The study of the behaviour of the ceramic composites $\text{ZrO}_2(\text{MgO})\text{-Al}_2\text{O}_3$ in a wide temperature range

Maxim Korobnikov^{1,2,*}, Sergey Kulkov¹, Vladimir Leitsin², and Alexander Tovpinets²

¹National Research Tomsk State University, 634050 Tomsk, Russia.

²Immanuel Kant Baltic Federal University, 236016 Kaliningrad, Russia.

Abstract. The paper presents the results of experimental studies of the temperature dependence of the strength characteristics of porous ceramic composites. It is known that the most significant factors affecting the mechanical characteristics of brittle ceramic composites are the pore structure parameters. Increase of porosity leads to decrease of strength characteristics of ceramic composites, however researches about mutual influence of porosity and temperature of tests on strength characteristics were not carried out. The results of studies to determine the strength characteristics of composites under compression showed that the increase in test temperature led to a decrease in compressive strength for specified types of composite porosity by an average of 10%. Experiments carried out at negative temperatures have shown that samples with a porosity of 21% have the greatest strength sensitivity to temperature test conditions.

1 Introduction

During the last years ceramic composites based on zirconia (ZrO_2) and alumina (Al_2O_3) have received special attention because they are promising materials for structural application [1-3]. Alumina was used for a long time for engineering ceramics in particular as motor turbines and aerospace applications due to its excellence technical properties. Zirconia was originally referred to as ceramic steel by Garvie because its Young's modulus and thermal expansion coefficient are similar to those of steel [4]. It is known that the development of zirconia based ceramics with high strength properties obtained through the transformation of tetragonal to monoclinic phase that increase the mechanical properties of these materials. This phase transformation is accompanied by a volume increase (~4%) that induces compressive stresses around a propagating crack and develops the toughening effect [5-7]. Alumina based ceramic has low fracture toughness, and zirconia was added to alumina to improve its fracture toughness, which is the most critical drawback for alumina ceramic. The phase transformation and microcracks toughening are the main toughening mechanisms that improve the mechanical properties of zirconia toughened alumina (ZTA) ceramics composite. However, pure ZrO_2 has been limited in its use as a structural ceramic due to phase transformation during cooling making manufacturing almost impossible. To avoid this, the ceramic based on ZrO_2 must be stabilized with other oxides such as yttria, magnesia or ceria, which stabilize total or partially, the tetragonal and cubic phase [8-11]. The system, zirconia ceramic based, like ZTA are promising materials for many applications.

Zirconia (ZrO_2) is a material with adequate mechanical properties for manufacturing medical devices, when a stress occurs on zirconia stabilized with MgO; a crystalline modification opposes the propagation of cracks [12, 13]. ZTA implants seem to have good biological and mechanical properties. ZTA implants could not affect the structure of zirconia ceramics, in hydrothermal conditions of the human body, promoting the transforming from tetragonal phase to monoclinic. On the other hand, it has been also observed that microstructure coarsening within ZTA may produce a relevant fracture toughness increment. Such correlation is associated with the important effect of zirconia particle size on phase transformation as well as with the influence of large matrix grains on promoting grain bridging and crack deflection [14]. Hence, the study of microstructure evolution of ZTA, in terms of matrix grain and zirconia particle sizes, and its effect on fracture toughness seem to be very interesting subjects.

Many authors studied the effect of porosity on the strength characteristics of the ceramic composites. It is known that the increase in porosity leads to a decrease in the strength characteristics of ceramic composites [15-18]. Control of technological parameters of production of the composite, such as the dispersity of the initial system of the powder mixture and the sintering temperature, allows you to create products with a given porosity and dispersity of the distribution of pore size. These data are confirmed by the works [19-22], which show that regardless of which method of porosity formation is chosen, the porosity value is mainly affected only by the sintering temperature. The increase in temperature leads to a decrease in the average

* Corresponding author: korobnikov@ftf.tsu.ru

porosity. In the works [23-25] it is confirmed both by methods of mathematical modeling and full-scale experiments that the increase in porosity leads to a sharp decrease in the compressive strength. All these works are carried out under normal conditions. However, there is insufficiently information in the literature about the mutual influence of porosity of ceramic composites and test temperature on the mechanical behavior of this class of materials.

The aim of this work was to study the strength characteristics of a ceramic composite at compression in a wide temperature range.

2 Method and materials

Zirconium dioxide powders stabilized by 3 mol. % magnesium oxide were obtained by denitration of aqueous solutions of zirconium salts and magnesium nitrate in a high-frequency plasma discharge. The morphology of the initial structures of the powder resembles hardened foam of spherical particles and irregular particles. The average size of spherical particles was 3 μm , and the size of other particles reached 20 μm .

Aluminium oxide was produced by heat treating of aluminum hydroxide with gibbsite modification $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ at 1300 $^\circ\text{C}$. At this temperature, the hydroxide decomposes into water and $\alpha\text{-Al}_2\text{O}_3$. The powder consisted of isolated polycrystalline particles with an average particle size of 50 μm .

The obtained powders in the ratio of 20% ($\text{ZrO}_2\text{-MgO}$) - 80% ($\alpha\text{-Al}_2\text{O}_3$) were mixed for 24 hours in ball mills. As a result of mechanical activation, conglomerates of polycrystalline particles with a good cut were formed, in the joints of which there were particles of zirconium dioxide. The average size of the obtained conglomerates is 64 μm . Figure 1 shows the obtained conglomerates.

The microstructure of the as-sintered specimens was examined with a scanning electron microscope (Vega Tescan).

Fig. 1. The SEM image of the obtained conglomerates.

Porosity of samples was measured by hydrostatic method in distilled water according to the following equation:

$$\theta = \frac{\rho_{th} - \rho_e}{\rho_k} * 100\%,$$

here ρ_{th} the theoretical density, ρ_e - experimental density of the material.

Study of the phase composition and crystal structure parameters of ceramic composites by x-ray diffraction. X-ray diffraction studies were carried out on the x-ray diffractometer "drone-3" with filtered $\text{CuK}\alpha$ radiation. Phase identification was performed by comparing the peaks of radiographs with ASTM card index. The content of zirconium dioxide phases was estimated by the ratio of integral intensities of tetragonal and monoclinic phases.

The properties of the samples were determined by testing them by a compression test method using the INSTRON 3369 test system with a climatic chamber. The test temperature was 250 $^\circ\text{C}$, 24 $^\circ\text{C}$ and -50 $^\circ\text{C}$. The value of tensile strength σ_{com} of ceramic composites was determined at a loading rate of 0.6 mm / min using five samples of the same series according to the following equation:

$$\sigma_{com} = \frac{P}{S},$$

here P is the limit load determined during the test sample, S is the surface area, mm^2 .

The microstructure of ZTA ceramic composites was studied by microtomography with detection of back-scattered electrons in a scanning electron microscope; the method is based on the formation of layered images of concealed subsurface microstructures using reflected electrons filtered in a narrow energy range. High resolution X-ray computer tomography was used in this work to control microstructure parameters of the ZTA composites, which allows assessment of the geometric characteristics with an error considerably lower than 10 μm . The method allow nondestructive testing inhomogeneities of composite structure, with analysis of the shape and geometry of the pore structure.

The nondestructive testing was carried out using a Y. Cheetan X-ray test system from YXLON, Germany. The basic component of the system are an open fine-focus X-ray tube that generated a conical X-ray beam and two-dimensional detector. The X-ray tube is fitted with a transmission-type target, which consist of a 6- μm tungsten layer sputtered over a diamond window 1.7 mm thick. The electron beam focusing system forms a focal spot with a size of less than 2 μm on the target, thus allowing assessment of the geometry and internal structure with high degree of accuracy.

The 3D visualization and analysis of the D images of the ZTA composites were performed using the VGStudio 2.2 software in which the data are reconstructed by the Feldkamp algorithm. The 3D visualization process consist in dividing voxel out of the entire set of data according to their intensity; this is so-called thresholding. The work with 2D images is performed in the software in the multiplanar reconstruction mode, which presents windows that

reflect profiles of the object under investigation in three planes.

Fig. 2. The 2D cross section of a 3D model of the ZTA composites.

The reconstruct of ZTA composites, the following parameters were chosen: a tube acceleration voltage of 90 kV, a current of 40 mA, and 10 projection by 1° rotation with an exposure time of 2 s for each samples. Figure 2 shows the 2D cross section of a 3D model of the ZTA composite.

3 Results and Discussion

The ceramic composite has been successfully prepared by uniaxial compaction at 10 kN followed by sintering at 1400 , 1500 and 1650 $^\circ\text{C}$ with isothermal exposure for one hour. The porosity of the ZTA composites was 21%, 11% and 6.5% respectively.

Fig. 3. The compression stress of the ZTA composite.

Figure 3 shows the ultimate compression stress of the obtained ZTA composites.

Figure 4 shows the porosity distribution of the different studied composites. The results showed that the average porosity size increases with the sintering temperature, and the distribution is subject to unimodal distribution. On the other hand, the sintering temperatures of 1400 $^\circ\text{C}$ and 1500 $^\circ\text{C}$ did not lead to a significant spread in the porosity distribution, the values

did not exceed 0.7 μm . However, at a sintering temperature of 1650 $^\circ\text{C}$, an increase in the porosity spread in size is associated with grain growth, with maximum values reaching 2 μm

a)

b)

c)

Fig. 4. The distribution of porosity of the ZTA composite: a) 1400 $^\circ\text{C}$, b) 1500 $^\circ\text{C}$, 1650 $^\circ\text{C}$.

Table 1. Variation in average grain size of ZrO_2 depending on the sintering temperature.

Sintering temperature, $^\circ\text{C}$	1400	1500	1600
Grain size, μm	0.409	0.998	0.848

Figure 5 shows the microstructure of the different studies ZTA composites. In the composites containing $\text{ZrO}_2(3\%\text{MgO})/\text{Al}_2\text{O}_3$, the grain boundaries are pointedly faceted at YSZ/alumina interfaces and triple grain junctions. The zirconia grain size tends to increase with the increase the sintering temperature. The zirconia grain size calculated from the above-mentioned figures is given in Table 1. The given data in Table 1 indicate that an increase in the size of the zirconium grain inhibits the growth of alumina grains, which in turn improves the compaction behavior and improves the relative density of composites.

a)

b)

c)

Fig. 5. The microstructure of different studied composite fired at: a) 1400 °C, b) 1500 °C, 1650 °C.

Figure 6 shows the microstructure of the different studies ZTA composites.

Fig. 6. X-ray diffraction patterns of the ZTA composites fired at 1400 °C.

X-ray diffraction pattern of the studied composites (Figure 6) indicate that $\alpha\text{-Al}_2\text{O}_3$, t-ZrO_2 and m-ZrO_2 are only crystalline phases present in the samples. The quantitative content of the phases of zirconium dioxide in ceramics was calculated by the ratio of the integral intensities of lines of (111) tetragonal (t) and (111) monoclinic (m) phases by the formula:

$$X_m = \frac{I^m(111) + I^m(-111)}{I^m(111) + I^m(-111) + I^t(111)}$$

Intensity of the XRD peaks has been represented the and the number in brackets are the miller indices of the pertinent crystallographic planes. Practically, a XRD scan between 25 and 32° of 2 theta covers the range necessary to observe all peaks used in the formula above. It was possible to improve the quality of the measure at short aging time by using XRD at grazing incidence angles (5° (2θ) with the copper K_α radiation); then, the penetration depth of X-ray is ever lower from ~3 μm.

The molar fraction of transformation from tetragonal to monoclinic after fired at different temperature of the ZTA ceramic samples presented in Table 2.

Table 2. The quantitative content of the phases of monoclinic zirconium dioxide in ceramics depending on the sintering temperature.

Sintering temperature, °C	1400	1500	1650
The quantitative content, %	40.46	46.64	74.61

It was denoted that hard alumina matrix conserved the zirconia monoclinic phase at room temperature. On the other hand, the transformation to monoclinic phase is easier in presence of t-ZrO₂. The change in crystallographic phase content is an additional factor that affected in strength characteristics of the ZTA composites.

The results obtained in the ZTA composites, as compared to those observed in alumina, evidence that addition of ZrO₂ particles effectively hinders the alumina matrix grain growth. Such effect may be related by toparticular aspect that induces a reduction of the grain growth driving force such as porosity increment. In the ZTA composite, zirconia particles tended to grow forming clusters. This factor explains the increase in pore sizes in fired samples at higher temperatures. On the other hand, the dilatancy effect is also one of the key factors of pore coalescence and the formation of large pores in the composite and pore clusters.

Fig. 7. The 3D model of the inclusion of zirconium in ZTA composites fired at 1400 °C.

The uniform distribution of zirconium dioxide particles in the aluminum matrix is shown by x-ray tomography, and the presence of consolidated particles is also seen. Figure 7 shows the 3D model of the inclusions of ZrO₂ particles in ZTA composite.

The presence of large inclusions indicates, most likely, the monoclinic phase. On the other hand, small inclusions are the tetragonal phase. This observation indicates that the use of MgO as a stabilizing additive leads to phase instability in ZTA composites. In this case, there may be residual deformations within the samples associated with the dilation effect, which lead to

critical consequences associated with strength disturbances. However, the experiments on compression of cylindrical samples showed high strength characteristics of the obtained composites.

At the same time, for the samples obtained at 1650 °C, a purely brittle fracture was observed, and the sample shattered into large fragments. The development of cracks corresponded to the direction of movement of the compressive sponges of the INSTRON 3369. For the rest of the samples, classical fracture was observed, accompanied by the development of maximum stresses, and, accordingly, main cracks, at an angle of 45 degrees. Figure 8 shows the difference in the nature of the destruction of ZTA composites.

Fig. 8. The 3D model of the destroyed ZTA composites fired at: a) 1650 °C; b) 1500 °C; c) 1400 °C.

As shown in the figures above in the samples fired at a temperature of 1400 and 1500 °C the material can retain its original shape, but cracks are observed in the internal structure. In the samples sintered at a temperature of 1650 °C, such a pattern of crack development is not observed, this can be explained by the low porosity of the samples, the presence of larger pores and the predominant brittle monoclinic phase, in contrast to the viscous tetragonal. On the other hand, the experiments carried out on the compression of samples showed that the increase in the test temperature to 250 °C leads to a decrease in strength. A possible cause may be a decrease in the transition energy from the tetragonal to the monoclinic phase. Experiments conducted at -50 °C showed a slight effect of the test temperature on the strength, in comparison with experiments conducted under normal conditions. At the same time there was a decrease in strength by only 10%.

4 Conclusions

The effect of test temperature on strength characteristic of ZTA composites was studied. From the microstructural evolution and mechanical characterization conducted in this work, the following conclusions can be drawn:

1. With the growth of the sintering temperature, the growth of zirconium grains occurs, which prevents the growth of grains of the oxide aluminum matrix.
2. An increase in the sintering temperature leads to a decrease in the overall porosity of the ZTA composite samples, due to the consolidation of the grains. But on the other hand there are larger pores.
3. The results of studies to determine the strength characteristics of composites under compression showed that the increase in test temperature led to a decrease in compressive strength for specified types of composite porosity by an average of 10%. Experiments carried out at negative temperatures have shown that samples with a porosity of 6.5% have the greatest strength sensitivity to temperature test conditions.
4. The study of the diffraction pattern of ZTA composites showed the presence of α -Al₂O₃ m-ZrO₂ and t-ZrO₂. The study of samples sintered at different temperatures showed that there is a destabilization of the high-temperature tetragonal phase. If the composite sintered at a temperature of 1400 °C monoclinic phase fraction is 40.46%, the composite sintered at a temperature of 1650 °C monoclinic phase fraction is 74.61 %.
5. In high-density composites cracks develop in the direction of compression. The destruction of the sample has an explosive character with the formation of large fragments. On the other hand, in porous composites, cracks develop at an angle of 45 degrees in the direction of the acting load.
6. The applicability of High-resolution tomography for testing the quality of the ZTA composites is shown. This method is universally applicable for the control of the initial obtained samples and for the sample of tested ones.

The reported study was funded by RFBR, according to the research project No. 16-31-60059 mol_a_dk. This Research was supported by the Russian Academic Excellence Project at the Immanuel Kant Baltic Federal University.

References

1. S. Pfeifer et al., J. Eur. Ceram. Soc. **36**, 725-731 (2016)
2. M.V. Korobnikov and S. N. Kulkov, *AIP Conf. Proc.* **1882**, 020035 (2017)
3. N. Chuankrerkkul et al., Chiang Mai J. Sci. **43**, 375-380 (2016)
4. R.C. Garvie et al., Nature **258**, 703-704 (1975)
5. A.G. Evans, J. Am. Ceram. Soc. **74**, 187 (1991)
6. C. Exare et al., J. Eur. Ceram. Soc. **35**, 1273-1283 (2015)
7. J. Chen et al., Ceram. Int. **43**, 3970-3974 (2017)
8. S.M. Naga et al. J. of All. and Comp. **695**, 1859-1862 (2017)
9. M.C. Aragon-Duarte et al., Ceram. Int. **43**, 3931-3939 (2017)
10. S. Kulkov et al., IOP Conf. Ser.: Mater. Sci. Eng. **140**, 012017 (2016)
11. T. Zhu et al., Ceram. Int. **44**, 505-510 (2018)
12. N.R. Silva et al., Materials **3**, 863-896 (2010)
13. Z.D.I. Sktani et al., Int. J. Refract. Mat. and Hard Mat. **74**, 78-86 (2018)
14. Y. Liu, Y. Ai, W. He, W. Chen, J. Zhang, Ceram. Int. **44**, 16421-16427 (2018)
15. A.S. Buyakov and S.N. Kulkov *AIP Conf. Proc.*, **1882**, 020010 (2017)
16. R.V. Levkov and S. N. Kulkov IOP Conf. Ser.: Mater. Sci Eng. **175**, 012045 (2017)
17. N.L. Savchenko et al., Rus. Phys. J., **58**, 1-5 (2016)
18. I. Zhukov et al., J. Sil. Based Comp. Mat., **68**, 74-78 (2016)
19. R.V. Levkov et al., J. Phys.: Conf. Ser. **1045**, 012027 (2018)
20. A. S. Buyakov et al., *AIP Conf. Proc.* **1760**, 020008(2016)
21. S. Buyakova, T. Sablina and S. Kulkov, *AIP Conf. Proc.* **1688**, 030009(2015)
22. R. V. Levkov and S. N. Kulkov, *AIP Conf. Proc.* **1760**, 020042 (2016)
23. M.V. Grigoriev et al., Tech. Phys. Let. **43**, 723-726 (2017)
24. M.V. Grigoriev et al., JSBCM **70**, 18-22 (2018)
25. A. Yu. Smolin et al., *AIP Conf. Proc.* **1893**, 030127 (2017)