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FACULTY OF CHEMICAL TECHNOLOGY AND BIOTECHNOLOGY
GEORGE OLAH DOCTORAL SCHOOL

Advanced ceramic composites produced by spark plasma sintering

Silicon nitride and silicon carbide based composites

PhD Thesis

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2018

1. Introduction and motivation

The humanity uses traditional ceramics since thousands of years; however, the development and application of advanced ceramics with special properties look back just a few decades. From the latter family of materials, silicon nitride (Si_3N_4) and silicon carbide (SiC) based systems are the most widely studied ones. It is reasoned by their special properties, such as high strength and hardness, excellent chemical and heat resistance. Due to these properties they can be applied even in conditions where other structural materials (polymers, metals) cannot.

Silicon nitride ceramics are widely used as bearings, cutting tools for metals and as engine parts in the car industry. Due to their high heat resistance, they are built-in high temperature furnaces[1]. Si_3N_4 is biocompatible, thus orthopedic and dental implants are also made of it [2]. Another field of its application includes micro electric chemical sensors [3].

Silicon carbide is an extremely hard material with high strength, and excellent wear and corrosion resistance even at high temperature. It is used primarily as abrasive material, but metalworking tools and power brake discs and brake pads for cars are also made of SiC [4]. Silicon carbide has electroluminescence properties, as well. Thus, it is widely used in the semiconductor industry [5]. Due to its biocompatibility and inertness in chemical terms, medical and biological devices are also produced from silicon carbide.

In spite of excellent mechanical, chemical and thermal properties, Si_3N_4- and SiC-based ceramics are characterized by low fracture resistance, as well. This drawback was eliminated in some extent due to developments in material science and technology more recently, however, the monolithic Si_3N_4 and SiC ceramics are still quite brittle and show catastrophic fracture behavior in certain cases. The critical fracture toughness can be improved by controlling the composition and microstructure of ceramic bodies, and thus, decreasing the development of critical stress on loading. Another possibility to improve mechanical properties is the inclusion of reinforcing

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[1] R. F. Riley, „Silicon Nitride and Related Materials," *Journal of the American Ceramic Society,* 8., pp. 245-265, 2000.

[2] R. Kue, A. Sohrabi és D. Nagle, „Enchanced proliferation and osteocalcin production by human osteoblast-like MG-63 cells on silicon nitride ceramic discs," *Biomaterials,* 20., pp. 1195-1201, 1999.

[3] P. R. Hernandez, C. Taboada és L. Leija, „Evaluation of biocompatibility of pH-ISFET materials during long-term subcutaneous implantation," *Sensors and Actuators B,* pp. 133-138, 1998.

[4] W. Dressier és R. Riedel, „Progress in Silicon-Based Non-Oxide Structural Ceramics," *International Journal of Refractory Metals & Hard Materials,* 15., pp. 13-47, 1997.

[5] H. J. Round, „ A note on Carborundum," *Electrical World,* 19., pp. 309, 1907.

additives into the ceramic matrix, i.e. to produce ceramic-based composites. The reinforcement in these systems can decrease the adverse effects of external strains.

A novel method of heat treatment, the spark plasma sintering (SPS) applies pressure and intensive Joule heating by pulsed electric current. SPS provides lower sintering temperature and faster sintering as compared to conventional sintering methods. Thus, it can hinder the extensive grain growth during heat treatment, and the microstructure of sintered ceramic material can be better controlled. Even nanostructured ceramics can be produced in this way.

As far as the production of ceramic based composites is concerned, one of the favorable reinforcing agent is zirconium dioxide (ZrO_2). Either as powder or fibre-like morphology, it can enhance the fracture toughness of ceramics by stress-induced transformation from tetragonal (t) to monoclinic (m) ZrO_2 [6] on the one hand and closes or deflects the path of the crack, on the other[7]. Another reinforcing agent of great potential is graphene, one of the favorite models in materials science and engineering nowadays, due to its excellent mechanical, thermal and electric properties [8,9].

In my PhD work I studied the correlation between microstructure and mechanical properties of Si_3N_4- and SiC-based advanced ceramic composites. For both systems, the effect of reinforcing materials and sintering conditions on the microstructure and mechanical properties of sintered bodies were studied. My main goal was to develop novel ceramic nanocomposites with improved properties and a method for their production, as well.

[6] M. Suárez, A. Fernández, J. L. Menéndez, R. Torrecillas, H. U. Kessel, J. Hennicke, R. Kirchner és T. Kessel, „Challenges and Opportunities for Spark Plasma Sintering: A Key Technology for a New Generation of Materials,” in *Sintering Applications,* InTech, 2013

[7] B. Basu és K. Balani, Advanced Structural Ceramics, New Jersey: John Wiley & Sons, Inc., 2011.

[8] L. S. Walker, V. R. Marotto, M. A. Rafiee, N. Koratkar és E. L. Corral, „Toughening in graphene ceramic composites, ACS Nano, 5 (2011) 3182-3190.,” *ACS Nano,* 5., pp. 3182-3190., 2011.

[9] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, R. D. P. E. A. Stach, S. T. Nguyen és R.S. Ruoff, „Graphene-based composite materials,” *Nature,* 442., pp. 282, 2006.

2. Experimental and methods

2.1. Preparation of reinforcing materials

To improve the mechanical properties of Si_3N_4- and SiC-based composites multilayer graphene (MLG) and ZrO_2 nanofibers were used as reinforcing agents.

Multilayer graphene (MLG) was prepared by exfoliation of nanographite in an attritor mill, developed by Thin Film Physics Research Group in the Centre for Energy Research of the Hungarian Academy of Sciences [10].

ZrO_2 nanofibers can be produced easily and at low cost by electrospinning. In my experimental work, I prepared 3 mol% Y_2O_3 partially stabilized ZrO_2 nanofibers by a laboratory scale electrospinning equipment.

2.2. Preparation of ceramics composites

The SiC based composites contained 1 and 3 wt% MLG, while the Si_3N_4 based composites were reinforced with 1, 3 and 5 wt% MLG.

In the case of reinforcement with ZrO_2 nanofibers, Si_3N_4- and SiC-matrices contained 5, 10 and 15 wt% fibres. For comparison, besides fibres, I also studied the reinforcing effect of ZrO_2 particles for the Si_3N_4 and SiC composites.

In all composite series I also prepared pure samples, as a reference. During the heat treatment I used liquid-phase and solid-phase sintering additives. Each sample was treating by spark plasma sintering (SPS) method.

2.3. Characterization of ceramic composites

Microstructural characterization

The surface composition of starting Si_3N_4 and SiC powders was studied by X-ray photoelectron spectroscopy (XPS). The density of sintered samples was measured by Archimedes method. The phase composition of the raw materials and the sintered bodies was determined by X-ray diffraction. The morphology and microstructure of sintered composites were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively.

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[10] Kun, F. Wéber és C. Balázsi, „Preparation and examination of multilayer graphene nanosheets by exfoliation of graphite in high efficient attritor mill,” *Central European Journal of Chemistry,* 9.kötet, pp. 47-51, 2011.

The structural changes in MLG on SPS were studied by Raman spectroscopy. The phase transformations of ZrO_2 fibres on mechanical loading was also studied by Raman spectroscopy.

Measurement of mechanical properties

The mechanical properties of sintered samples were characterized by measuring their Vickers hardness and Young's modulus with an instrumented indentation tester. The fracture toughness was calculated by the Niihara equation using cracks lengths and other data from the indentation measurements. The flexural strength was determined by three points bending test.

3. Results

The **Si_3N_4/MLG nanocomposites** were produced by SPS at 1500 and 1600°C with holding time of 3 and 10 minutes, respectively.

It has been proved that MLG can effectively improve the fracture toughness of composites, due to its homogeneous distribution in the matrix and thus, many interactions between the matrix and the reinforcing material.

According to microstructural investigations, 1 wt% MLG was dispersed in the matrix relatively evenly. The highest fracture toughness was obtained for Si_3N_4-based composite containing 1 m/m% MLG and sintered at 1500°C: an improvement of ~60% was achieved against the monolithic ceramics (Figure 1. a). It is attributed to the partial pull out of MLG layers from the matrix on one hand and the deflecting of the cracks paths, on the other. TEM studies revealed nanopores on the MLG/matrix interface (Figure 1. b), which refer to reaction during heat treatment between MLG and SiO_2 on the surface of Si_3N_4 particles. At higher MLG content, the MLG layers slid together and agglomerate in the matrix.

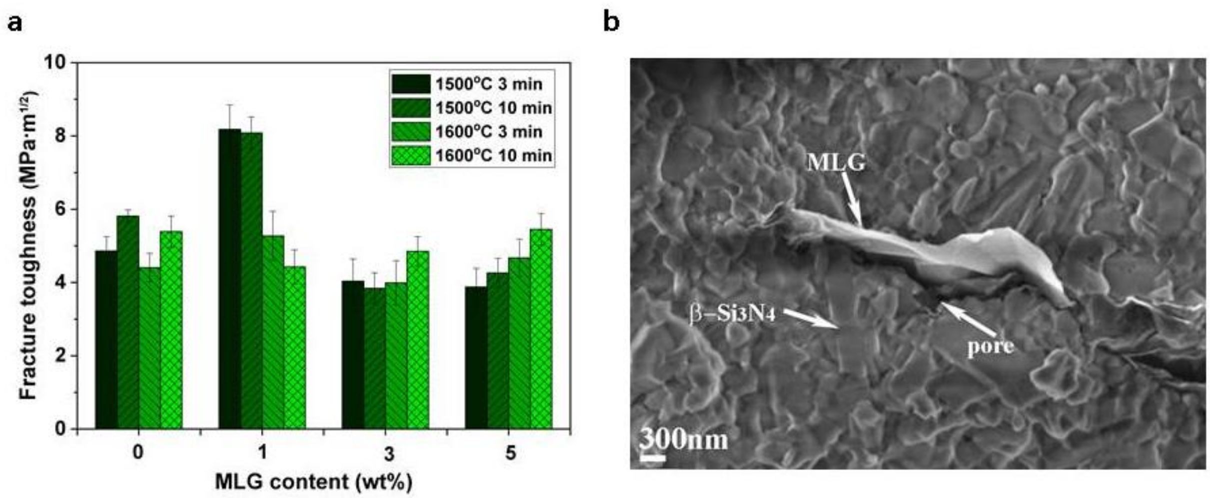

Figure 1. (a) Fracture toughness and (b) SEM micrographs of Si_3N_4/MLG nanocomposite

At MLG contents of 3 and 5 wt%, respectively, the mechanical properties fall, because of the MLG agglomeration and the increasing number of nanopores on the matrix-MLG interfaces.

In the case of **Si_3N_4/ZrO_2 composites,** higher fracture toughness and flexural strengths were obtained for those reinforced with ZrO_2 fibres, than with particles. The highest fracture toughness and bending strength was obtained for sample containing 15 m/m% ZrO_2 fibre and sintered at the 1600°C (Figure 2. a).

The fracture toughness of Si_3N_4-based composites reinforced with ZrO_2 fibres improved due to several effects: (a) the randomly located fibres deflect cracks and absorb the fracture energy along their length (Figure 2. b) and (b) a tetragonal to monoclinic-ZrO_2 phase transformation took place under the stress of cracks. Thus, a complex toughening mechanism was developed, which resulted in a twofold fracture toughness and flexural strength as compared to the monolithic reference sample.

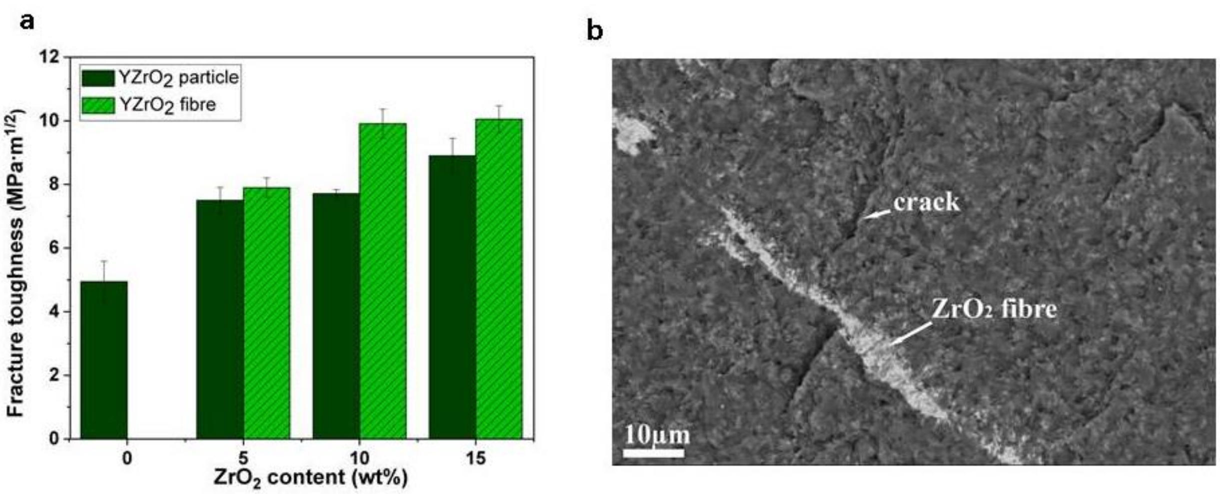

Figure 2. (a) Fracture toughness of Si_3N_4/ZrO_2 nanocomposites (b) SEM micrographs of the toughening mechanisms of ZrO_2 fibres

It was shown that the fracture toughness and flexural strengths of **SiC/MLG composites** can be enhanced by 20% with 1 wt% MLG as reinforcing material (Figure 3. a). This improvement can be explained by the double toughening mechanism of MLG, namely crack bridging and pull out (Figure 3. b).

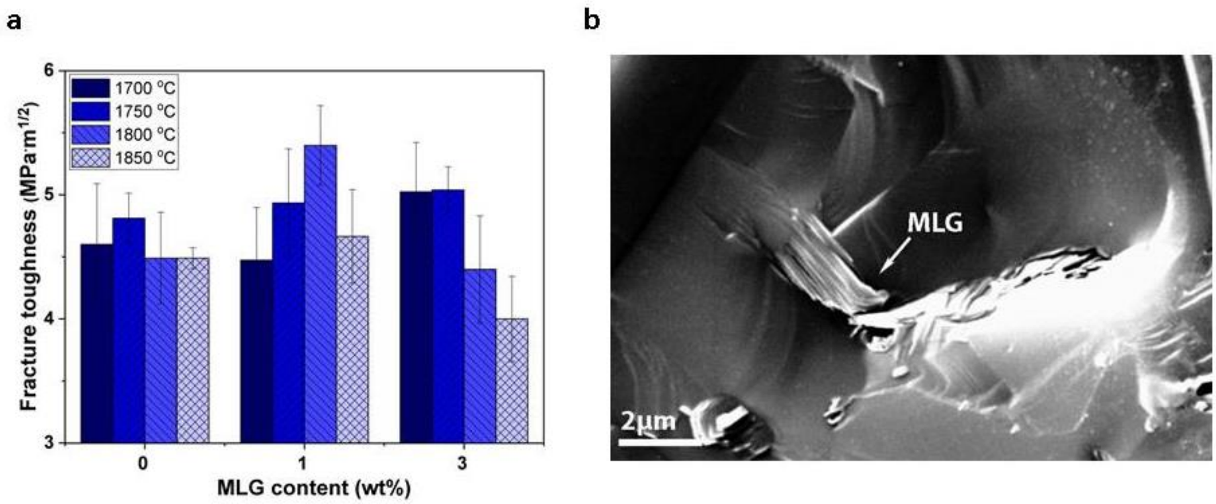

Figure 3. (a) Fracture toughness and (b) fractured surfaces of SiC/MLG composites

When the MLG content was increased to 3 wt%, the graphene layers agglomerated and partially transformed to graphite on SPS. At the same time, SiC-based composites with 3 wt% MLG content can be sintered actually pore-free; it leads to an increase of 17% in Vickers hardness as compared to monolithic ceramics sintered in same conditions. Microstructural studies revealed that particular improvement could be attributed to formation of intergranular B_4C on SiC/MLG grain boundaries, which occurred during the reaction between the boron sintering additive and the MLG.

During SPS of **SiC/ZrO_2 fibres** and **SiC/ZrO_2 particles composites** complex process occurred at 1700°C. On the bottom of sintered discs ZrC was detected as a new product, while on their top it was not observed (Figure 4. a). According to thermodynamic calculations, ZrC is forming in the reaction of SiC with ZrO_2 at ~1750°C. Consequently, the differences in the phase compositions on the opposite sides of the sintered bodies can be attributed to temperature differences between the sides: on the bottom the temperature was higher than on the top of discs. My microstructural studies refer to formation of ZrC as a process accompanied by c-ZrO_2 $\rightarrow$ c-ZrC isostructural transformation.

Addition of ZrO_2 improved the mechanical properties of SiC composites, as well. However, in this case ZrO_2 particles had more favorable effect on the mechanical properties than ZrO_2 fibres.

It is reasoned by the preferred isostructural transformation of c-ZrO_2 to c-ZrC in the case of ZrO_2 particles: ZrC improves the Vickers hardness, Young modulus and flexural strength of composites (Figure 4.b).

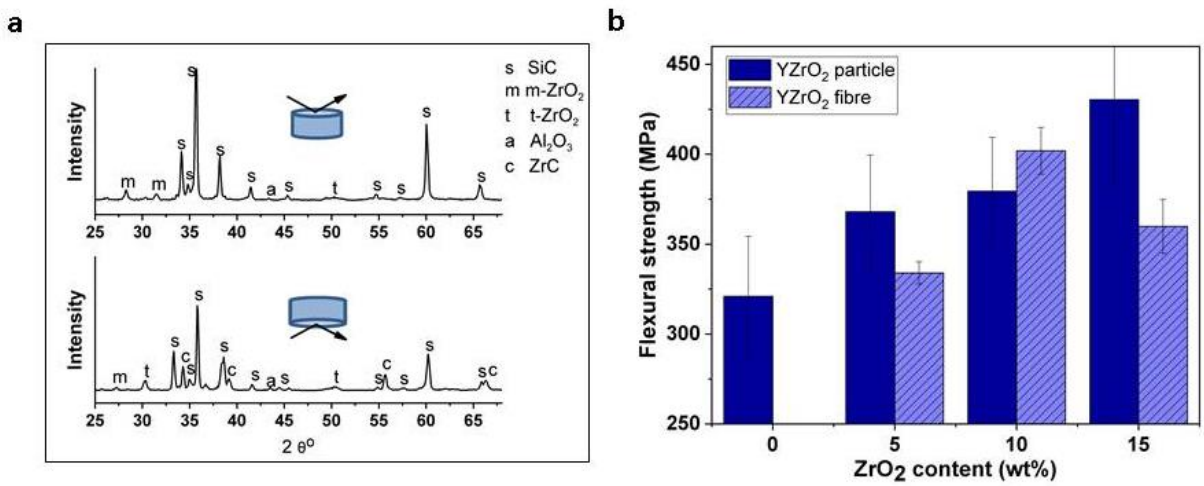

Figure 4. Microstructure and flexural strength of SiC/ ZrO_2 composites

During my thesis work, Si_3N_4 and SiC-based composites were developed with better mechanical properties as compared to the monolithic reference ceramics. I managed to clarify some details of correlations among the microstructure and mechanical properties of sintered composites. I do hope that these results can be regarded as good bases for further development of particular advanced ceramics.

4. List of theses

1. Correlation was established between the microstructure and mechanical properties of the Si_3N_4-based composites containing multilayer graphene (MLG) as reinforcing material. It was found that MLG can deflect the cracks in the matrix on the one hand, and it can pull-out from the matrix on the other, thereby it reduces the fracture energy in the matrix. Due to the combined effect of these two toughening mechanisms, the fracture toughness of Si_3N_4 composite containing 1 wt% MLG and sintered at 1500°C was improved by one and half times compared to the monolithic reference sample (I. Publication).

2. It was shown that in the case of MLG content of 3 and 5 wt%, MLG agglomerated in the Si_3N_4 matrix and nanopores were formed on the matrix/graphene interface. It weakened strength of interactions among MLG and Si_3N_4 grains and thus, the mechanical properties of the reinforced composites do not differ from the reference samples (I. Publication).

3. As a new material, Si_3N_4 matrix reinforced with ZrO_2 fibres and sintered by SPS was developed. It was proven that addition of ZrO_2 increased the mechanical properties of Si_3N_4-based composites, the higher ZrO_2 content the better properties. For composites containing 15wt% ZrO_2, application of fibres resulted in higher fracture toughness and flexural strength as compared to ZrO_2 particles. The favourable effect of ZrO_2 fibres could be attributed to a complex toughening mechanism. The ZrO_2 fibres deflected and bridged the cracks, thereby reduced the fracture energy in the matrix on one hand, and there also was a stress-induced t→m-ZrO_2 phase transformation, which absorbed the fracture energy, on the other (II. Publication).

4. It was shown that multilayer graphene improved the mechanical properties of SiC-based composites. In the case of 1 wt% MLG content and sintering temperature of 1800^{o}C, the fracture toughness and flexural strength were increased by 20% against the monolithic reference sample. The beneficial effect of MLG is associated with complex toughening effects, such as MLG pull-out and cracks bridging (III. Publication).

5. It was proved that the SiC/MLG composite could be sintered to almost pore-free under given conditions (3 wt% MLG content, 1850ºC). In this case the Vickers hardness increased by 17% as compared to the monolithic reference sample. This increase was partly attributed to the pore-free structure and partly to formation of intergranular B_4C (III. Publication).

6. Comparison of the microstructure and mechanical properties of composites of SiC/ZrO_2 fibres and SiC/ZrO_2 particles produced by SPS revealed that at sintering temperature of 1700ºC, different microstructures have been formed on the bottom and the top of sintered samples, respectively. On the bottom ZrC formed in the reaction of SiC with ZrO_2, while on the top ZrC was not detected. Particular distribution of ZrC was attributed to the temperature difference between the bottom and the top of discs during sintering: on the bottom temperature was higher than on the top (IV. Publication).

7. It was proven that the mechanical properties of SiC-based ceramics could be improved by ZrO_2 reinforcement. The extent of improvement depended on the morphology of reinforcing material: ZrO_2 particles are more preferred than fibres. It was attributed to the preferred formation of ZrC in the presence of ZrO_2 particles. The Vickers hardness, Young modulus and flexural strength were all increased due to the presence of ZrC in the SiC matrix (IV. Publication).

5. Publications

Publications related to the dissertation

I. Bódis E., Tapasztó O., Károly Z., Fazekas P., Klébert Sz., Keszler A. M., Balázsi K., Szépvölgyi J., Spark plasma sintering of Si_3N_4/multilayer graphene composites, ***OPEN CHEMISTRY* 13:**(1) pp. 484-489. (2015) (IF_{2015}:1,207, independent citations: 6)

II. Bódis E., Molnár K., Mucsi A., Károly Z., Móczó J., Klébert Sz., Keszler A. M., Fazekas P., Szépvölgyi J., Silicon nitride-based composites reinforced with zirconia nanofibers, ***CERAMICS INTERNATIONAL* 43:** pp. 16811-16818. (2017) (IF_{2016}: 2,986, independent citations: 1)

III. Bódis E., Cora I., Balázsi Cs., Németh P., Károly Z., Klébert Sz., Fazekas P., Keszler A. M., Szépvölgyi J., Spark plasma sintering of graphene reinforced silicon carbide ceramics, ***CERAMICS INTERNATIONAL* 43:**(12) pp. 9005-9011. (2017) (IF_{2016}: 2,986, independent citations: 3)

IV. Bódis E., Fábián Á., Bán K., Károly Z., Klébert Sz., Keszler A. M., Fazekas P., Szépvölgyi J., Microstructure and sintering mechanism of SiC ceramics reinforced with nanosized ZrO_2, ***EUROPEAN CHEMICAL BULLETIN* 6:**(11) pp. 484-490. (2017) (IF:0)

Presentations related to the thesis

Oral presentations in English

1. Conference for Young Scientists in Ceramics, The Tenth Students' Meeting (SM-2013), Novi Sad, Serbia (2013)
2. 15th International Conference of European Ceramics Society, Student Speach Contest, Budapest (2017)

Oral presentations in Hungarian

1. „XIII. PhD hallgatók anyagtudományi napja."MTA Műszaki Kémiai Tudományos Bizottság, Anyagtudományi és Szilikátkémiai Munkabizottsága, Pannon Egyetem, Veszprém (2013)
2. „XV. PhD hallgatók anyagtudományi napja."MTA Műszaki Kémiai Tudományos Bizottság, Anyagtudományi és Szilikátkémiai Munkabizottsága, Pannon Egyetem, Veszprém (2015)
3. Szilikátipari Tudományos Egyesület Finomkerámiai szakmai nap, MTA TTK, Budapest (2015)
4. Változatok Négy Intézetre: Doktori Konferencia, MTA TTK, Budapest (2016)

Poster presentations

- Eszter Bódis, Oorsolya Tapasztó, Csaba Balázsi, Zoltán Károly, János Szépvölgyi: Spark plasma sintering of Si_3N_4/multilayer graphene composites , 5th Central-European Symposium on Plasma Chemistry, Balatonalmádi (2013)

- Eszter Bódis, Orsolya Tapasztó, Csaba Balázsi, Zoltán Károly, János Szépvölgyi: Spark plasma sintering of Si_3N_4/multilayer graphene composites, IX. Országos Anyagtudományi Konferencia, Balatonkenese (2013)

- Eszter Bódis, Zoltán Károly, László Szabó, Kolos Molnár, János Szépvölgyi: ZrO_2 nanofibre reinforced Si_3N_4 structural ceramic, 14th International Conference of European Ceramics Society, Toledo, Spanyolország (2015)

- Eszter Bódis, Zoltán Károly, János Szépvölgyi: Graphene reinforced SiC ceramics sintered by Spark Plasma Sintering, Oláh György Doktori Konferencia Budapest (2015)

- Eszter Bódis, Zoltán Károly, János Szépvölgyi: Graphene reinforced SiC ceramics sintered by Spark Plasma Sintering International Conference and Exposition on Advanced Ceramics and Composites , Daytona Beach, Florida, USA (2016)

- Eszter Bódis, Kolos Molnár, Anna Mária Keszler, Szilvia Klébert, Péter Fazekas, Zoltán Károly, János Szépvölgyi: Novel ceramics reinforced with ZrO_2 nanofibers 15th International Conference of European Ceramics Society, Budapest (2017)

Publications not closely related to the thesis

Marosné B. M., Németh A. K., Károly Z., Bódis E., Maros Zs., Tapasztó O., Balázsi K., Tribological characterisation of silicon nitride/multilayer graphene nanocomposites produced by HIP and SPS technology, ***TRIBOLOGY INTERNATIONAL*** **93:**(Part A) pp. 269-281. (2016)

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Károly Z., Klébert Sz., Bódis E., Sajó I., Szépvölgyi J., Spark Plasma Sintering of Plasma Synthesized Nanosized SiC Powder, ***EUROPEAN CHEMICAL BULLETIN*** **3:**(2) pp. 157-160. (2014)

Fazekas P., Bódis E., Keszler A. M., Czégény Zs., Klébert Sz., Károly Z, Szépvölgyi J., Decomposition of Chlorobenzene by Thermal Plasma Processing, ***PLASMA CHEMISTRY AND PLASMA PROCESSING*** **33:**(4) pp. 765-778. (2013)

Further Publications:

Fazekas P., Czégény Zs., Mink J., Szabó P. T., Keszler A. M, Bódis E., Klébert Sz., Szépvölgyi J., Károly Z.,Decomposition of Poly(vinyl chloride) in Inductively Coupled Radiofrequency Thermal Plasma, ***PLASMA CHEMISTRY AND PLASMA PROCESSING*** *38* pp: 771-790. (2018)

Keszler A. M., Fazekas P., Bódis E, Drotár E., Klébert Sz., M. Boselli, E. Ghedini, P. Sanibondi, Károly Z., Szépvölgyi J., Optical emission spectroscopic study of the synthesis of titanium boride nanoparticles in RF thermal plasma reactor ***PLASMA CHEMISTRY AND PLASMA PROCESSING*** **37:**(6) pp. 1491-1503. (2017)

Fazekas P., Czégény Zs., Mink J., Bódis E., Klébert Sz., Németh Cs., Keszler A. M., Károly Z., Szépvölgyi J., Decomposition of Poly(vinyl chloride) in Inductively Coupled Radiofrequency Thermal Plasma, ***CHEMICAL ENGINEERING JOURNAL*** **302:** pp. 163-171. (2016)

Fazekas P., Keszler A. M., Bódis E., Drotár E., Klébert Sz., Károly Z., Szépvölgyi J., Optical emission spectra analysis of thermal plasma treatment of poly(vinyl chloride), ***OPEN CHEMISTRY*** **13:** pp. 549-556. (2015)

Klébert Sz., Keszler A. M., Sajó I., Drotár E., Bertóti I., Bódis E., Fazekas P., Károly Z., Szépvölgyi J., Effect of the solid precursors on the formation of nanosized TiBx powders in RF thermal plasma, ***CERAMICS INTERNATIONAL*** **40:**(3) pp. 3925-3931. (2014)

Fazekas P., Bódis E., Keszler A. M., Czégény Zs., Klébert Sz., Károly Z, Szépvölgyi J., Decomposition of Chlorobenzene by Thermal Plasma Processing, ***PLASMA CHEMISTRY AND PLASMA PROCESSING*** **33:**(4) pp. 765-778. (2013)

Publication in Hungarian:

Fazekas P., Bódis E., Keszler A. M., Czégény Zs., Szépvölgyi J., Klórbenzol lebontása termikus rádiófrekvenciás plazmában, In: Jurecska L, Kiss Á (szerk.)**Környezettudományi Doktori Iskolák Konferenciája 20**12. 253 p. ,Konferencia helye, ideje: Budapest, Magyarország, 2012.08.30-2012.08.31. Budapest: Eötvös Loránd Tudományegyetem, 2012. pp. 236-243.