Novel development of functionally graded bioceramics by spark plasma sintering
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Final report

Functionally graded materials (FGM) have attracted considerable attention in material research because of their gradually changing properties (composition and/or microstructures) makes them exceptionally suited for various application area, particularly biomedical applications.

The main goals of the research were: 1) to create thermal gradient during spark plasma sintering (SPS) process; 2) comprehensive study of various mechanisms and effects of thermal gradient occurring during SPS process as well as 3) fabrication of functionally graded Al_2O_3-ZrO_2 bioceramics, in particular investigate the micro- and nanostructure properties and mechanical behaviour of the Al_2O_3-ZrO_2 bioceramics having different morphologies.

Our investigations and characterizations revealed new information in terms of the in-situ formation of thermal gradient during SPS process. We developed a novel as well as simple technique for fabrication of FGM, which does not require extra tools or additives, thereby offering new directions in FGMs research as well as in the application of SPS equipment. We reported that the thermal gradient contributes a gradient microstructure (namely porosity) along the cross-section of the Al_2O_3-ZrO_2 ceramic composite, resulting in unique multifunctional feature for ceramic composites. These composites can be attractive for biomedical applications such as bone or dental implants. We pointed out that the obtained gradient structure similar to the natural bones; the porous part of the Al_2O_3-ZrO_2 ceramic composite can promote rapid osseointegration of the bone cells, while the opposite, non-porous part provides ceramic with high mechanical resistance. According to the achieved results, we also predicted the use of these bioceramics in biomedical applications and enhanced the bioactivity of Al_2O_3-ZrO_2 ceramics. The gradient pores were successfully impregnated with nano-hydroxyapatite (HAp) improving the bioactivity of ceramics.

The project was successful, and its outcome was not influenced by several hindering circumstances, such as Covid-19 pandemic, which affected the one-year extension of the research work. In addition, my pregnancy, and the birth of my child in October also affected my laboratory and research work this year. However, for the last year a BSc student, Bálint Tulik was involved in a minor segment of the project that is the basis of his thesis. The thesis entitled "Production of zirconia toughened alumina (ZTA) ceramic composite for biological application" was submitted into Budapest University of Technology in December 2023.

The most significant results have been published in material science journals. The results of the projects also reported at national and international conferences and seminars.

Major results:

1) Development of temperature gradient during spark plasma sintering process

We developed a new approach to synthetizing functionally graded ceramics by SPS, using alumina nanopowder as model material. (Al_2O_3 powder was prepared by the hydrothermal method in laboratory scale.)

Our investigations pointed out that during SPS heating process, an in-situ, exceptional high thermal gradient can be generated inside the sample when the graphite tools were placed in an asymmetric position, which resulted in a continuously changing microstructure in the cross-section of the Al_2O_3 sample. To demonstrate the extension of temperature gradient in the sample and gain exact temperature values during the sintering process, minor improvement was made to the SPS equipment, as well. S-type thermocouples were installed into the SPS, which were inserted into the wall of the graphite tools as close at the top and bottom parts of the samples as possible. The temperature gradient and microstructure of the samples were studied systematically. Different graphite configurations were studied during the sintering process, where the powder samples were shifted vertically downward into an asymmetric position, hereinafter ASY. We also performed experiments in normal (standard) graphite configurations hereinafter STD, where the powder samples were placed in the centre, these results served the refence. In order to understand the mechanism of the SPS, further sintering conditions including temperature, pressure, and heating rate were also varied during the experiments.

The experimental results showed that as asymmetry increased in the graphite tool configuration, a relatively large vertical temperature gradient developed within the sample. While the top temperature of the samples was nearly identical to the set temperature in each test, the temperature at the bottom significantly differed. Both greater asymmetry and higher sintering temperature significantly affected the temperature difference, and it increased between the opposite part of the sample. We pointed out, that the largest temperature differences (225 °C) can be recorded for the most asymmetric of the graphite tools, with a temperature of 1300 °C and a pressure of 25 MPa applied 200 °C min^{-1} heating rate. The explanation of this large thermal gradient can be related to the inhomogeneous distribution of current density for the asymmetric graphite configuration during the SPS sintering process. Inhomogeneous distribution of the current density also occurs at the contacting points of the particles leading to large temperature differences inside the ceramics body during sintering. Hence, the ceramic sample placed in asymmetric position in the graphite tools represent a new function and possibility for the use of SPS equipment, thereby broadening its possibilities of use.

The generated large temperature gradients cause discontinuous densification and consequently graded microstructures in the vertical cross-section. Namely, crystalline size and pore structure also exhibit a gradual change through the vertical cross-section as a result of the temperature gradient. The microstructure of the obtained sample consists of a nanosized grains with open and interconnected pore structure on one part and a pore-free, completely dense structure on the opposite part of the sample resulting in porosity gradient along the cross-section of the ceramics body. These investigations show that a gradient ceramic can be produced with a single-step SPS process, which offers new directions in FGMs research as well as in the use of SPS equipment.

The new results were published in International Journal of Advances Manufacturing Technology [1]. The project leader was the first and the corresponding author of the paper. The major results were also presented on the international evening (a).

In order to acquire comprehensive knowledge about nano- and microstructure characterization method, such as high-resolution scanning electron microscopy analysis, the nanostructured SiC ceramic composites was also studied in the first year of the project [2].

2. Investigation of composition and microstructure graded Al_2O_3-Ce-ZrO_2 ceramics composites

Both ceramics, Al_2O_3 and ZrO_2, have biocompatible properties beside excellent mechanical properties. They are already used in various medical area, for example in bone or dental implants. While Al_2O_3 is more preferred in medical applications due to its good biocompatibility and hypoallergenic properties, ZrO_2 with tetragonal crystal structure outperforms Al_2O_3 with respect those mechanical properties like fracture toughness and strength. Consequently Al_2O_3 - ZrO_2 composites provide obvious solution combining the advantages of both ceramics.

In this contribution, laminated Al_2O_3- ZrO_2 ceramic composites were developed by varying the chemical composition through four layers by layering the starting nanopowders with different Al_2O_3 to ZrO_2 ratios, from 100% to 50% regarding Al_2O_3. Thus, the effect of the change in composition on the formation of temperature gradient during SPS process as well as on the microstructural and mechanical properties were investigated.

Regarding to experimental details, the four powder mixtures were homogenized by conventional milling process in a planetary ball mill. 16 mol% CeO_2 was used as a stabilizing agent for tetragonal ZrO_2 (Ce-ZrO_2) since it shows more resistance to the so-called low temperature degradation (LTD) compared to the other commonly used 3 mol% Y_2O_3 stabilized tetragonal ZrO_2. (LTD results in uncontrollable tetragonal to monoclinic phase transformation in ZrO_2 causing difficulties during operation e.g., in the implanted protheses.)

The investigations confirmed that regardless of changes in composition, significant temperature differences are formed between the top and bottom part of the samples according to the former developed SPS technology, applying ASY configuration. The difference increased with increasing sintering temperatures and reached as much as 120 °C at a sintering temperature of 1300 °C. At the same time, the temperature at the top side was also invariably higher than the set temperature. In contrast with the reference sample, fabricated in STD configuration, where thermal gradient was not detected.

Detailed microstructure analysis as well as Mercury-porosimetry supported the formation of a gradient pore structure for the samples heat treated in ASY. Total porosity varied between 40 and 5%, and it decreased with the increasing sintering temperature regardless of the type of graphite configuration. However, it was lower in the ASY configuration, due to the evolved high local temperature at the bottom part of the samples. In spite of that, in parallel, the relative pore volume distributed in wide range for the ASY samples, and pores of up to 100 μm were detected in a significant ratio, as well. Scanning electron microscopy (SEM) analysis showed that porosity and pore size distribution is anisotropic densification increased toward the bottom part of the samples as compared with the reference materials fabricated in STD, where the porosity distribution was homogenous along the cross-section of the ceramics. High magnification SEM analysis also confirmed a smooth transition of the material in terms of composition and porosity without any sign of delamination or cracks at the imaginary interfaces of the layers, which was attributed to the continuous temperature gradient during the heating process.

Microhardness and flexural test results also indicate the changes in the composition and porosity of the Al_2O_3-Ce-ZrO_2 material. Hardness increased gradually along the axis particularly for the asymmetric configuration samples. A difference of nearly 10 GP in hardness was achieved between the top and bottom part of the sample heat treated at 1300 °C. For these samples, hardness distribution was more homogenous within the sample compare with the samples made in STD, therefore the formation of internal stresses inside the materials can be avoided and better load capacity can be obtained. The flexural strength of the samples for both series (ASY and STD) shows an increasing tendency with higher sintering temperatures. However, the samples sintered in ASY achieved improved strength due to the lower total porosity of the sample. XRD and SEM analysis revealed that an unexpected, newly formed $CeAl_{11}O_{18}$ phase in structure, as a result of a solid-state reaction between the Ce_2O_3 and Al_2O_3 during the sintering process, which may also affect the mechanical properties of Al_2O_3-Ce-ZrO_2 FGM samples. However, the achieved mechanical properties of the Al_2O_3-Ce-ZrO_2 composites match or even exceed those of natural bone.

The achieved new results were published in Materials [3] and presented on the international conferences (b), as well.

3. Fibrous alumina and zirconia toughened alumina ceramics with gradient porosity

In this contribution we highlighted a new aspect in the application of starting ceramic materials and thus a novel approach to production of highly porous ceramic composites with improved mechanical strength. Electrospunned ceramic composite nanofibers were used as the starting material for fabrication of porous ceramic, which investigations has been appear only limited in the literature. However, these ceramic fibres already exhibit highly porous structure, which contains several so-called interfibre-bondings. This highly connected porous ceramic bodies contribute the increasing stiffness irrespective of material properties and loading conditions.

Based on the previous results, the composite fibres were fabricated by sol-gel synthesis offering several advantages such as a a) highly homogeneous distribution of the phases compared with the conventional mixing/milling synthesis methods; b) enhance the mechanical properties and c) reduce the unexpected in-situ reactions during the sintering process in addition d) improve the resistance of Y_2O_3 stabilized ZrO_2 against LTD.

In this contribution, we investigated three different composition of ceramic fibres and produced gradient ceramic body in SPS by various conditions. Pure Al_2O_3, as a reference, and two different 20 wt% ZrO_2 toughened Al_2O_3, hereinafter ZTA and composite fibers was studied. (The production of two types of fibers with various compositions was necessary in order to examine the advantages of the sol-gel synthesis method.) In the case of composite fibers, we used the two most studied stabilizer agents of tetragonal ZrO_2 and produced 3 mol% Y_2O_3 stabilized ZTA (hereinafter Y-ZTA) and 16 mol% CeO_2 stabilized ZTA (hereinafter Ce-ZTA) composite fibers.

According to the major founds, ASY configuration of the graphite tools resulted in considerable temperature differences on the opposite sides of the samples, particular for the Ce-ZTA sample, where the highest temperature difference (143 °C) was detected between the opposite sited of the sample at a sintering temperature of 1300 °C. The microstructure analysis confirmed that the prevailing temperature difference between the opposite sides of the samples yielded gradient microstructures in terms of porosity similarly as in the previous studies. Additionally, it has been proved that the use of fibres as a raw material contributes to the high apparent porosity of the samples, despite to the high local temperatures at the bottom side of the samples. The porosity varied between 42 and 75%, which was also influenced by the as-formed hollow characteristics of the fibres. The hollow fibres contributed to bimodal pore structure in the ceramics.

The XRD analysis confirmed that the higher temperature gradient for Ce-ZTA samples induced a moderate t→m- ZrO_2 phase transformation, as well as the formation of $CeAl_{11}O_{18}$, in minor amounts. Hence, it should be noticed that the sol-gel synthesis is more effective than traditional milling/mixing homogenization, since the $CeAl_{11}O_{18}$ phase appeared only in a small amount in the phase composition. More extensive phase transformations were hindered by the intragranular position of ZrO_2 within Al_2O_3 grains, which exceptional structure was demonstrated by high-resolution microstructure analysis. Furthermore, the developed intragranular nanostructure of ZTA composites offer solution to the long-standing disadvantage of Y-ZrO_2, the so-called LTD resistance, as well.

Strong correlation has been showed between the gradient microstructure and the mechanical properties. Despite the achieved high porosity of the ceramics bodies, the decreasing porosity toward the bottom side of the samples resulted in significantly improved mechanical properties in terms of hardness and compression strength. The highest hardness and was obtained for the Ce-ZTA composite, while the compressive strength of the composites reached similar values for Y-ZTA and Ce-ZTA, respectively sintered in ASY. Several works have reported that high porosity of the composites leads to a drastically reduced compression strength. In contrast, our results represented a relatively high strength, more than double values, which was attributed to the gradient microstructure in the composites.

We believe that such fibrous ZTA nanocomposites represent a new approach in the production of functionally graded ceramics, especially since the developed ZTA composites enable the combination of contrary properties (high porosity and strength) within a single body. Furthermore, they are attractive for biomedical applications, due to the porosity gradient structure is similar to natural bone: the highly porous part of the ceramic promotes e.g., rapid osseointegration of the bone cells, while the opposite, non-porous part provides ceramic with high mechanical resistance. The new results were published in Nanomaterials [4] and presented on an international conference (c).

Regarding to the obtained results of ZTA ceramics with interesting inter- and intragranular microstructure, a student Bálint Tulik was involved in this segment of the research project. He's task was to investigate the formation of inter- and intra-granular microstructures for Y-ZTA composites as his thesis work. According to the results, we successfully produced a Y-ZTA composite that shows high LTD resistance, which result represent a significant advance in the to produce biomedical grade Y-ZTA composites. The thesis entitle ”Production of zirconia-reinforced alumina (ZTA) ceramic composite for biological application” was submitted into the Faculty of Chemical Technology and Biotechnology of BME in December 2023. Regarding to the encouraging results, we plan to publish it in scientific paper, as well.

4. Comparative study of ZTA ceramics with fibrous and granular morphology

Regarding to previous results, we performed a comparative study on nanofibrous and nanogranular Y-ZTA and Ce-ZTA composites having gradient microstructure, particularly considering the effect of the different morphologies of the starting materials on the formation of temperature gradient in the sample during SPS and the final microstructure and the mechanical properties, as well (5). The mechanism of SPS sintering still raises many questions, and only a few papers address the influence of raw powder morphology on SPS heating mechanisms. However, according to the different morphologies of the starting materials, Joule heating and/or sparks can be formed differently at the connection points, which also affects the microstructure of the sample.

We pointed out that the morphology of the starting materials did not have significant influence on temperature gradient, it was similarly great for the fibrous and granular samples with the same composition. However, in all cases, samples with a fibre morphology showed a higher temperature gradient. This is probably due to the difference in compaction of materials with different morphologies during SPS sintering. For the spherical nanoparticles have far more contact points among the particles than continuous fibres, which cause more discharges among the particles during SPS, and in turn results in a smaller temperature difference inside the samples.

However, the microstructure of the composite is showed significant difference particularly the porosity and the morphology of pore network. We pointed out that the pore structure of the ceramic body can be tailored by varying the morphology of the precursor or the graphite configuration. Fibrous samples for a given temperature, graphite configuration and composition exhibit 10–20% higher porosity than granular samples, which reflect the microstructure of the composites as well. The gradient microstructure is clearly apparent for the ASY samples, regardless of the fibrous or granular morphology of the sample. While the top part of the ASY samples consists of fine particles or fibres with substantial porosity— especially for the granular samples —the bottom part consists of coarser grains and fibres, leaving less room between them, which results in decreased porosity. In contrast the microstructure of the granular ZTA samples was almost pore-free at the lower part.

The morphological differences contribute significantly to the mechanical properties, particularly to the strength of samples. Samples with granular morphology typically exhibit greater hardness than samples with a fibrous structure under the same sintering conditions. The higher hardness of granular sample can be ascribed to the significantly different porosity and pore structure of the sintered sample. While the trend was similar to hardness and the strength of the granular samples was ~50% higher than that of the fibrous samples. The higher compressive strength can be attributed to the more stable and compact pore structure in the granulated samples.

The results emphasis that a combination of ceramics with mixed morphologies would also be appropriate e.g. in a layered arrangement. For increased porosity, ceramics fibres are more suitable, while granular ceramics resulted in an enhanced strength.

One of the goals of this project was develop a bioceramics for potential application in biomedical area, therefore, in this contribution, we also anticipated the possible use of these ceramics in biomedical applications, and we integrated bioactive nano- HAp material into the pore structure. Deposited HAp inside the pores is known to possess bone-bonding properties.

High-resolution microstructure analysis revealed that nanosized- HAp can pass into the pore structure of the samples with either fibrous or granular morphologies, regardless of composition, furthermore in addition to individual particles, agglomerated HAp also infiltrate to the pore structure. We showed that HAp can integrate more into the fibrous samples due to the larger porosity and interconnected pore structure on one hand to and bimodal pore structure of fibrous samples (large pores between the fibers and small pores inside the fibers) on the other.

Our results suggest that such ZTA ceramic bodies with porosity gradient are suitable for biomedical use, furthermore biocompatibility can be enhanced by integrating HAp into the pore system.

The new results were published in Micromachines [4] and presented on a national conference (d), as well.

Use of the project results

Our new results propose fundamental interest in ceramic material science, particularly in bioceramic research.

The investigated Al_2O_3-ZrO_2 ceramics composites fabricated by a novel SPS technology are excellent candidates for biomedical applications, due to its unique gradient microstructure. In particular, Al_2O_3-ZrO_2 composite with porosity gradient are suited for different implants and bone scaffolds with their exceptional multifunctional properties: the biocompatible or even bioactive feature by adequate porosity is combined with improved mechanical strength.

Furthermore, the newly developed technology for creating in-situ temperature gradient during SPS sintering process can be easily apply for other ceramic or materials, as well. Hence FGM can be simply produced for additional application area, such as for lightweight structural materials (thermal insulator) as well as for energy production (solid oxide fuel cells).

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Papers

[1] Bódis E., Károly Z., Fabrication of graded alumina by spark plasma sintering, INTERNATIONAL JOURNAL OF ADVANCED MANUFACTURING TECHNOLOGY 117 pp. 2835-2843., 9 p.(2021) IF_{2021}:3.4

[2] Bódis E. ;Cora, I.; Fogarassy, Z.; Veres, M. ;Németh, P., High-temperature evolution of diamond-SiC composites, PROCESSING AND APPLICATION OF CERAMICS 16 : 1 pp. 69-77. , 9 p. (2022) IF_{2022}: 1.1

[3] Bódis E. ;Jakab M.; Bán K.; Károly Z., Functionally Graded Al_2O_3–CTZ Ceramics Fabricated by Spark Plasma Sintering, MATERIALS 15 : 5 Paper: 1860 , 18 p. (2022) IF_{2022}: 3.4

[4] Bódis E. ;Molnár K.; Móczó J.; Károly Z., Preparation and characterization of fibrous alumina and zirconia toughened alumina ceramics with gradient porosity, NANOMATERIALS 12 : 23 Paper: 4165 , 19 p. (2022) IF_{2022}: 5.3

[5] Bódis E. ; Károly Z., Zirconia-Toughened Alumina (ZTA) Nanoceramics with a Gradient Microstructure: A Comparative Study of ZTA Ceramics with Fibrous and Granular Morphology, MICROMACHINES 14 : 9 Paper: 1681 , 15 p. (2023) IF_{2022}: 3.4

Talks in conferences and seminars.

a) E. Bódis, “Functionally graded bioceramics fabricated by spark plasma sintering” on the “Nanofabrication and Technologies” training course, 04- 24 February 2020, Bengaluru, India
b) E. Bódis, Functionally Graded Ceramics Fabricated by Spark Plasma Sintering, 11th Global Conference on Materials Science and Engineering (CMSE 2022), 8-11 August 2022, Shenzhen, China
c) E. Bódis, Porous Bioceramic NanoComposites with Improved Strength by Gradient Microstructure, 7th International Conference on “Material Science and Engineering” 29-30 June 2023, Barcelona, Spain
d) E. Bódis, Z. Károly, Gradiens szerkezetű kerámiák előállítása SPS módszerrel, Anyagtudományi és Szilikátkémiai Munkabizottság szakmai ülés, 7 September 2023, Budapest (in Hungarian)