Structure and mechanical properties of ZrO$_2$-MgO composites with bimodal pore structure

A Buyakov$^{1,2,3}$, S Buyakova$^{1,2,3}$, S Kulkov$^{1,2,3}$

$^1$Tomsk State University, 36, Lenina ave., Tomsk, 634050, Russia
$^2$Institute of Strength Physics and Materials Science of Siberian Branch Russian Academy of Sciences 2/4, Akademicheskii ave., Tomsk, 634021, Russia
$^3$Tomsk Polytechnic University, 30, Lenina ave., Tomsk, 634050, Russia

E-mail: alesbuyakov@gmail.com

Abstract. Porous ceramic ZrO$_2$-MgO composite in a wide range of component content was studied. The effect of content and sintering parameters on pores size, its distribution, lattice structure, coherently diffracting domains and lattice microdistortion, tensile strength was investigated. It has been shown that the adding of pore-forming particles into the initial powder makes it possible to obtain a bimodal pore structure of composites. Sintering time and MgO content in ceramics are stipulated a changing of the average size of macro- and micropores and microstresses, which determine the macroscopic strength of the material.

1. Introduction
Ceramics, such as zirconia and alumina compounds, are widespread as dental and osteoprosthetics materials. These ceramics have identical type of chemical bonds with inorganic bone matrix, do not participate in electrochemical interaction with the body tissues and mechanical parameters do not degrade over time. However, their high strength, significantly exceeding similar characteristics of bone tissue, restricts using of ceramics as osteo replacement material.

Significant prospects for the osteo replacement materials creation may have the "Bio-inspired" approach, which consists in reproducing natural structures in artificially created materials. Bone tissue is a complex composite with heterogeneous structure and developed porosity. It is well known from studies that osteo replacement materials with bimodal porosity have good conditions for bone tissue integration – macropores, with an average size of about 100 μm, play the role of niches for the osteoblast cells proliferation and micropores and micropore channels, with an average size of 30 μm, are necessary for the vascular system development and cell cultures nutrition [1]. Ensuring the structural and biomechanical identity with natural bone tissue will allow making a new kind of osteo replacement materials.

Among ceramic materials, promising for osteoimplantation, materials based on ZrO$_2$ and MgO are of particular interest [2, 3]. Zirconia is included in the ISO registry (ISO 13356:2015) as a biocompatible material for prosthetics. Magnesium ions are participating in the DNA and RNA molecules synthesis and stabilization processes, creating favorable conditions for the bone tissue regeneration stimulating in the contact area [4]. However, currently knowledge of porous ceramics based on ZrO$_2$ and MgO system are not enough and require further study.

The purpose of this work is to study pore structure formation in the ZrO$_2$-MgO composite, depending on the composition and sintering parameters.

2. Materials and experiments
Porous ceramic materials based on partially magnesium-stabilized zirconium dioxide and magnesium oxide were studied. Samples were obtained by mechanical mixing of ZrO$_2$ and MgO powders in a wide range of components
concentration followed by cold uniaxial pressing of ceramic mixtures and sintering in air. The pore structure was formed by adding 50 vol. % of ultrahigh molecular weight polyethylene particles (UHMWPE) with an average particle size of 80 μm. Samples sintering were carried out according to the following conditions: heating at a speed of 0.5 °C/min with holding at 300 °C for 3 hours to remove pore-forming particles and sintered at 1600 °C with holding time 10 minutes up to 10 hours.

The phase content, the average size of coherently diffracting domains and lattice microdistortion were estimated by the Williamson-Hall method [5] based on the X-ray diffraction patterns obtained under conditions of filtered Cu Kα radiation and an angular range of 20-80°.

Microstresses were evaluated by microdistortions and the Young's modulus values of the corresponding phase. The average value of microstresses was calculated by the mixture rule, according to the ceramic sample phase content.

The microstructure of ceramics was studied by using scanning electron microscopy Tescan. Porosity was measured by using the Archimedes method [6].

The tensile strength was estimated by the method of "Brazilian test" [7], with a constant traverse speed of 0.01 mm/min.

3. Results and discussions
The porous structure of ceramics is represented by two types of pores, fig. 1. Macropores inherited the structure of burnt UHMWPE particles and mostly have a regular spherical shape. The micropores did not have a clearly defined form and were formed due to the presence of interparticle voids formed during the powders compaction. Porosity of studied ceramics basically did not change and was 48 ± 2%.

![Figure 1. The destruction surface of 50 wt. % ZrO₂ + 50 wt. % MgO ceramics after sintering at 1600 °C with a 1 hour holding time.](image)

In ceramics sintered for 10 minutes, the average size of macropores decreases from 36 to 24 μm with increasing of MgO content. The average size of micropores decreases from 3.8 to 2.5 μm, Figure 2 (a). Increasing of sintering time up to 10 hours leads to decreasing of the macropores average size to 25 μm, due to the continuing volumetric shrinkage, however, the average size of micropores increases to 7 μm, which is a due to the pores coalescence mechanism [8], Figure 2 (b).
Figure 2. The dependence of the average pore size on the MgO content after sintering for 10 minutes (a); dependence of the zirconia average pore size on the sintering time (b).

X-ray diffraction analysis showed that sintered zirconia is represented by the cubic phase with low-intensity peaks of monoclinic phase on the X-ray patterns of ZrO$_2$ samples sintered with holding more than 3 hours, which is corresponds with the ZrO$_2$ - MgO [9] state diagram. Increase of MgO content in the composite leads to a full stabilization of ZrO$_2$ in the cubic phase. Cubic zirconia lattice parameter was 5.090±0.017 Å, magnesia parameter was 4.213±0.009, which corresponds with JCPDS crystallographic base cards [Cubic ZrO$_2$ card # 27-997; Cubic MgO card # 4-829].

Figure 3 shows the changes of the coherent ly diffracting domains size and the lattice microdistortion of cubic ZrO$_2$ and MgO phases with varying sintering time. It can be seen that the cubic zirconia coherently diffracting domains size increases from 600 to 1600 Å, both with MgO content increasing and with time of sintering, figure 3 (a). The average size of MgO coherently diffracting domains varies from 900 to 1100 Å with increasing of MgO content in the composite and increases with the time of sintering, Figure 3 (b).

A cubic ZrO$_2$ lattice microdistortion decreases from 14 to $4 \times 10^{-4}$ with increasing of MgO content, Figure 1 (c). Increasing of sintering up to 10 hours leads to increasing of ZrO$_2$ lattice microdistortions, Figure 1 (d). MgO microdistortions decrease from 2 to $1 \times 10^{-4}$ with increasing of MgO content and time of sintering.
Figure 3. Cubic ZrO$_2$ CDD, the legend is valid for all the figures (a); MgO CDD(b); Cubic ZrO$_2$ microdistortion (c); MgO microdistortion (d).

Figure 4 shows the plotted data between the microstresses and macroscopic tensile strength. As one can seen there is a correlation between these values - microstresses, formed during sintering of the composite, determine the decreasing of macrostrength.

4. Conclusions
It has been shown that the adding of pore-forming particles into the initial powder makes it possible to obtain a bimodal pore structure of ceramics. Change of the sintering time and content of the ZrO$_2$-MgO leads to changing the average sizes pores, both macro- and micropores. Macro-strength of the material is determined by microstresses formed during sintering of the composite.

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