Structure and Percolation Thresholds in Magnesia Stabilized ZrO$_2$-MgO Porous Composite

Ales Buyakov, Sergei Kulkov
National Research Tomsk State University, Tomsk, 634050 Russia
Institute of Strength Physics and Materials Science SB RAS, Tomsk, 634055 Russia
National Research Tomsk Polytechnic University, Tomsk, 634050 Russia

E-mail address: kulkov@ms.tsc.ru

Abstract
This work reports the influence of porous ZrO$_2$-MgO ceramic composition on its structure and mechanical properties. The bimodal pore structure were formed by introduction of organic pore forming particles into the initial powder composition and due to the voids between ceramic powder particles. It was shown, that the mechanical parameters of the porous ZrO$_2$-MgO composite are substantially defined by the value of the microstresses, the MgO content, and, apparently, the formation of a percolation structure. Thus, it was shown that by varying the composition and the size of the pore-forming particles, it is possible to achieve a high degree of identity with the structure and properties of natural bone tissue.

Keywords: Zirconia, magnesia, porosity, biomaterial, percolation, strength, microstress

1. Introduction
Zirconia-based ceramic composites are widely used materials in medicine and other applications. Due to its high hardness, strength and wear resistance, zirconia is a good material for the manufacture of medical tools, and the high resistance to chemically aggressive media and the biological inertness of zirconia make it possible to produce a wide range of different parts for replacement of damaged bone tissue as a result of diseases and injuries, elements of joints and dental implants production [1].

To ensure the biological compatibility of the bone tissue endoprosthesis with the organism, it is necessary not only to obtain the biochemical compatibility of the material, which prevents the development of carcinogenesis induced by a foreign body, but also it is necessary the structural identity and correspondence of the mechanical parameters of the implant with the mechanical parameters of the bone tissue.

Despite the works of a number of authors devoted to the reproduction of the natural bone tissue structure in artificial ceramic materials, most of them consist in organizing a single-level pore structure, but it is known that bone tissue has hierarchically organized porosity. So, the aim of this work is to study the mechanical properties of the ZrO$_2$-MgO composite with a multiscale pore structure, close to the structure of an inorganic bone matrix [2].

2. Materials and methods
In the work, porous ceramic composites based on magnesium oxide stabilized zirconium oxide and magnesium oxide in a wide range of component concentrations were studied. Ceramics were
obtained by cold uniaxial pressing followed by high-temperature sintering at 1600 °C. A particles of ultrahigh molecular weight polyethylene in an amount of 50 vol. % were added to the initial powder compositions.

Studies of the pore microstructure were performed using a scanning electron microscope. The macroscopic strength of the studied composites was measured under axial compression of ceramic cylinders. The value of the microstresses were estimated as the multiplication of the microdistortions of the crystal lattice calculated by graphically plotting the Hall-Williamson dependence based on X-ray diffraction patterns and the theoretical value of Young's modulus.

3. Results and discussion
Studies of the microstructure of porous ZrO$_2$-MgO composites obtained in this work showed that their pore structure is represented by two types of pores. Macropores, with an average size of 77 and standard deviation 9 μm, were formed during the burning of organic particles of ultra-high molecular weight polyethylene during high-temperature sintering of ceramic composites, and inherited the spherical shape of polyethylene particles. Micropores are formed by the presence of voids between particles of ceramic particles formed during the compaction process. The average micropore size was 3 with standard deviation 0.7 μm.

![Microstructure images](image1.jpg)

Fig. 1. Microstructure of inorganic bone matrix, (a,b); microstructure of ceramic ZrO$_2$-MgO sample with 50 wt. % of MgO, (c,d)
On Figures 1a and b are shown the pictures of the microstructure of cancellous bone tissue, annealed at 800 °C to remove the organic component. Figures 1c and d shows the pictures of the ZrO$_2$-MgO composite with a 50 wt. % content of MgO pore structure. As one can see that the structure of the obtained ceramic material has a high degree of identity with the structure of the inorganic bone matrix.

Studies of the compressive strength of the obtained ceramic composites depending on the composition showed that sintered pure zirconia has the maximum strength, about 78±4 MPa, Figure 2. With increase of the MgO content in the composition up to 50% leads to a linear strength decrease to a minimum value of 28±3 MPa. However a further increase in the MgO content, on the contrary, is accompanied by strength increasing up to 37±5 MPa. Apparently, such a dependence of the compressive strength on the composition of the studied ceramics may be due to the forming of the percolation structure in the composite [3].

![Fig. 2. The dependence of the average value of the compressive strength on the composition](image)

X-ray diffraction analysis showed that the zirconia in the composite is represented by a cubic modification of the crystal lattice. The dependence of the microdistortions of the crystal lattice value is shown in Figure 3a. It can be seen that increasing of the MgO content leads to increasing of the ZrO$_2$ crystal lattice microdistortions, while at the same time, a decreasing of microdistortions of the magnesia crystal lattice is observed [4].

![Fig. 3. The dependence of crystalline lattice microdistortion value vs. MgO content, (a); Microstresses average value dependence vs. the content of MgO, (b)](image)
Estimation of the average value of the microstresses in the composite by the additivity rule on the composition showed that the minimum level of microstresses corresponds to pure MgO. When the content of magnesia is about 50%, a maximum of the average microstress is observed, Figure 3b.

The dependence of macro-strength vs. microstresses showed that the strength of the composite is largely determined by the values of microstresses acting in internal structure of composite, Fig. 4. These properties of sintered ceramics are correspond well to materials for osteointplant [5].

![Fig. 4. The effect of microstresses on the compressive strength of a composite.](image)

4. Conclusions
It has been shown that by introducing organic pore-forming particles into the initial powder compositions of ZrO$_2$-MgO ceramics, it is possible to obtain a bimodal pore structure and the pore size will be determined by the average particle size of the ceramic powder and pore former and sintering temperature. The mechanical parameters of the porous ZrO$_2$-MgO composite are substantially defined by the value of the microstresses, the MgO content, and, apparently, the formation of a percolation structure. Thus, it was shown that by varying the composition and the size of the pore-forming particles, it is possible to achieve a high degree of similarity with the structure and properties of natural bone tissue for these materials for osteoreplacement.

Acknowledgements
This work was carried out according to the Program III.23 of Fundamental Scientific Research of the State Russian Academy of Sciences for 2013–2020.

References
[1] C. Hadjicharalambous, A. Buyakov, S. Buyakova, S. Kulkov, M. Chatzinikolaidou 2015 *Bio. Mat.* 10 025012. [http://dx.doi.org/10.1088/1748-6041/10/2/025012](http://dx.doi.org/10.1088/1748-6041/10/2/025012)
[2] G.K. Williamson, W. Hall 1953 *Acta Metallurgica* 1 (22) 22 [https://doi.org/10.1016/0001-6160(53)90006-6](https://doi.org/10.1016/0001-6160(53)90006-6)
[3] F. C. Fonseca, R. Muccillo 2004 *Solid State Ionics* 166 (1-2) 157 [https://doi.org/10.1016/j.ssi.2003.10.002](https://doi.org/10.1016/j.ssi.2003.10.002)
[4] A.S. Apkaryan, S.N. Kulkov, L. A. Gömzc 2014 *Építőanyag-JSBCM* 66 (2) 38. [http://dx.doi.org/10.14382/epitoanyag-jsbcm.2014.8](http://dx.doi.org/10.14382/epitoanyag-jsbcm.2014.8)
[5] P. Ammann, R. Rizzoli 2003 *Osteoporosis int.* 14 13 [https://doi.org/10.1007/s00198-002-1345-4](https://doi.org/10.1007/s00198-002-1345-4)