputtering. The TNTs showed a good photocatalytic activity by the removal of two model pollutants rhodamine B and bisphenol A.

ACKNOWLEDGMENT

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Preparation and properties of functionally graded SiC-graphene composites

O. Hanzel¹, R. Sedlák², Z. Lenčoš¹, P. Šajgalík¹

¹*Institute of Inorganic Chemistry SAS, Dúbravská cesta 9, 845 36 Bratislava*

²*Institute of Materials Research SAS, Watsonova 47, 040 01 Košice*

ABSTRACT

Functionally graded materials (FGM) based on silicon carbide with yttria and alumina as a sintering additives and graphene nanoplatelets as a conductive phase were sintered at 1800°C in vacuum by rapid hot-pressing (RHP) technique. Functional properties (thermal diffusivity and electrical conductivity) as well as density, microstructure, hardness and elastic modulus of 3-layered composites were investigated with regard to applied pressure during sintering in RHP (minimum contact pressure, 30, 40 and 50 MPa). Electrical conductivity increased in all composites with increasing applied pressure during sintering and increased in all layers with increasing amount of GNPs. The highest electrical conductivity (1442 S/m) was observed in layer which contains 15 wt. % of GNPs in 3-layered composites sintered at 50 MPa.

Keywords: SiC, graphene, layered composites, thermal diffusivity, electrical conductivity

INTRODUCTION

FGM are advanced engineering materials consisting of two or more phases, in which gradation in composition or microstructure allow us to tailor mechanical and/or functional properties for a specific function. The term “functionally graded materials” was first used in Japan in 1984 for development of thermal barrier materials [1]. The main goal of this study is the preparation of dense SiC materials with gradually changed content of graphene nanoplatelets along one direction. The microstructure, electrical conductivity, thermal diffusivity, hardness, elastic modulus across the 3-layered composites have been measured and investigated.

EXPERIMENTAL

In this work, for preparation of 3-layered composite materials, three different powder mixtures were used. For preparation of composite powders, SiC (Superior graphite, USA, β -SiC, d_{50} = 0.6 μ m), Y₂O₃ (HC Starck, purity > 99.99%), Al₂O₃ (Taimei Chemicals Ltd., α -Al₂O₃, purity > 99.99 %, particle size 100 nm) and graphene nanoplatelets – GNPs (Cheap Tubes Inc., USA, thickness < 3 nm, lateral size 1-2 μ m) were used. The first step was strong ultrasonication of water based suspension with different amount of GNPs (5; 15 wt. %) for 60 min. by ultrasound probe. After that, SiC powder together with Y₂O₃ and Al₂O₃ powders in 93:5:2 wt. % ratio were added and ball milled in a plastic jar with SiC balls on rollers for 24 h. Final suspension was sprayed into the liquid nitrogen and subsequently freeze dried. This procedure is crucial for ensuring homogeneous distribution of all components and especially graphene nanoplatelets, throughout the composite materials. After stacking layer by layer of each accurately weighted composite powder mixture in graphite die, uniaxial pressing at 30 MPa was applied. Sintering was performed in rapid hot press (DSP 507, Dr. Fritsch GmbH., Germany) at 1800°C for 5 min and at various uniaxial pressure (minimal contact pressure 30, 40 and 50 MPa), under vacuum atmosphere and with the heating rate of 100°C/min. In the 3-layered samples the layer sequence was 0-5-15 % GNPs. The electrical resistivity of the sintered samples was determined by using a standard four-point Van der Pauw method (Loresta-AX MCPT370) with linear configuration of probe tips. The thermal diffusivities were measured using the laser flash analyzer (Linseis LFA 1000, Germany) in the temperature range from room temperature to 400 °C in a vacuum.

RESULTS

Relative densities (RD) of samples were higher than 97 %, except the 3-layered composite sample (C3_m), which was sintered at 30 MPa contact pressure (RD = 92.23 %). Thermal diffusivity of 3-layered sample sintered at minimum contact pressure is around 22 mm²/s mainly due to the lower relative density compared to three other samples sintered at higher pressure and therefore with higher densities. Thermal diffusivities of samples sintered at higher pressure were in the range from 26 to 29 mm²/s (Fig. 1b). Electrical conductivity was measured from both sides (SiC side and side which contains 15 wt. % of GNPs) and was investigated as a function of applied pressure during sintering (Fig. 1a). Electrical conductivity of sample with the lowest contact pressure (C3_m) was 588 S/m and with increasing applied pressure during sintering increased up to 1442 S/m. In case of SiC side, electrical conductivity increased linearly from $\sigma = 12$ S/m (for C3_m sample) up to $\sigma = 122$ S/m (for C3_50 sample). Thus, the electrical conductivity of layered composites was strongly influenced by side which was measured, because in standard four-point Van der Pauw method electric current goes mainly through the surface layer and only partially through the bulk. Electrical conductivity increased in both cases with increasing applied pressure during sintering and therefore with increasing relative density. However, the improvement of electrical conductivity was much more pronounced on the side which contains 15 wt. % of graphene nanoplatelets.

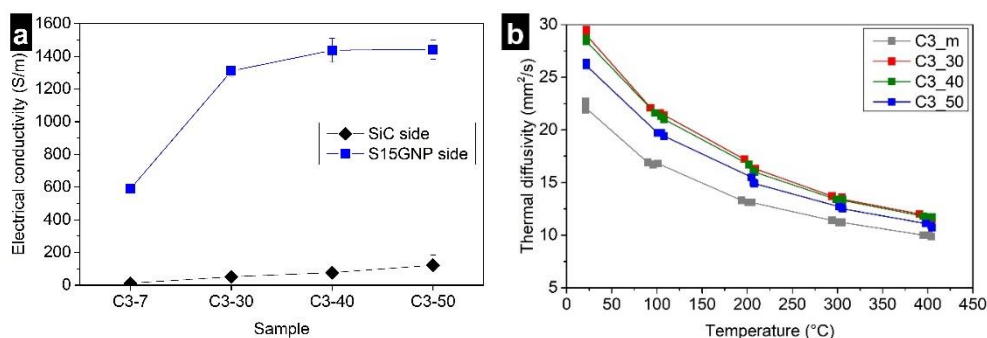


Fig.1. Electrical conductivity and thermal diffusivity of 3-layered composites

CONCLUSION

Dense functionally graded SiC-graphene materials consisting of 3 layers with gradually increased content of graphene were successfully prepared by RHP. Electrical conductivity of layered composites increased with increasing applied pressure during sintering as well as with increasing amount of GNPs in matrix and was strongly dependent on arrangement of layers.

ACKNOWLEDGMENT

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Fabrication of Magnesium Aluminosilicate Glass-Ceramics Reinforced by 3Y-ZrO₂ Addition

Ali Talimian¹, Dusan Galusek^{1,2}, Lothar Wondraczek³

¹*Centre for Functional and Surface Functionalised Glass, Alexander Dubcek University of Trencin, Trencin, Slovakia*

²*Joint Glass Centre of the IIC SAS, TnUAD and FChPT STU, Trencin, Slovakia*

³*Otto Schott Institute of Materials Research, University of Jena, Jena, Germany*

ABSTRACT

In the present work, the effect of the addition of zirconia particles on the densification behaviour of a magnesium alumino-silicate glass matrix is investigated. The glass powder was synthesised by melting, quenching and milling. The crystallisation of the glass matrix was analysed using differential scanning calorimetry; bulk samples were prepared by spark plasma sintering of mixtures of glass powder and 3Y-TZP (15 vol.%). Spark Plasma Sintering (SPS) enables producing the glass-zirconia composite below the glass transition temperature.

Keywords: Glass-ceramics, ZrO₂, Densification, Spark Plasma Sintering.

INTRODUCTION

Most, if not all, studies failed to obtain high toughness in zirconia-containing glass-ceramics; this is mainly related to the low elastic modulus of the glassy matrix that cannot provide the required constraints to zirconia in order to activate the transformation toughening mechanism. Moreover, the fabrication of glass-ceramics containing large amounts of zirconia is difficult using melting-crystallisation methods. Spark plasma sintering (SPS) can be employed to produce highly dense glass-ceramic bodies containing relatively large amounts of zirconia inclusions. In the present study, bulk magnesium aluminosilicate glass-ceramic bodies containing ZrO₂ particles were produced by spark plasma sintering, and the impacts of crystallisation and zirconia inclusions on the densification behaviour of glass-ceramic bodies were investigated. The influences of ZrO₂ addition were examined in terms of Vickers indentation fracture toughness and critically discussed.

EXPERIMENTAL

Magnesium aluminosilicate glass, MAS, (20MgO-20Al₂O₃-60SiO₂) was synthesised by the melt-quenching method. Afterwards, glass powder, with a particle size < 80 µm, was prepared by milling. The glass powder was mixed with zirconia powder (TZ-3YS, Tosoh) and consolidated using spark plasma sintering at 850 °C. The effects of glass powder particle size and heating rate on the crystallisation of glass matrix were investigated under non-isothermal

conditions using differential scanning calorimetry (DSC). The indentation fracture toughness of the composites was measured using the Vickers' indentation method.

RESULTS

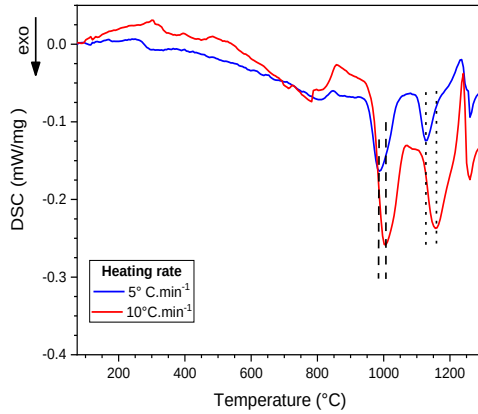


Figure 1. DSC curves for glass matrix powder with a particle size $< 80 \mu\text{m}$ upon heating to 1300°C at 5 and $10^{\circ}\text{C min}^{-1}$

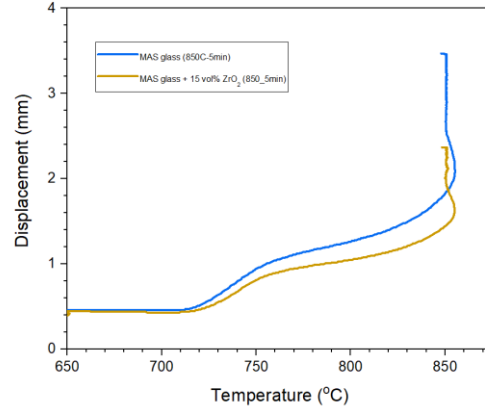


Figure 2. Punch displacement vs temperature during the consolidation of samples using SPS

CONCLUSION

The viscous flow of the glassy matrix under pressure enables the fabrication of dense glass-ceramic containing ZrO_2 particles by using spark plasma sintering. Moreover, the short sintering process prevents the reactions between 3Y-TZP and glass matrix whose effects on densification and toughening are detrimental.

ACKNOWLEDGMENT

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Wetting and reactive melt infiltration of transition metal disilicides during the development of Ultra-High Temperature Ceramic Matrix Composites

H. Ünsal¹, F. Valenza², B. Matovič³, A. Kovalčíková⁴, P. Tatarko¹

¹*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava*

²*Institute of Condensed Matter Chemistry and Technologies for Energy, CNR, Genoa, Italy*

³*Institute of Nuclear Sciences Vinča, University of Belgrade, Belgrade, Serbia*

⁴*Institute of Materials Research, Slovak Academy of Sciences, Košice*

ABSTRACT

This study was focused on the thorough investigation of the wettability and infiltration of molten ZrSi₂ into C_f/SiC composites to understand the interfacial interactions that occur during the development of C_f-SiC-ZrC composites. The effect of different porosities of C_f/SiC substrates on the wetting and melt infiltration of molten ZrSi₂ was investigated.

Keywords: Ceramic matrix composites, Zirconium disilicide, Wettability

INTRODUCTION

Substantial advancements in hypersonic flight technology and development of new low-cost space launch systems require new advanced materials to survive temperatures above 2000°C [1]. The maximum working temperature of Ceramic matrix composites (CMCs), such as C_f/SiC, is limited to 1600°C - 1800°C [2]. The addition of ultra-high temperature ceramics (UHTCs), such as ZrC, has been shown to increase the oxidation and ablation resistance of CMCs, due to its extremely high melting temperature, 3532°C [3]. The aim of this study was to investigate the high temperature interactions of molten ZrSi₂ and two different C_f/SiC composites during the formation of C_f/SiC-ZrC composites.

EXPERIMENTAL

The high-purity ZrSi₂ powder were compacted into the pellets with dimensions of Ø 4 mm x 2 mm by cold isostatic pressing using the pressure of 400 MPa for 60 seconds. Two different C_f/SiC substrates having different overall porosities (21% for C_f/SiC-I3; 12% for C_f/SiC-I6) were supplied by Airbus Defense and Space GmbH, Germany.

The compacted ZrSi₂ pellets were placed onto the substrate surfaces and heated up to the maximum temperature of 1670°C in argon, followed by the dwell of 5 minutes. The microstructures of the cross sections of the wetted couples were characterised using SEM.

RESULTS

No liquid phase formation was observed when the ZrSi₂ pellets were tested on the surface of C_f/SiC-I3 (Fig. 1a), so no contact angle was measured for this substrate. A completely different situation occurred for the C_f/SiC-I6 substrate (Fig. 1b). The alloy melted, spread over the surface of composite and apparently infiltrated into the composite body. Such better wetting behaviour was also confirmed by a relatively low apparent contact angle: 23°.

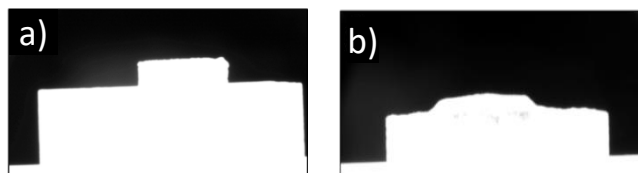


Fig. 1. High temperature (1670°C) contacts between ZrSi_2 pellet and a) $\text{C}_f/\text{SiC-I3}$ substrate or b) $\text{C}_f/\text{SiC-I6}$ substrate.

The SEM analysis (Fig. 2) revealed that the molten alloy uniformly infiltrated into the $\text{C}_f/\text{SiC-I3}$ body (up to $\sim 900 \mu\text{m}$), leaving behind an extremely porous alloy on the surface of the substrate (Fig. 2a). Such a porous pellet detached from the $\text{C}_f/\text{SiC-I3}$ substrate upon cooling from the testing temperature. Even though the alloy infiltrated into the similar distance in the case of $\text{C}_f/\text{SiC-I6}$ substrate, the homogeneously infiltrated subsurface layer was not achieved (Fig. 2b). A denser SiC matrix in C_f/SiC inhibited infiltration, which led to the less porous solidified alloy, which was strongly attached to the surface of $\text{C}_f/\text{SiC-I6}$ after the wetting tests. The EDX and XRD analysis (not shown here) confirmed that the desired composition ($\text{ZrC}+\text{SiC}$) was obtained in the matrix, so can be concluded that the uniform UHTC composition was obtained in the subsurface layer of $\text{C}_f/\text{SiC-I3}$.

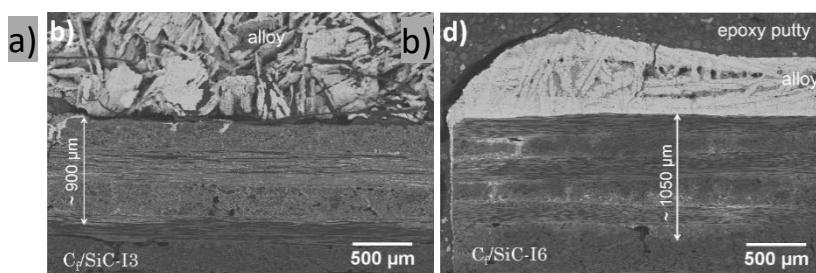


Fig. 2. SEM microstructures of the cross sections of ZrSi_2 on a) $\text{C}_f/\text{SiC-I3}$ substrate or b) $\text{C}_f/\text{SiC-I6}$ substrate after a wetting experiment done at 1670°C in argon.

CONCLUSION

The porosity of C_f/SiC played an important role during melt infiltration of molten ZrSi_2 . A very uniform infiltrated region (up to $\sim 900 \mu\text{m}$) with a desired UHTC composition ($\text{ZrC}+\text{SiC}$) was obtained for the substrate with a higher overall porosity ($\sim 23\%$), i.e. $\text{C}_f/\text{SiC-I3}$.

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Porosity evolution of the 45S5 bioactive glass porous microspheres by adjusting the alkali activation conditions

S. Chen^{1*}, J. Kraxner¹, D. Galusek^{1,2}, M. Michálek¹

¹ FunGlass, A. Dubček University of Trenčín, Študentská 2, 911 50 Trenčín, Slovakia

² VILA – Join Glass Centre of the IIC SAS, TnUAD, FChPT STU, Študentská 2, 911 50 Trenčín, Slovakia

* The corresponding author e-mail: si.chen@tnuni.sk

ABSTRACT

Porous 45S5 bioactive glass microspheres were successfully fabricated through alkali activation with NaOH and flame synthesis. In this study, the effect of three main parameters of alkali activation, such as concentration of NaOH solution, activation time and activation temperature, on the porosity and pore size was investigated in order to achieve the control of the texture properties of the microspheres.

Keywords: Bioactive glass, Porous microspheres, Alkali activation, Flame synthesis

INTRODUCTION

45S5 bioactive glass (BG) was developed by Hench et al. in 1971 [1]: it contains 45% SiO₂, 24.5% CaO, 24.5% Na₂O, and 6% P₂O₅, in wt%. 45S5 BG is commonly applied to fabricate ceramic/glass scaffolds [2], or to be incorporated in composite scaffolds [3] for bone regeneration applications. It is able to form a chemical bond with bone tissue [4]. The ions of Si, Ca and P released from 45S5 BG promote osteogenesis and angiogenesis [4]. Highly porous structure is one of the criteria for ideal bone tissue engineering scaffolds [2]. After alkali activation with NaOH of the 45S5 bioactive glass, porous and hollow microspheres can be fabricated via flame spheroidization process [5]. In this study, we followed three parameters - concentration of NaOH solution, activation time and activation temperature - of alkali activation with the aim to study their effect on the porosity and pore size of the 45S5 bioactive glass microspheres.

EXPERIMENTAL

The 45S5 powder with the particle size less than 40 µm was treated by alkali activation systematically varying three process parameters: concentration of NaOH solution (0.5M, 1M, 2M), activation time (0.5h, 1h, 3h) and activation temperature (25°C, 50°C). After alkali activation, the powder would aggregate together because silica would dissolve and produce sodium silicate during this process. Milling and sieving were performed again to obtain new powder between 40 to 80 µm which was further treated through flame synthesis process. The structural, morphological and chemical characteristics of the microspheres were analysed in detail by XRD, SEM and EDX, respectively. BET measurement was carried out to analyse the textural properties of the porous microspheres.

RESULTS

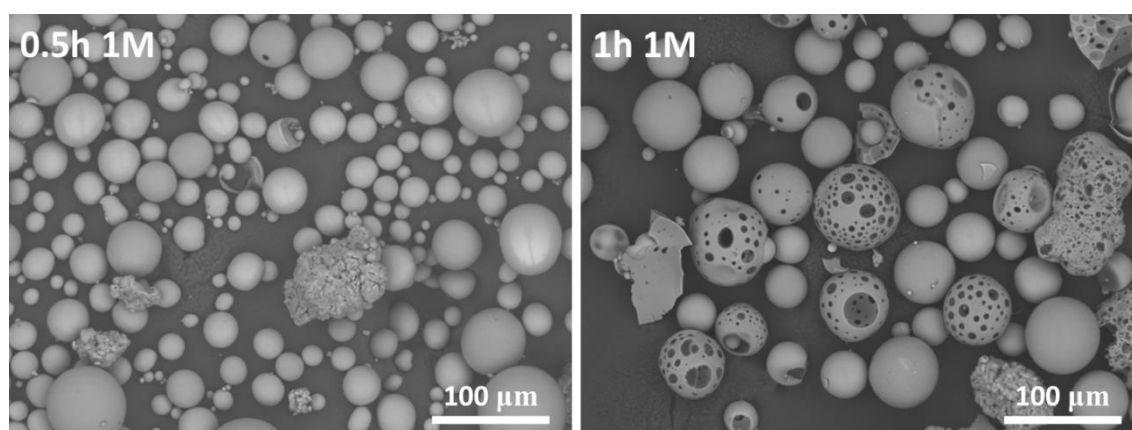


Figure 1. SEM images of microspheres after alkali activation for 0.5h and 1h.

45S5 powder was treated by all processes of alkali activation including 2M-1h-25°C, 1M-1h-25°C, 0.5M-1h-25°C, 1M-3h-25°C, 1M-0.5h-25°C, 1M-1h-50°C. All microspheres were successfully fabricated through flame synthesis process. Figure 1 shows the increase of the number of the porous microspheres with the increase of alkali activation time.

CONCLUSION

All processes of microspheres were successfully fabricated. XRD, SEM, EDX and BET measurement are in progress.

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Cerium and gallium containing mesoporous bioactive glass nanoparticles for biomedical application

F. Kurtuldu ^{1, 2}, N. Mutlu ^{1, 2}, M. Michálek ¹, L. Liverani ², D. Galusek ³ and A.R. Boccaccini ²

¹ *FunGlass, Alexander Dubček University of Trenčín, 911 50 Trenčín, Slovakia*

² *Institute of Biomaterials, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, 91058 Erlangen, Germany*

³ *Joint Glass Centre of the IIC SAS, TnU AD and FChFT STU, Centre for Functional and Surface Functionalized Glass, Trenčín, Slovakia*

The abstract cannot be published due to the ongoing publishing process.

Inorganic Waste Upcycling: The lessons learned, and the outlook for the future

Miroslava Hujova¹, Patricia Rabello Monich², Jozef Kraxner¹, Enrico Bernardo²

¹*FunGlass, Alexander Dubcek University of Trencin, Trencin, Slovakia*

²*Dipartimento di Ingegneria Industriale Università degli Studi di Padova, Padova, Italy*

ABSTRACT

Inorganic waste upcycling offers a solution how to avoid landfilling and how to save raw materials at the same time. Its implementations in Slovakia are rather limited despite the potential it has as a country with closely-knitted inorganic materials industry. This contribution provides a short overview of wastes that can be possibly used for upcycling, i.e. fly ashes, red mud, glass cullets, vitrified bottom ashes. These wastes can be processed, by the means of alkali activation, into novel materials. These materials are characterized by a comprehensive means (X-Ray Fluorescence, Diffraction methods, Thermal Analysis, Scanning Electron Microscopy, Mechanical tests and Chemical stability) to demonstrate their competitive properties against traditional materials available at the market. Therefore, it is appropriate to discuss reasons why these materials as such do not receive more significant attention from industry and how this issue could be fixed.

Keywords: upcycling; inorganic wastes; glass ceramics; alkali-activation

INTRODUCTION

In 21st century, waste management has become one of the most frequently discussed topics in the society, due to growing amounts of waste and increasingly limited space on landfills [1]. Government pressure on environmental precautions in industry, exposed limitations of closed-loop recycling and growing prices of raw materials singlehandedly support research and implementation of upcycling [2], process, during which a waste is reused into a new, different kind of material. Inorganic wastes, such as glass cullets [3], fly ashes [4], slags [5], red mud [6], vitrified bottom ash [7], are excellent candidates for upcycling. One of the most straight-forward ways is alkali-activation, process during which the original bonds are partially dissolved, and reformed into new and stable Si-O-Si, or Al-O-Si networks depending on the chemical composition of the original material.

We discuss some of the novel materials prepared from vitrified bottom ashes (VBA), glass cullets, red mud and slags. These materials indeed maintain excellent chemical and mechanical properties, which are explained via microstructure and mineralogy. However, it is yet left for the discussion, how these materials can become more attractive for the industry and have them implemented as regularly used materials in civil and construction engineering.

EXPERIMENTAL

A chemical composition of various inorganic wastes has been estimated by XRF. These were activated by alkaline solutions of differing strengths (0-8 M NaOH), mixed and treated to either monolithic samples or glass foams. The mineralogy has been observed via XRD, microstructure has been obtained via SEM. Mechanical properties have been investigated in 3- or 4- point flexural or crushing modes. Density and porosity was established by means

of He pycnometry. Finally, simple hydrolytic resistance tests have been assessed and leachates have been evaluated by ICP-OES to check the safety according to 2003/33/EC.

RESULTS

Glass ceramic foams from VBA and glass cullet mixtures demonstrated even-celled, uniform structure, and while the maximum compressive strength reached 3.7 MPa, it strongly depended on the ability to control gehlenite and amount of residual amorphous phase.

Monolithic samples from smelting slags have shown strong reactivity with water connected with crystallization of phases similar to those in Portland cement. Upon curing, these samples could be categorized in IV category of cements, but chemical stability needs to be controlled and maintained.

Finally, by a vitrification of red mud, fly ashes and glass cullets, was prepared a glass containing magnetite, which upon alkali activation formed magnetic geopolymer of excellent mechanical properties (flexural strength up to 12.5 MPa). These materials show promising results for functionalization in the future (i.e. electromagnetic shielding).

CONCLUSION

All materials demonstrate suitable chemical stability, good chemical properties and their preparation can be even more fine-tuned towards higher environmental suitability. However, some obstacles need to be overcome, before upcycling as such would be the acceptable way of waste processing.

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