Influence of nanopowders and pore-forming additives on sintering of alumina-zirconia ceramics

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Abstract. This work reviews the influence of nanopowders and pore forming additives on sintering and on properties of fine-pored alumina-zirconia ceramics. The optimum ratio of additives for ceramics’ sintering, as well as the content of additives to obtain microporosity have been determined.

1. Introduction
At present, zirconium and aluminum oxide-based ceramics is widely used in machinery and medicine. Aluminum oxide-based ceramic materials are characterized by high durability and high resistance to abrasion [1]. Zirconium dioxide is also considered to be a promising material due to its high mechanical strength and fracture toughness [2, 3]. Nevertheless, each of these oxides has its limitations, such as high cost of zirconium dioxide-based ceramics, low fracture toughness of aluminum-based ceramics, and high temperatures of sintering. At this time ceramic materials based on the mixture of these oxides are being intensively developed. These ceramics appear to be rather promising due to their favorable physical and chemical properties [4, 5]. Medicine is a potential area of application for these ceramic materials. Implant materials should have specific porosity [6]. The optimal pore size of the tissue ingrowth into an implant varies from 5 to 10 µm and from 50 to 100 µm [7]. Introduction of various additives into ceramic mass allows to modify the temperature of sintering, porosity and strength of the obtained ceramics. Usually, the impact of small quantities of pore-forming additives (up to 1.5 mas. %) is generally disregarded, as their introduction to materials can lead to mixed results.

2. Experimental Part
This research was aimed at studying the influence of nanopowders and pore-forming additives on sintering and on properties of fine-pored alumina-zirconia ceramics. During the experiment the initial charge mixture was made of micron powders of aluminum oxide (produced by Nabalox, Germany, average particle size 1.20 µm) and of zirconium dioxide (produced by the Chepetsk Mechanical Factory in Glasov, average particle size 0.23 µm) with mass ratio 70:30. Specific surface area of powders was determined by Surface Area and Pore Size Analyzer Quantachrome Nova-2200-e. Formation of the porous structure with channels of the necessary size was achieved by introduction of a burnable fibrous material. To improve sample strength, a pore-forming additives in the form of synthetic fiber (thread length – 1-2 mm) or polyvinyl alcohol (PVA) granules with nanopowder of one of the oxides were added in the obtained charge mixture. The average size of the zirconium dioxide nanopowder particles was 0.065 µm, of the aluminum oxide – 0.070 µm. The choice of nanopowders of similar oxides as additives guarantees lack of impurities in the sintered material. Oxides nanopowders were studied using analytical Field Emission SEM JEOL JSM-7500FA. To achieve even distribution of the additives in the micron powder, prepared mixture was blended in the Mini-Mill (Pulversisette 23). Cylinder shaped samples were molded from prepared charge mixture using uniaxial compaction method under specific pressure of 600 MPa. Samples were heat treated at
1550° C and 1580°C in air, rate of temperature rise ~ 2°C per a minute, curing at finishing temperature for 2 hour. Behavior of the synthetic fiber during heating was analyzed using thermal analyzer NETZSCH STA 449 F3 Jupiter®. After thermal treatment shrinkage, density, porosity and water absorption of the samples were defined using hydrostatic weighing with vacuum blowing method. For tensile strength determination at three-point bending, the samples were prepared in the form of beams with size 50 × 5 × 5 mm. For determination of strength at compression, the samples were prepared in the form of cubes, with size 5 × 5 × 5 mm.

3. Results and Discussion

Line charts showing relationship between shrinkage/total porosity and quantity/additive type

**Figure 1.** Relationship between shrinkage/total porosity and the quantity of Al₂O₃ and ZrO₂ nanopowder at the firing temperatures of 1550° C and 1580° C (types of nanopowder additive and firing temperatures are specified on the graphs).

Nanopowders in the content range under study at 1550°C carry out a function of a sintering additive, which appears from the increase in shrinkage of the samples and from the reduction of the total porosity when introducing nano-Al₂O₃ to 1 mas.% and nano-ZrO₂ to 0.75 mas.% (Fig.1). Sinterability at 1580°C is limited by the nanopowders’ content at 0.25 mas. % of Al₂O₃ and 0.5 mas.% of ZrO₂. Porosity of the samples tends to increase with the increase of nanopowders’ content greater than these values. It must be noted that properties of the initial powders greatly influence properties of the obtained samples. Therefore, pictures of the initial nanopowders were taken and a specific surface area of the initial powders was determined.

Microphotos (Fig. 2, Fig. 3) demonstrate that zirconium dioxide nanopowder has sphere structured hollow particles (0.065 µm), which later will influence the samples’ porosity. Aluminum oxide nanopowder has spherical particles (0.070 µm) and “loose” structure. On the one hand, it complicates pressing process; on the other hand, it provides closer packaging of the particles in a raw material (density increases by 10%).
Not only PVA, but also small amounts (up to 0.1 mas.%) of synthetic fiber increase sinterability: they contribute to density of sintered materials, increase of shrinkage and decrease of porosity. (Fig. 4).

With the increase of polyvinyl alcohol and fiber content in the sinter mixture, the role of PVA and fiber is progressively changing. At 0.5-1.0 % these additives contribute to the increase of porosity and to the formation of fine-pored structure. It was noted that with firing temperature increase by 30°C, linear shrinkage increases by 2.0-2.5%; total porosity increases by 4.0% (for samples without pore-forming additives), and by 10.0 % (for samples with 1 mas.% PVA).

Differential thermal analysis of the synthetic fiber was conducted to determine the role of the fibrous material. This material has to perform the pore forming function, i.e. to burn out completely when heated in air.

Thermogram (Fig. 5) shows that fiber starts melting at low temperatures 219.4 and 306.4 °C, that results in two small endothermic effects (circles in Fig. 5); fiber starts oxidation at 359°C, and at 564.2° C the mass loss is 99%. This reaction is exothermic and it is accompanied by two effects at temperatures 375.5° C and 492.8° C through primary oxidation, formation of capsules and their additional oxidation. Thus, it is arguable that in the initial interval of the thermal treatment fiber melts, creating a small quantity of the melt that contributes to attraction of solid particles, so, up to a certain content in the charge mixture, it promotes material densification.
At mass content greater than 0.5 mas.%, fiber creates porous structure while burning out. However, it is necessary to take into account, that fiber content greater than 1 mas. % complicates the pressing process and leads to formation of hairline cracks in samples. Microphotos of the samples confirm received results (Fig. 6, Fig. 7).

Microphotos demonstrate that the increase in the amount of fiber leads to the increase in porosity of samples. It is noted that pores created by fiber are cylindrical in shape with diameter about 30 µm. The combined effect of nanopowder and fiber on the properties of sintered ceramics was also researched. At 1580º C, the presence of fiber (0.1 mas.%) contributes to sintering of the ceramics, containing nano-ZrO$_2$ at 0.25 mas.% as an additive (without the fiber this additive activates sintering at 0.5 mas.%) (Fig.8). With introduction of nano-Al$_2$O$_3$ additive, sintering takes place when its contents is not greater than 0.5 mas.% (while without introduction of the fiber sintering occurs at the contents not greater than 0.25 mas.%). At 1550º C, sintering is limited by nanopowders’ contents of 0.25 - 0.75 mas.%. Thus, when comparing shrinkage of samples with both nanopowder and fiber additives as opposed to samples with the nanopowder additive only, it can be concluded that the introduction of fiber in the amount of 0.1 mas.% insignificantly improves sintering of samples (shrinkage of samples is approximately the same), but it increases the content range of nanopowders, which leads to improvement of sintering. This fact has technological importance, since it allows adjusting additive amounts at a larger range.
Figure 8. Relationship between shrinkage/total porosity and quantity of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanopowder at 0.1 mas.% fiber at firing temperatures of 1550°C and 1580°C.

Comparison of micropictures (SEM) shows that in samples without additives, separate agglomerates of grains and pores between grains are visible (Fig. 9).

Figure 9. Photo of sample consist of 70%-$\text{Al}_2\text{O}_3$ and 30%-$\text{ZrO}_2$ ($T_{\text{bur}}=1580°C$)

Figure 10. Photo of sample with 1.5 mas.% of $\text{Al}_2\text{O}_3$ nanopowder ($T_{\text{bur}}=1580°C$)

Figure 11. Photo of sample with 1.5 mas.% of $\text{Al}_2\text{O}_3$ nanopowder and 0.1 mas.% of fiber ($T_{\text{bur}}=1580°C$)

Nanopowder additive activates firing and creates small number of pores (Fig.10), also confirmed by the data demonstrated in Fig 1. Adding fiber to this structure, on the one hand, promotes proximity of particles at sintering, on the other hand, creates porous structure due to burn out (Fig.11). Samples with fiber and nanopowders have compact structure with large number of pores (Fig.11).

Tensile strength of samples on compression exceeds their flexural strength (Fig.12) approximately two times. The data obtained revealed that synthetic fiber as a pore-forming additive increases strength of the samples both at compression and at bending. PVA as a pore-forming additive increases strength of samples only at its content of no greater than 0.1 mas.%. Further increase of PVA content leads to decrease in strength properties of the ceramics, which is explained by the increase in the total porosity of the obtained samples. Increase in nanopowder content leads to increase of ceramics’ strength. It is noted, that when combining nanopowder and synthetic fiber additives, a possibility of stronger ceramics can be achieved, compared to using a nanopowder or fiber additive alone. It can be explained by the fact that pores created by burning out of the pore-forming agent are strengthened by the powder, which makes the sample more durable.
4. Conclusion

Results of this research indicate that introduction of small amounts of additives of different nature and varying their ratio can significantly change properties of obtained ceramics (increased durability, porosity, degree of sintering). The nature of pore-forming substances has a great influence on ceramics’ sintering and strength properties. Therefore, even small amounts of additives as well as processes occurring in the material at low heat treatment temperatures must be taken into account. Burning out, synthetic fiber as pore-forming additive in amounts greater than 0.5 mas.% produces pores with sizes about 30 µm.

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