SPS-RS technique for solid-phase “in situ” synthesis of biocompatible ZrO₂ porous ceramics

O O Shichalin¹,², M A Medkov¹, D N Grishchenko¹, V Yu Mayorov¹, A N Fedorets², A A Belov¹,², A V Golub¹, E A Gridasova², E K Papynov¹²

1 Institute of Chemistry, Far Eastern Branch of Russian Academy of Sciences, Vladivostok, 690022, Prospect 100-let Vladivostoku 159, Russia
2 Far Eastern Federal University, Vladivostok, 690920, Suhanova street 8, Russia
E-mail: oleg_shich@mail.ru

Abstract. The prospective method of spark plasma sintering-reaction synthesis (SPS-RS) for fabrication of ceramics based on ZrO₂ and biocompatible with living tissue is presented. Nanostructured ceramics has high mechanical strength (more than 400 MPa) and controlled porosity depending on specified sintering conditions. Biocompatible phases Ca₁₀(PO₄)₆(OH)₂ are formed “in situ” during SPS sintering of ZrO₂ powder due to chemical interaction of phosphate precursors preliminary introduced into the mixture. The effective method to improve (to develop) porous structure of bioceramics obtained by SPS or SPS-RS techniques using poreforming agent (carbon black) is proposed. Suggested original SPS-RS “in situ” technique provides fabrication of new ZrO₂ ceramics containing biocompatible phosphate components and possessing unique structural and mechanical characteristics. Such ceramics is indispensable for bone-ceramic implants that are able to activate processes of osteogenesis during bone tissue recovery.

1. Introduction
Ceramic materials for bone implants raise a great interest of scientific community due to growing demand in orthopedics. Inertness to biological medium and high mechanical properties of the ceramics based on ZrO₂ allow successful implementing it in the production of porous constructions implanted into organism [1]. ZrO₂ is referred to bioinert type of materials, which means that negative chemical reactions with tissues and intertissular liquids in organism are avoided. Nevertheless, it has a significant drawback: due to shielding of mechanical loads the gradual resorption of nearest bone tissues occurs [1].

There are several approaches to the problem indicated above. One of them is to increase the bioactive properties of ZrO₂ ceramics. In that case ceramics have its own ability to bioresorption and during implantation executes the function of building material, participates in the process of recovery of bone material. This can be made via creating on the basis of ZrO₂ ceramics composite materials with resorbable phase, in place of which the calcium-phosphate compounds, for example hydroxyapatite, which has the closest composition to the mineral part of bone tissue [2]. Secondly, stimulating activity during reparative osteogenesis is affected also by microstructure of bone implant, in particular, porosity is responsible for the depth of accretion of biological tissue into implant. In that case, during synthesis of bioactive composites such parameters as curvature, degree of crystallinity and porosity are modified in the first place and by a variety of methods [3]. Also, in order to achieve desired mechanical characteristics of ZrO₂ composites methods of powder metallurgy are used: hot/cold or...
isostatic pressing, sintering under pressure, slip casting, microwave synthesis and oth. [4], as results obtaining composite ceramics of high mechanical strength. However, it is known that conventional routines do not ensure preservation of material’s porous structure, which collapses and forms highly dense compound with density more than 99.5% from theoretical [5]. This is caused by severe technological conditions of the process, under which the grain growth and destruction are intensified leading to distortion and demolition of porous framework in the solid body.

High level of modern technologies allows eliminating complications connected with preservation of porous framework of bulk ceramics. In that case one is advisable to use innovative technology of powder metallurgy known as Spark Plasma Sintering (SPS). Main purpose of SPS technology is high-speed sintering (consolidation) of powder materials of any origin resulting in formation of ceramics with novel compositions and properties [6]. Successful application of SPS technology for synthesis of nanostructured ceramics based on ZrO₂ and on its composite forms is shown by a number of researchers in [7]. Almost all of the works in the field contain limited description of correlations between porous structure changes and SPS conditions. Recommendations or suggestions concerning control of organization or development of porous structure of ceramic composites based on ZrO₂ during SPS synthesis are practically absent. In addition, in our point of view, more prospective direction in this scientific field is search and study of original ways of synthesis of such ceramics, for example Spark Plasma Sintering-Reaction Synthesis (SPS-RS) based on conducting chemical reaction under spark plasma exposure onto reacting mixture during SPS synthesis Information about SPS-RS preparation of bioactive ZrO₂ ceramic composites containing bioactive phase are absent.

Present research is devoted to fabrication of multiphase biocompatible ceramics based zirconium dioxide via reactive spark plasma sintering. Given that the aim of this work is establishing capability of formation of bioactive phase within the composition of ceramics in the course of chemical reaction during SPS consolidation of ZrO₂ powder, doped with reactive mixture. Also studying of possibility of regulation of porous structure of obtained ceramics via using carbon template as a poreforming agent with conservation of high mechanical strength. The suggested in present work original method ensures fabrication of new bioceramics for medical purposes, prospective as bone-ceramic implants.

2. Experimental

2.1. Materials

To prepare initial dry mix (IM) we used ZrO₂ powder of analytical grade. Crystal structure of ZrO₂ ceramics was stabilized by introduction of magnesium oxide (chemically pure). As a reactive mixture (RM) for the formation of bio-compatible phase we used a (NH₄)₂HPO₄ (pure) and CaCO₃ (chemically pure). Proportion of these components was adjusted to reach Ca/P = 1.66. Dispersed technical carbon (TC) with particle size 1-500 µm was used as a poreforming agent during ceramic synthesis.

2.2. Synthesis

Ceramic synthesis was carried out in an equipment of SPS-515S “Dr.Sinter*LAB™ (Japan) according to following scheme: 3 g of IM containing ZrO₂ powder (80 wt.%), reactive mixture (RM) of CaCO₃ and (NH₄)₂HPO₄ (15 wt. %) and stabilizing agent MgO (5 wt.%), was placed into a graphite die (15.5 mm diameter), prepressed (20.7 MPa), then the stock was placed into vacuum chamber (pressure 6 Pa) and then sintered. To prevent baking of sintered powder on the die and on the plungers as well as to remove obtained compound easily we used carbon foil 200 µm thick. Sample sintering was conducted at 900, 1000 and 1300 °C with heating rate 170 °C/min. Samples were being held at the maximal temperature for 5 min and then were cooled down to room temperature. Pressure onto the sample during sintering was 22.3 MPa and remained constant throughout the process. Periodicity of generated low-voltage pulse in ON/OFF regime is 12/2, duration 3.3-329 ms.

To increase porous volume of the obtained ceramic samples the poreforming agent was additionally introduced. As an agent we used low dispersed technical carbon (TC) of 1-500 µm fraction in the amount 2, 5, 10 and 15 wt.% of total IM. After SPS-RS consolidation obtained ceramic samples were
exposed to 900 °C (heating rate 5 °C/min, holding time 30 min) temperature in air atmosphere to remove TC in the furnace “Nabertherm GmbH” (Germany).

2.3. Characterization methods
Crystal phases of initial powders and sintered pellets based on uranium dioxide were identified by XRD on a multipurpose X-ray diffractometer D8 Advance “Bruker AXS” (Germany). Microstructure of the samples was carried out using scanning electron microscopy (SEM) on TM 3000 and S 5500 “Hitachi” (Japan) devices. Samples’ elemental composition based on quantitative and qualitative determination of the elements in the investigated materials was carried out using energy dispersive microanalysis (EDX) on Bruker station within TM 3000 microscope “Hitachi” (Japan).

3. Results and discussions
During experiment the SPS consolidation of ZrO$_2$ powders, containing reactive mixture of initial compounds of bioactive phase including poreforming agent, was carried out. According to the goal of investigation, primarily it was necessary to establish a fact of formation of bioactive phases of HAP in the course of chemical reaction between (NH$_4$)$_2$HPO$_4$ (pure) and CaCO$_3$ during SPS-RS consolidation of ZrO$_2$ powder (“in situ”). Ratio of RM was chosen as described in [8] and corresponded to Ca/P=1.66. In that case there are two reactions possible with the first being dominating.

10CaCO$_3$ + 6(NH$_4$)$_2$HPO$_4$ = Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ + 10CO$_2$ + 8H$_2$O + 12NH$_3$
3CaCO$_3$ + 2(NH$_4$)$_2$HPO$_4$ = Ca$_3$(PO$_4$)$_2$ + 3CO$_2$ + 3H$_2$O + 4NH$_3$

According to reaction (1) and (2) thoroughly described in [8] thermal treatment of the indicated reaction mixture the final products are calcium phosphates Ca$_3$(PO$_4$)$_2$ and Ca$_{10}$(PO$_4$)$_6$(OH)$_2$. Formation of one from the two phosphates or of their mixture is ruled by several factors, like partial interaction of the initial components, destruction of reaction products and synthesis conditions such as components’ ratio, treatment temperature and holding time. As a result, the series of dense ZrO$_2$ ceramics with various physico-chemical characteristics have been obtained (Table 1).

We considered 1300 °C as the optimal SPS-RS temperature for the studied system, because it is enough for sintering of ZrO$_2$ powder and for deep chemical interaction of the components in the reaction mixture resulting in hydroxyapatite phase. As a blank experiment we conducted SPS-RS at 900 and 1000 °C to evaluate the depth of reaction between the components during SPS-RS.

Table 1. Characteristics of ceramics based on ZrO$_2$.

| No. | Sample composition          | P$_s$ MPa | T$_{sintering}$ °C | Compressive strength MPa | S$_{spec}$ (BET), m$^2$/g |
|-----|----------------------------|-----------|--------------------|--------------------------|---------------------------|
| 1   | IM (80% ZrO$_2$ + 15% RM)  | 22.3      | 900                | 9                        | 0.68                      |
| 2   | IM (80% ZrO$_2$ + 15% RM)  | 22.3      | 1000               | 373                      | 0.12                      |
| 3   | IM (80% ZrO$_2$ + 15% RM)  | 22.3      | 1300               | 400                      | 0.12                      |
| 4   | IM (80% ZrO$_2$ + 15% RM)+TC 2% | 22.3 | 1300               | 362                      | 0.24                      |
| 5   | IM (80% ZrO$_2$ + 15% RM)+TC 5% | 22.3 | 1300               | 242                      | 0.25                      |
| 6   | IM (80% ZrO$_2$ + 15% RM)+TC 10% | 22.3 | 1300               | 150                      | 0.29                      |
| 7   | IM (80% ZrO$_2$ + 15% RM)+TC 15% | 22.3 | 1300               | 47                       | 0.35                      |

According to XRD (Fig. 1), solid composition depends on SPS temperature and includes zirconium oxide in monocline and(or) tetragonal modifications, containing calcium phosphates in its bulk. SPS treatment of reaction mixture with ZrO$_2$ at 900, 1000 and 1300 °C provides formation of crystalline HAP, while the phase composition of the samples is identical (Fig. 1, curves 1 and 2). However, diffraction peak intensities are obviously different, in particular, ceramics obtained at 1300 °C possesses higher crystallinity of the phases (Curve 2) compared to 900 and 1000 °C samples (Curve 1). It is noteworthy that adding the poreforming agent does not change the final ceramics’ composition as found from XRD patterns of samples 3-5 that are identical and correspond to Curve 2.
Figure 1. XRD patterns of composite ceramics based on ZrO$_2$ and calcium phosphates obtained via SPS-RS: (1) – samples No. 1, 2; (2) – samples No. 3, 4, 5, 6, 7. Sample description is given in Table 1.

Investigations of surface morphology showed that microstructure of consolidated ZrO$_2$ sample is represented by agglomerates of spherical particles with mean diameter 1-1.5 µm (Fig. 2). Also there are melted, shapeless units that somehow stick together spherical particles. According to EDX, particles consist of ZrO$_2$ with small amount of calcium and phosphorus (Fig. 2b, area 1, spectrum 1 and Table 2). Shapeless regions, which are observed mainly inside pores, composed of calcium phosphates with little zirconium content (Fig. 2b, area 2, spectrum 2 and Table 2). Mixed composition, obtained by energy-dispersive spectra and indicated in the table – is the result of scattering from particles that are close to the imaging area.

Table 2. Element composition of ZrO$_2$ composite ceramic obtained by SPS-RS using carbon template (sample No. 6, table 1). Spectrums on Fig.2.

| No. | Zr  | Ca | P   | Mg | O     | C   |
|-----|-----|----|-----|----|-------|-----|
| 1   | 49.21 | 7.26 | 0   | 1.74 | 34.59 | 7.20 |
| 2   | 61.27 | 3.81 | 1.46 | 1.64 | 14.24 | 17.58 |
| 3   | 56.71 | 3.16 | 1.38 | 1.85 | 21.27 | 15.63 |
| 4   | 15.95 | 16.22 | 10.53 | 4.79 | 33.63 | 18.87 |
| 5   | 6.17  | 14.55 | 12.68 | 3.50 | 46.69 | 16.40 |

SEM images of obtained composite ceramics clearly show the presence of macroporous formations with pore diameter ~5-10 µm (Fig. 2b). In order to structure porous framework of the ceramics we suggested to introduce poreforming agent (TC) into the initial system subjected to sintering with its consequent removal. Prospect of such approach was confirmed by us earlier on the example of synthesis of highly porous bioinert silicate ceramics [9]. Suggested method allows controlling pore size and volume in the SPS ceramics. However, such solution requires additional stage of thermooxidative treatment of final samples. It is caused by SPS operation procedure, which is carried out in vacuum in order to avoid burning of the materials. Oxygen-free gaseous medium prevents removal of TC. Thermooxidative treatment of consolidated samples solves the mentioned problem. Intrusion curves presented on Fig. 3 indicate the influence of carbon additive on sample’s microstructure. First, the increase of porous volume depending on quantity of introduced TC is observed (2, 5, 15 wt.%). Second, material with various pore size distribution is formed. Sample obtained without carbon additive has micro- and mesopores that is reflected on intrusion curves in high pressure region (Fig. 3a, curve 1), and also on differential curve (Fig. 3b, curve 1) within the range 5-50 nm, and also a number of macropores sized ~500 nm. Formation of this type of pores is connected primarily due to packing of fine particles of sintered powder. Volume of such pores depends directly on the degree of interconnectivity of particles, shape change (deformation or grain growth), density of their mutual packing and also on the sintering parameters.
Figure 2. SEM-images of ZrO$_2$ composite ceramic obtained by SPS-RS using carbon template (sample No. 6, table 1).

Figure 3. Cumulative and differential mercury intrusion curves of ZrO$_2$ ceramic samples, obtained via SPS-RS at 1300 °C: (1)-IM without carbon (sample 3); (2)-IM+2 wt.% TC (sample 5); (3)-IM+5 wt.% TC (sample 6); (4)-IM+15 wt.% TC (sample 7). Sample’s description is given in Table 1.

Introducing of pore forming agent leads to eliminating of micro- and mesopores (Fig. 3b) that results in reduction of specific surface area (Table 1). However, large macropores are formed with size 1 μm and above (Fig. 3b).

Another plausible reason of variety of pore sizes in ceramic samples, in particular, synthesized without TC, is the consequences of chemical reaction according to reaction equations 1 and 2. During interaction of RM there are a lot of volatile products formed. While those gases are liberated in the process of sintering formation of defects in the volume of ceramics can possibly occur. Such defects are voids (pores) in the volume of the material and have various size and shape. One can reasonably suggest that surface of such pore type is enriched by HAP that cover pore’s inner surface (Figure 2b).

In addition, one should note that quality of ceramics of any type besides structural characteristics is defined by mechanical parameters. Suggested in present work method provides formation of ZrO$_2$ ceramics with bioactive phosphate basis of macroporous structure with wide pore size range from 1 to 100 μm and more, high mechanical strength, compressive strength reaches 400 MPa (Table 1). While the sintering cycle does not last longer than 10 minutes of heating and holding at 1300 °C. However, the suggested SPS-RS method to control porous structure of the ceramics is plausible but at the expense of mechanical strength, which linearly depends on the amount of poreforming agent (TC).
4. Conclusions
In present work an original way of synthesis of biocompatible ceramic material based on zirconium dioxide via SPS-RS is presented. Obtained ceramics possess unique set of structural and mechanical characteristics: wide range of macropore size, from 1 to 100 μm and more, compressive strength reaches 400 MPa. We have shown for the first time that chemical interaction between CaCO$_3$ and (NH$_4$)$_2$HPO$_4$ (reaction mixture) can be caused by spark plasma with formation of biocompatible phases HAP “in situ” during sintering of ZrO$_2$ ceramics. It is supposed that volatile products of reaction are the reason of structural defects as macropores, on the surface of which bioactive phase is formed in a thin layer. The effectiveness of using poreforming agent (carbon additive) to organize macroporosity of ceramics along with preserving its high mechanical strength has been shown. It was established by structural analysis (BET and mercury porosimetry) that pore size and volume depend on the quantity of introduced poreforming agent, which avoids presence of micro- and mesopores, however ensures formation of large macropores when template content is higher than 2 wt.%.

Presented ZrO$_2$ ceramics is characterized by a number of unique properties: chemical, corrosive and mechanical stability, developed macroporous structure that is similar to bone tissue texture and is able to execute its main functions, high mechanical strength, which is responsible for durability, and also presence of biocompatibility with living tissues of the organism and stimulates the osteogenesis processes, all these make ceramics of this type very prospective solution for medical practice.

References
[1] Dubok V A 2001 Bioceramics - Yesterday, Today, Tomorrow Powder Metall. Met. Ceram. 39 381–94
[2] Medkov M A, Rudnev V S, Grishchenko D N, Djuizen I V, Lukiynchuk I V, Papynov E K, Portnyagin A S and Gridasova E A 2016 Nano-Sized Calcium-Phosphate Powders and Glass-Ceramic Coatings for Medical Purposes Bioglass: Properties, Functions and Applications ed L Cannon (Nova Science Publisher, Inc) pp 55–96
[3] Izhizaki K, Komarneni S and Nanko M 1998 Porous materials vol 15, ed R Ford (Springer US) p 240
[4] Lashneva V V., Shevchenko A V. and Dudnik E V. 2009 Bioceramic based on zirconium dioxide Glas. Ceram. 66 140–3
[5] Hu C, Li F, Qu D, Wang Q, Xie R, Zhang H, Peng S, Bao Y and Zhou Y 2014 Developments in hot pressing (HP) and hot isostatic pressing (HIP) of ceramic matrix composites Advances in Ceramic Matrix Composites ed I M Low (Woodhead Publishing Limited) pp 164–89
[6] Tokita M 2013 Spark Plasma Sintering (SPS) Method, Systems, and Applications Handbook of Advanced Ceramics: Materials, Applications, Processing and Properties ed S Somiya (Elsevier Inc.) pp 1149–78
[7] Li W and Gao L 2000 Rapid sintering of nanocrystalline ZrO$_2$(3Y) by spark plasma sintering J. Eur. Ceram. Soc. 20 2441–5
[8] Safronova T V., Putlyaev V I, Ivanov V K, Knot’ko A V. and Shatalova T B 2016 Powders Mixtures Based on Ammonium Pyrophosphate and Calcium Carbonate for Preparation of Biocompatible Porous Ceramic in the CaO–P$_2$O$_5$ System Refract. Ind. Ceram. 56 502–9
[9] Papyonov E K, Mayorov V Y, Portnyagin A S, Shichalin O O, Kobyllyakovt S P, Kaidalova T A, Nepomnyashyi A V., Sokol’nitskaya T A, Zub Y L and Avramenko V A 2015 Application of carbonaceous template for porous structure control of ceramic composites based on synthetic wollastonite obtained via Spark Plasma Sintering Ceram. Int. 41 1171–6

Acknowledgements
This study was supported by grant for young scientists from the President of the Russian Federation (grant MK-177.2017.3).