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## Study of the effect of variation of thermal annealing conditions on the structural ordering and phase formation processes in ZrO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> ceramics

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<p>Received: November 8, 2024 Peer-reviewed: November 29, 2024 Accepted: December 4, 2024</p>	<p><b>ABSTRACT</b> Interest in composite refractory ZrO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> ceramics is due to the great prospects for their use in extreme conditions (radiation exposure, thermal cycling, exposure to aggressive environments) due to the high resistance to external influences of these ceramics. Moreover, the features of high resistance to external influences for this type of ceramics are due to their structural features and phase composition, which are controlled by the synthesis method and its conditions. This paper presents the results of studying the influence of variations in the annealing temperature of ZrO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> ceramics obtained by solid-phase synthesis, as well as establishing the effect of variations in the phase composition on strengthening and resistance to thermal cycling. In the course of the research, using the X-ray phase analysis method, it was found that at temperatures above 1200 °C, the formation of an impurity substitution phase of the AlZrO<sub>2</sub> type is observed, the formation of which leads to strengthening and increased resistance to external influences. For ZrO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> ceramic samples, in which the AlZrO<sub>2</sub> phase content was about 15-20 % (samples obtained at annealing temperatures of 1400 – 1500 °C), the change in strength characteristics after 5 successive cycles was less than 3 %, which is more than 9 times lower than the similar change for two-phase samples obtained at an annealing temperature of 1000 °C.</p>
	<p><b>Keywords:</b> ZrO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> ceramics; thermal annealing; phase transformations; strengthening; resistance to thermal influences.</p>
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### Introduction

Interest in composite ceramics based on zirconium and aluminum oxides is due to their properties, in particular, high strength, wear resistance and resistance to mechanical stress, including compression, tension, corrosion resistance, and the ability to operate at elevated temperatures (about 700 – 1000 °C) due to low thermal expansion rates, etc. [[1], [2], [3]]. The combination of these properties makes these ceramics one of the promising materials in nuclear energy, in particular, when used as structural

materials for high-temperature reactors or the basis for creating inert matrices of dispersed nuclear fuel [[4], [5]]. At the same time, the combination of aluminum and zirconium oxides makes it possible to increase the thermal conductivity of the composite due to the higher thermal conductivity of aluminum oxide, as well as to increase resistance to mechanical damage and thermal shocks due to the strength properties of zirconium dioxide. Also, high melting temperatures (about 2000 – 2700 °C) allow the use of these materials in extreme conditions [[6], [7]].

ZrO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> ceramics with an equal ratio of components during mechanochemical mixing (0.5 M ZrO<sub>2</sub> – 0.5M Al<sub>2</sub>O<sub>3</sub>) were selected as objects of study to determine the variability of thermal annealing temperature on changes in structural parameters, as well as the possibility of initializing phase transformation processes associated with the formation of substitution phases [[8], [9], [10]]. The choice of these objects for research is due to the possibility of combining the features of zirconium dioxide, such as high levels of resistance to mechanical and thermal influences (low rates of thermal expansion of the crystalline structure as a result of external influences), as well as good radiation and corrosion resistance, with high thermal conductivity of aluminum oxide (the thermal conductivity of aluminum oxide is an order of magnitude higher than that of zirconium dioxide), as well as good electrical insulating properties of these oxides, which makes it possible to create high-strength structural materials based on this composite [[11], [12], [13], [14]]. At the same time, the choice of a method for producing a composite is based on the need to simplify the technological processes for manufacturing composite materials with the possibility of scaling production technology to create high-strength ceramic materials, both in the form of powders and pressed ceramics. The use of the method of mechanochemical solid-phase grinding combined with thermal annealing of the resulting homogeneous mixtures of powders to obtain composite ceramics makes it possible to control not only the sizes of the resulting ceramics by varying the grinding conditions but also to initiate the processes of phase transformations associated with thermal effects on the ceramics [[15], [16], [17], [18]]. As a result, this method is quite simple for the production of ceramic materials, including composite or multiphase ceramics. However, despite the simplicity of the method, a comprehensive study of the influence of synthesis conditions is necessary to determine the optimal conditions for the manufacture of ceramics, as well as to determine the possibilities of using thermal annealing to initiate phase transformation processes [[19], [20]].

If the synthesis conditions change, in particular, variations in the annealing temperature, not only structural ordering processes associated with the relaxation of deformation distortions and structural stresses that arose during solid-phase grinding can be initiated, but also, under certain conditions, can provoke phase formation processes associated with

the partial replacement of one type of atoms by others with the subsequent formation of new phases or recrystallization processes, during which a complete restructuring and mixing of simple oxide compounds into new, more complex formations occur. The most accurate and reliable method for determining the influence of annealing temperature on the processes of structural ordering and phase transformations is the method of X-ray phase analysis, the use of which allows one to determine with high accuracy all the structural changes that occur in samples caused by external influences. Moreover, the comparison of the observed changes in the obtained diffraction patterns makes it possible to determine the kinetics of structural parameters depending on the annealing temperature or other external influences.

### Experimental part

Powders of zirconium (ZrO<sub>2</sub>) and aluminum (Al<sub>2</sub>O<sub>3</sub>) oxides with a chemical purity of about 99.95 % were chosen as the starting components. These powders were purchased from Sigma Aldrich (USA).

The preparation of composite ZrO<sub>2</sub> –Al<sub>2</sub>O<sub>3</sub> ceramics was carried out through a sequence of actions that included mechanochemical grinding of the initial components in a PULVERISETTE 6 (Fritsch, Berlin, Germany) planetary mill at a grinding speed of 250 rpm for 30 minutes, followed by thermal annealing of the ground samples in a Nabertherm LE 4/11/R6 (Nabertherm, Lilienthal, Germany) muffle furnace at a given temperature, followed by cooling of the samples to room temperature together with the furnace for 24 hours until they cool down completely (the samples reached room temperature). Determination of the variation in the thermal annealing temperature on the phase transformation processes, as well as the structural ordering resulting from the thermal effect on the ground mixtures of oxides, was carried out in the thermal annealing temperature range from 1000 to 1500 °C. Annealing was carried out in a muffle furnace in an oxygen-containing atmosphere for 5 hours, followed by cooling the samples to room temperature without removing them from the furnace. Regarding the annealing temperature of powders, in particular, the range of 1000 – 1500 °C, this range was chosen to assess the influence of the sintering temperature on the processes of structural ordering and the initialization of phase transformation processes, associated with this case with processes of polymorphic transformations of

the  $m - \text{ZrO}_2 \rightarrow t - \text{Zr}(\text{Al})\text{O}_2$  type, which arises according to experimental data at temperatures above 1100 °C. It is important to note that the samples in the crucibles were placed in such a way as to avoid the effect of the sintering of the powders in the near-surface bulk layer, while the inner part was not subjected to heat treatment. To do this, the powders were poured in a uniform thin layer onto the bottom of the crucible, which made it possible to uniformly anneal the powdered samples.

The study of the phase composition of  $x\text{ZrO}_2 - (1-x)\text{Al}_2\text{O}_3$  ceramics depending on the annealing temperature was carried out using the X-ray phase analysis method. X-ray diffraction patterns were obtained on a D8 ADVANCE ECO powder diffractometer (Bruker, Karlsruhe, Germany). Diffraction patterns were recorded in the Bragg-Brentano geometry in the angular range  $2\theta=20-100^\circ$ , with a step of  $0.03^\circ$ . The diffraction patterns were interpreted using the PDF-2(2016) database, from which the main phases, as well as impurity inclusions, the appearance of which is associated with phase transformation processes, were determined by selecting and comparing experimentally obtained diffraction patterns with reference values.

Determination of the crystal lattice parameters and volume for all established phases in the composition of the ceramics under study contingent upon the annealing temperature, alongside their refinement, was carried out in the DiffracEVA v.4.2 program code. The parameters were refined by comparative analysis of the positions of the main (most intense) diffraction reflections of the experimentally obtained samples for each phase with the positions of the lines of card values of the most suitable cards from the PDF-2 database (the accuracy of the match for the analysis was at least 90 %). The parameters were refined considering the possible effects of deformation distortion caused by mechanical action and thermal relaxation occurring during the manufacturing process of ceramics.

The structural ordering degree (crystallinity degree) was assessed by calculating the weight contributions of diffraction reflections and background radiation characteristics of disordered inclusions in the samples.

The determination of the phase composition data, in particular, the establishment of the weight values of each phase, was conducted considering the corundum numbers for each established phase,

as well as their weight contribution, based on the ratio of the areas of reflections.

Microstructural studies aimed at investigation of the morphology of the synthesized samples were carried out using scanning electron microscopy and transmission electron microscopy, implemented using a Phenom™ ProX scanning electron microscope (Thermo Fisher Scientific, Eindhoven, the Netherlands) and a Jeol JEM-1400Plus transmission electron microscope (Jeol, Tokyo, Japan). To determine the elemental composition, a mapping method was used to determine the uniformity of the distribution of elements in the composition of the samples under study.

To measure the strength and thermophysical parameters of the  $x\text{ZrO}_2 - (1-x)\text{Al}_2\text{O}_3$  ceramics under study, the resulting powders were pressed into tablets with a diameter of about 10 mm and a thickness of 3 mm. The pressing of the samples was carried out using a special mold, the pressing pressure was 250 MPa, the time was about 30 minutes. After pressing, the samples were subjected to thermal annealing of deformation stresses caused by pressing in a muffle furnace at a temperature of 700 °C for 10 hours, which made it possible to achieve the values of structural parameters characteristic of samples in an unpressed form. According to the X-ray diffraction data of structural parameters before and after thermal annealing of tablets at a temperature of 700 °C, almost complete relaxation of deformation distortions in the structure of tablets is observed, without changes in the phase ratio, as well as enlargement of grains or their merging.

The thermal conductivity coefficient was determined using the absolute stationary method of longitudinal heat flow, implemented on a KIT-800 thermal conductivity meter (KB Teplofon, Russia) [21]. A uniform heat flux  $q$  was created at one end of a ceramic sample with a given cross-sectional area. The temperature difference is measured between two cross-sections of the sample located at a given distance  $\delta$ . In the absence of lateral heat losses, the thermal conductivity coefficient of the sample is calculated using formula (1) [21]:

$$\lambda = \frac{q\delta}{t_{C1} - t_{C2}}, \quad (1)$$

where  $\lambda$  is the thermal conductivity coefficient of the wall material,  $\text{W}/\text{m}\cdot\text{K}$ ;  $q$  is the heat flux density,  $\text{W}/\text{m}^2$ ;  $\delta$  is the wall thickness,  $\text{m}$ ;  $t_{C1}$  and  $t_{C2}$

are temperature constants on the hot and cold sides of the wall, respectively, K.

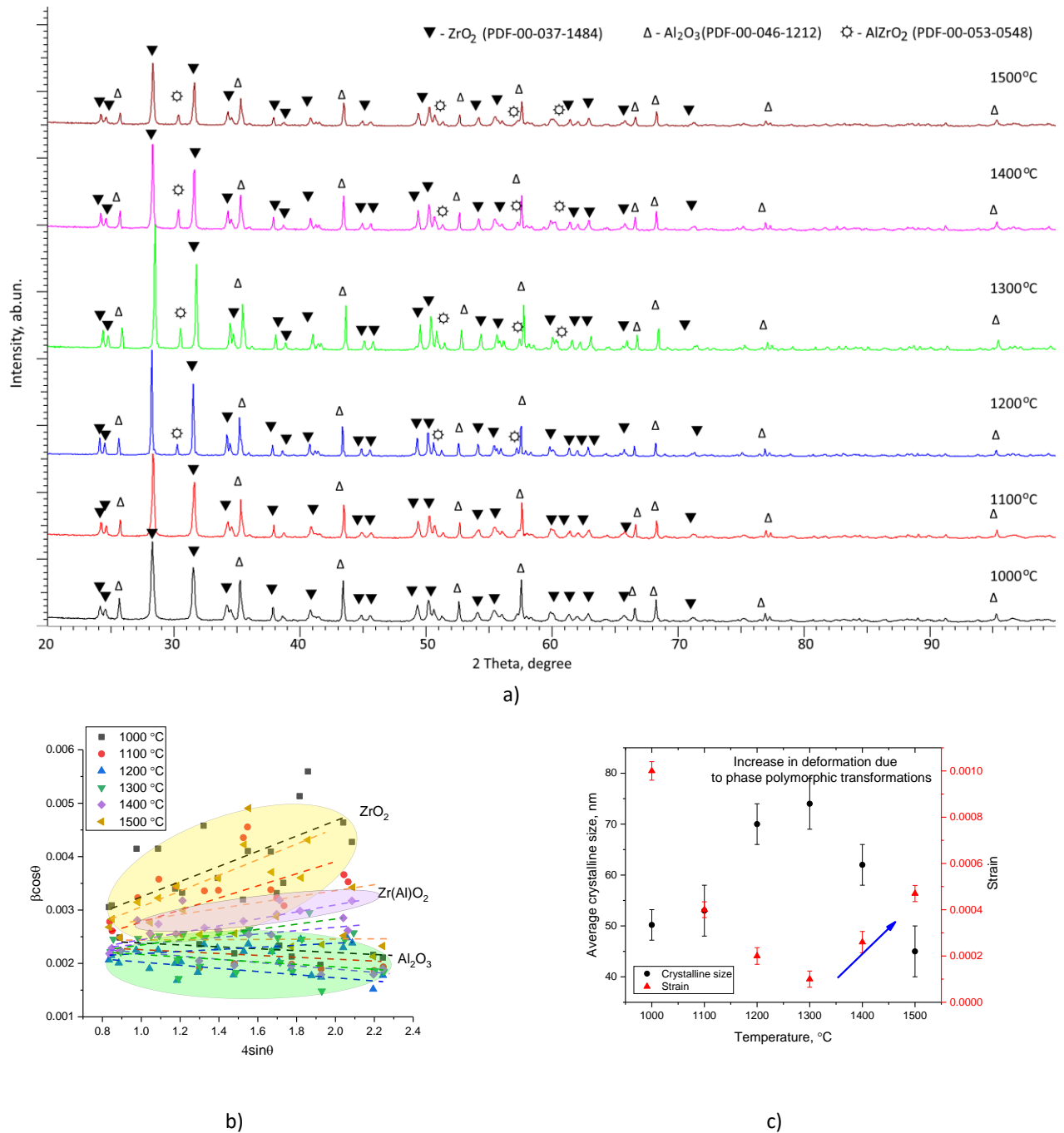
The determination of the strength parameters of  $x\text{ZrO}_2 - (1-x)\text{Al}_2\text{O}_3$  ceramics, as well as the establishment of the relationship between strengthening factors and synthesis conditions, was carried out using the following methods. Hardness determination was carried out using the sample indentation method using a Duroline M1 microhardness tester (Metkon, Bursa, Turkey). A Vickers diamond pyramid was used as an indenter (the angle between opposite faces was  $136^\circ$ ), the load on the indenter was about 100 N, and the indentation time (holding the load on the indenter) was 15 seconds per measurement. To determine the uniformity of the hardness of the samples, measurements were carried out in various areas, which made it possible to determine not only the isotropy of the hardness over the surface but also the average value, as well as the standard deviation. Determination of the resistance to cracking of the samples under study, depending on the conditions of their production, was carried out according to the single compression method on a Unitest framework SKU UT-750 (Unitest, USA) testing machine. This technique involves placing ceramic samples in the form of cylindrical tablets in a special holder, on one side of which pressure is applied (the load increases) at a constant speed of 10 mm/min. Monitoring the formation of microcracks during a single compression is carried out using the extensometry method and visual observation of the sample. Also, to determine the possibility of obtaining ceramics in the form of tablets with repeatable isotropic strength properties, cracking measurements were carried out in the form of serial tests (at least 10 - 15 samples in a series).

Determination of resistance to thermal influences - thermal shocks that occur during rapid heating of samples and subsequent rapid cooling by extraction into air was carried out according to the following experimental scheme. The samples were placed in a muffle furnace in special crucibles (made of zirconium dioxide, capable of withstanding high-temperature changes while quickly releasing crucibles from the furnace chamber to air) and then heated to a temperature of about  $1000^\circ\text{C}$  (heating rate  $50^\circ\text{C}/\text{min}$ ), held at this temperature for 1 hour and then removed from the furnace to air. The determination of resistance to thermal shocks was assessed by changes in strength parameters (hardness and cracking resistance) depending on the number of thermal stability test cycles.

The combination of X-ray diffraction analysis methods and scanning and transmission electron microscopy, combined with mapping methods, made it possible to establish phase transformations in  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  ceramic samples resulting from thermal annealing. Using methods for determining thermal conductivity and hardness, as well as resistance to cracking, the dependences of changes in the strength parameters of  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  ceramics were established. Based on them, conclusions were drawn about the connection between phase changes and the strength properties of ceramics, and optimal compositions were proposed for future studies of the applicability of these ceramics as materials for inert matrices of dispersed nuclear fuel.

## Results and Discussion

Figure 1 demonstrates the results of X-ray phase analysis of the studied  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  ceramics depending on the thermal annealing temperature, the variation of which leads to changes in structural parameters characteristic of structural ordering processes, as well as the initialization of phase transformation processes characteristic of the formation of substitution or interstitial phases. The general appearance of the presented X-ray diffraction patterns of the studied samples of  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  ceramics, depending on the annealing temperature, indicates the polycrystalline structure of the obtained samples, represented by a combination of two phases, the diffraction reflections of which have a well-developed shape (high-intensity values, as well as an unbroadened shape, indicating fairly high structural ordering degree values). Moreover, according to the obtained X-ray phase analysis data, all presented diffraction patterns reflect the presence of two main phases: the monoclinic  $\text{ZrO}_2$  phase (PDF-00-037-1484) and the rhombohedral  $\text{Al}_2\text{O}_3$  phase (PDF-00-046-1212), the presence of which indicates the formation of composite ceramics, which are a solid solution of two phases. At the same time, the obtained X-ray phase analysis data are in good agreement with the results obtained by Pulgarín H. L. C. et.al. [22], according to which thermal annealing of  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  compounds in the range from  $1000$  to  $1600^\circ\text{C}$  leads to the formation of ceramics in which  $\text{ZrO}_2$  grains are located inside an  $\text{Al}_2\text{O}_3$  matrix, thereby preventing the coarsening of  $\text{Al}_2\text{O}_3$  grains, characteristic of high-temperature annealing of aluminum oxide. In turn, an increase in the annealing temperature from  $1000$  to  $1100^\circ\text{C}$



**Figure 1** - a) Results of X-ray phase analysis of the studied ZrO<sub>2</sub>– Al<sub>2</sub>O<sub>3</sub> ceramics at annealing temperature variations; b) W-H plots reflecting changes in deformation and dimensional contributions in samples during annealing temperature variation; c) Comparative analysis of changes in the average grain size and deformation distortion of the crystal structure

does not lead to the formation of any new diffraction reflections characteristic of phase transformation processes, as well as associated with the possible formation of intermetallic inclusions of the AlZr<sub>3</sub> type [23], the formation of which can occur at grain boundaries under severe deformation distortions of the crystal structure.

At an annealing temperature of 1200 °C in the region  $2\theta=29-30^\circ$  and  $2\theta=49-50^\circ$ , the formation of pronounced diffraction reflections characteristic of

the tetragonal phase of AlZrO<sub>2</sub> (PDF-00-053-0548) is observed. The appearance of these reflections, as well as an increase in their intensity for samples annealed at temperatures above 1200 °C, indicates phase transformation processes that occur as a result of thermal effects on ceramics.

It should be noted that diffraction reflections near  $2\theta=30^\circ$  can be interpreted for these samples as reflections of the tetragonal phase t-ZrO<sub>2</sub>, which in turn confirms the influence of the presence of



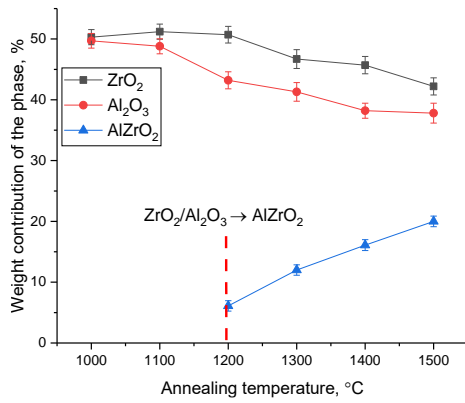
aluminum oxide in the composition to initiate processes of polymorphic transformations of the  $m - \text{ZrO}_2 \rightarrow t - \text{ZrO}_2$  type, the formation of which can be initiated at temperatures above 1100 °C. Moreover, the presence of aluminum oxide in the composition of ceramics, especially a fairly large amount, can accelerate the processes of polymorphic transformations in zirconium dioxide, as a result of which aluminum is incorporated into the tetragonal phase of  $\text{ZrO}_2$ , partially replacing zirconium at sublattice sites. In this case, aluminum oxide can be considered as a stabilizing additive, when added to the composition of ceramics, polymorphic transformations of the  $m - \text{ZrO}_2 \rightarrow t - \text{Zr}(\text{Al})\text{O}_2$  type occur. At the same time, analyzing alterations in the crystal lattice parameters, and mapping data (see Figures 3-4), it can be concluded that the  $t\text{-Zr}(\text{Al})\text{O}_2$  phase formation occurs in the ceramics due to differences in the ionic radii of Zr (0.079 nm) and Al (0.053-0.067 nm), since the established changes in parameters are less than the characteristic parameters of the tetragonal phase  $t - \text{ZrO}_2$  ( $a=3.5984 \text{ \AA}$ ,  $c=5.152 \text{ \AA}$  PDF-00-050-1089).

The formation of this phase is possible as a result of the partial replacement of aluminum with zirconium in the rhombohedral lattice, followed by the formation of  $\text{AlZrO}_2$  grains near the interphase boundaries. At the same time, such a substitution mechanism can be explained by the lower melting temperature of  $\text{Al}_2\text{O}_3$  ( $T_{\text{melt, Al}_2\text{O}_3}=2072 \text{ °C}$ ), as a result of which, when thermal annealing temperatures are higher than  $0.5T_{\text{melt, Al}_2\text{O}_3}$ , initialization of phase transformation processes associated with partial substitution processes is possible. It should also be noted that with a growth in the  $\text{AlZrO}_2$  phase contribution in the case of thermal annealing of samples at temperatures of 1400 – 1500 °C, a broadening of the diffraction reflections of the main phases is observed (most pronounced for samples annealed at a temperature of 1500 °C), which indicates a reduction in the size of crystallites, which in turn indicates that the formation of the  $\text{AlZrO}_2$  phase is also accompanied by recrystallization processes and grain fragmentation of the main  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  phases, which is accompanied by an increase in dislocation density. The appearance of such effects in the structure of ceramics can help increase resistance to external influences, in particular, dislocation strengthening, which can have a positive effect on resistance to external influences [24]. The dislocation density was estimated based on data on

changes in crystallite sizes, using the assumption of an inverse square dependence of the dislocation density on crystallite sizes [25].

Using the Williamson – Hall (W-H) method, the dependences  $\beta \cos\theta(4\sin\theta)$  were constructed, which made it possible to estimate the contribution of deformation distortions in the structure of ceramics, as well as determine the average crystallite size, the results of which are shown in Figure 1b-c. During assessment of deformation distortions in the structure based on W-H plots, it is clear that the annealing temperature growth from 1000 °C to 1300 °C leads to a decline in the slope angle  $\beta \cos\theta(4\sin\theta)$ , which indicates a decrease in the strain distortion of the  $m - \text{ZrO}_2$  phase, while the  $\beta \cos\theta(4\sin\theta)$  dependences characteristic of the  $\text{Al}_2\text{O}_3$  phase indicate a small influence of thermal effects on the strain distortion degree of the  $\text{Al}_2\text{O}_3$  phase, for which the  $\beta \cos\theta(4\sin\theta)$  dependences characterize the presence of compressive stresses, while the deformation  $m - \text{ZrO}_2$  is tensile. At the same time, analysis of changes in the average size of crystallites for samples annealed at temperatures of 1100 – 1300 °C indicates an enlargement of sizes by more than 1.2 – 1.5 times compared with these sizes obtained for samples annealed at a temperature of 1000 °C. An elevation in the annealing temperature above 1300 °C, which is characterized by a rise in the contribution of the  $t\text{-Zr}(\text{Al})\text{O}_2$  tetragonal phase, a growth in the deformation distortion of the  $m - \text{ZrO}_2$  phase is observed. Moreover, these changes are accompanied by a reduction in the crystallite size, the value of which at an annealing temperature of 1500 °C is about  $45 \pm 5 \text{ nm}$ . Assessing changes in crystallite sizes and deformation distortions of the crystal lattice, it can be concluded that the observed broadening of reflections of ceramic samples annealed at a temperature of 1500 °C is largely associated with crystallite size reduction, alongside an elevation in deformation distortion of the crystal structure of  $m - \text{ZrO}_2$ , due to an increase in the contribution of the  $t\text{-Zr}(\text{Al})\text{O}_2$  phase, the content of which is initiated by the processes of polymorphic transformations.

Based on the obtained X-ray diffraction patterns, using the method of weight estimation of the established phase contributions, a diagram of phase transformations was constructed depending on the annealing temperature, characterizing the temperature dependence of the formation of the  $\text{AlZrO}_2$  substitution phase in the ceramic composition. The results are presented in Figure 2.



**Figure 2** - Assessment results of changes in the phase composition of ZrO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> ceramics depending on the thermal annealing temperature

As can be seen from the data presented in Figure 2, in the case of annealing temperatures of 1000 and 1100 °C, the main changes in the phase composition of ceramics occur due to a slight redistribution of the weight contributions of the monoclinic ZrO<sub>2</sub> phase and the rhombohedral Al<sub>2</sub>O<sub>3</sub> phase, the contribution of which, according to the estimate, is approximately equal. These changes in this case are due to the effects of structural ordering, and as a consequence, an increase in the intensities of diffraction reflections for the ordered

phase in the diffraction pattern. At an annealing temperature of 1200 °C, as shown above, the formation of reflections characteristic of the tetragonal AlZrO<sub>2</sub> phase, the content of which is no more than 6 % in the ceramic composition, is observed. A further increase in the annealing temperature (above 1200 °C) leads to the displacement of the rhombohedral Al<sub>2</sub>O<sub>3</sub> phase and an increase in the contribution of the tetragonal AlZrO<sub>2</sub> phase, which indicates the formation of this phase by partial replacement of aluminum with zirconium as a result of thermal action, and as a consequence of the formation of a similar substitution phase.

Table 1 presents the assessment results of the structural parameters of the studied ZrO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> ceramics depending on the thermal annealing temperature, which was obtained by comparing the experimentally obtained positions of diffraction reflections with reference values, which in turn makes it possible to determine the influence of temperature on changes in the parameters of the crystal lattice and its deformation changes associated with the processes of synthesis and subsequent thermal exposure.

**Table 1** - Structural parameter data

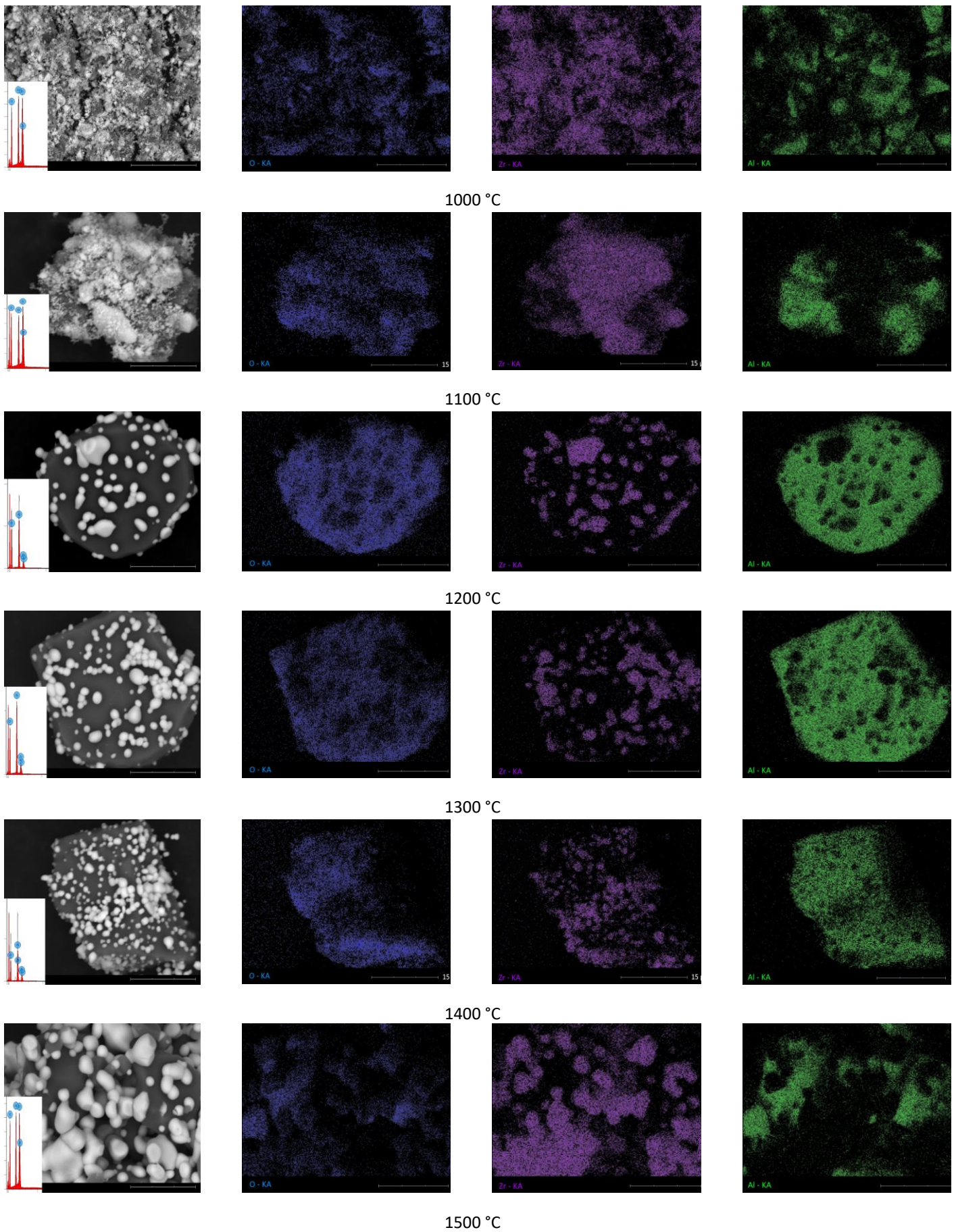
Phase	Crystal lattice parameters					
	Thermal annealing temperature, °C					
	1000 °C	1100 °C	1200 °C	1300 °C	1400 °C	1500 °C
ZrO <sub>2</sub>	a=5.3107 Å, b=5.1937 Å, c=5.1319 Å, β=98.978°, V=139.81 Å <sup>3</sup>	a=5.2982 Å, b=5.18149 Å, c=5.1278 Å, β=99.173°, V=138.97 Å <sup>3</sup>	a=5.25463 Å, b=5.17590 Å, c=5.12936 Å, β=99.834°, V=137.46 Å <sup>3</sup>	a=5.20759 Å, b=5.16348 Å, c=5.13551 Å, β=99.188°, V=136.22 Å <sup>3</sup>	a=5.3044 Å, b=5.1917 Å, c=5.1359 Å, β=99.095°, V=139.69 Å <sup>3</sup>	a=5.3024 Å, b=5.1958 Å, c=5.1379 Å, β=98.822°, V=139.87 Å <sup>3</sup>
AlZrO <sub>2</sub>			a=3.5915 Å, c=5.1093 Å, V=65.90 Å <sup>3</sup>	a=3.5522 Å, c=5.1638 Å, V=65.16 Å <sup>3</sup>	a=3.5747 Å, c=5.1436 Å, V=65.73 Å <sup>3</sup>	a=3.5747 Å, c=5.1497 Å, V=65.80 Å <sup>3</sup>
Al <sub>2</sub> O <sub>3</sub>	a=4.7484 Å, c=12.9343 Å, V=252.57 Å <sup>3</sup>	a=4.7298 Å, c=12.9445 Å, V=250.78 Å <sup>3</sup>	a=4.7260 Å, c=12.8885 Å, V=249.30 Å <sup>3</sup>	a=4.7503 Å, c=12.9649 Å, V=253.36 Å <sup>3</sup>	a=4.7484 Å, c=12.9598 Å, V=253.06 Å <sup>3</sup>	a=4.7335 Å, c=12.9598 Å, V=251.48 Å <sup>3</sup>
Degree of structural ordering, %	86.64	88.76	91.22	91.96	92.35	92.85

The general appearance of the observed changes in the parameters and volume of the crystal lattice can be divided into two stages, corresponding to various processes occurring in ceramics with variations in the annealing temperature. The first stage is typical for temperatures of 1000 – 1200 °C, which is characterized by a decrease in the crystal lattice parameters for both established phases  $ZrO_2$  and  $Al_2O_3$ , which indicates the structural ordering of the crystal structure, caused by relaxation processes of deformation distortions and structural stresses that arose during mechanochemical grinding of the samples. At the same time, the structural ordering degree (crystallinity degree) in this temperature range increases from 86.6 to 91.2 %, which indicates a fairly intense relaxation of deformation structural distortions, the reduction of which is manifested in an increase in the asymmetry of the diffraction reflections of samples annealed at temperatures of 1100 – 1200 °C in comparison with the shape of the diffraction reflections of samples obtained at a temperature of 1000 °C. At an annealing temperature of 1300 °C, an increase in the crystal lattice parameters is observed, the change in which is due to the effects of the emergence and subsequent increase in the contribution of the tetragonal  $AlZrO_2$  phase, the formation of which is accompanied by deformation processes of distortion of the main phases due to phase formation processes. With a subsequent increase in the annealing temperature, the relaxation nature of deformation distortions in the crystal structure of ceramics is retained, however, the presence of the  $AlZrO_2$  impurity phase leads to a decrease in the trend of increasing the degree of structural ordering, which is caused by deformation distortions associated with the formation of an impurity phase in the interphase space. It is also worth noting that the dynamics of changes in crystal lattice parameters indicate the absence of effects of broadening of crystal parameters and volume associated with thermal expansion of the crystal structure of ceramics.

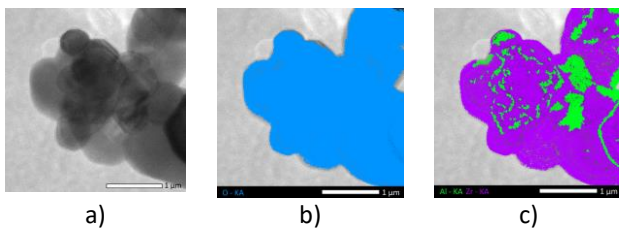
Figure 3 reveals the microstructure assessment results of the studied  $ZrO_2 - Al_2O_3$  ceramics, performed using the scanning electron microscopy method. Determination of elemental analysis was performed using the assessment method of energy-dispersive spectra and mapping (assessing the distribution of elements in samples). As is evident from the data presented, at annealing

temperatures of 1000 – 1100 °C, the morphology of the samples is represented by a mixture of powdery (fine particles) covering larger particles, which, according to energy dispersive analysis, are aluminum oxide. At the same time, fine particles, according to mapping data, are zirconium dioxide. This type of microstructure of ceramics obtained at temperatures of 1000 – 1100 °C indicates that at these temperatures sintering processes do not manifest themselves in a pronounced form, and the ceramics themselves are a mixture of two oxides. At a thermal annealing temperature of 1200 °C, the formation of large grains of aluminum oxide is observed, with inclusions of spherical or sphere-shaped particles, most of which, according to mapping data, correspond to zirconium dioxide. At the same time, a detailed analysis of energy dispersion analysis data revealed (see mapping data) that several particles also contain aluminum in low content (less pronounced color contrast), which confirms the results of X-ray phase analysis data, indicating the formation of the tetragonal  $AlZrO_2$  phase. Further growth of the annealing temperature above 1200 °C leads to a rise in the number of such grains in the composition of the samples, which is one of the indirect confirmations of the growth in the contribution of the  $AlZrO_2$  phase in the composition of the ceramics, alongside the structural ordering of the ceramics with thermal annealing temperature growth. It should be noted that the analysis of the morphological features of the obtained ceramics indicates that the samples obtained at temperatures above 1100 °C are formed as a matrix of aluminum oxide with inclusions of grains of  $ZrO_2$  and  $AlZrO_2$ , which is in good agreement with the results of the review [26]. Moreover, the formation of  $AlZrO_2$  grains in ceramics can be explained by polymorphic transformation processes such as  $m-ZrO_2 \rightarrow t-Zr(Al)O_2$ , the initialization of which occurs due to the partial substitution of zirconium by aluminium, which in turn results in phase transformations. Figure 4a-c illustrates a TEM image and the results of mapping  $ZrO_2$  and  $AlZrO_2$  grains of ceramic samples obtained at an annealing temperature of 1500 °C, reflecting the distribution of elements in the composition of the grains, according to which it is clear that aluminum is present in the structure of the grains, which confirms the presence of inclusions in the form of  $AlZrO_2$  grains, the formation of which is due to the partial substitution of zirconium by aluminium.

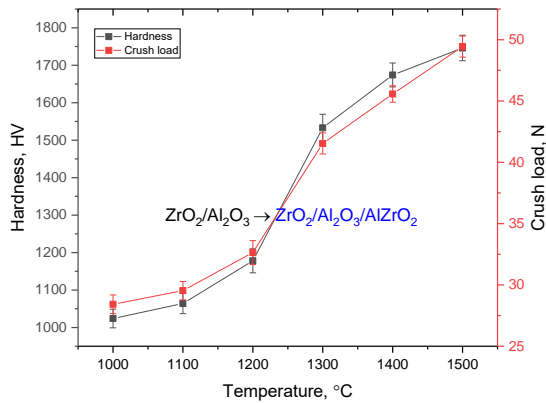




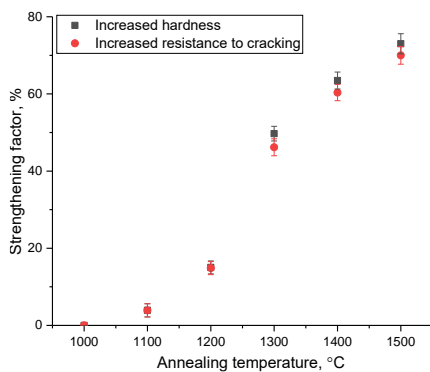
**Figure 3** – Results of microstructural analysis of the studied ceramics with the given element distribution maps



**Figure 4** - a) TEM image of spherical inclusions characteristic of  $ZrO_2$  and  $AlZrO_2$  grains; b) Mapping results for oxygen distribution; c) Mapping results for the distribution of aluminum and zirconium



a)



b)

**Figure 5** – a) Results of alterations in the values of hardness and resistance to cracking of  $ZrO_2 - Al_2O_3$  ceramics in the case of changes in the temperature of thermal annealing of samples, leading to structural ordering and phase transformations; b) Comparative analysis of the assessment results of the strengthening factors associated with changes in hardness and cracking resistance in  $ZrO_2 - Al_2O_3$  ceramics with changes in the thermal annealing temperature

Figure 5a reveals the assessment results of alterations in hardness and cracking resistance values (i.e., the maximum pressure that ceramics can withstand under external influence in the case of a single compression). The figure shows the results of strengthening factors (changes in

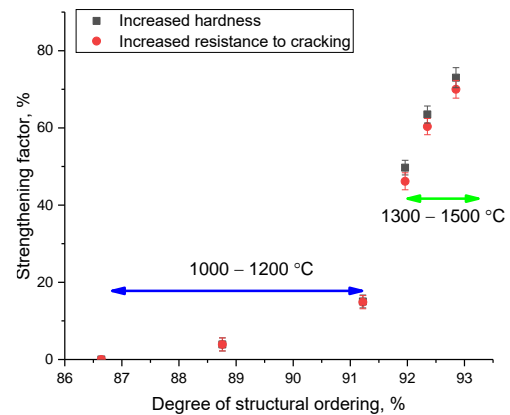
hardness and cracking resistance) calculated for  $ZrO_2 - Al_2O_3$  ceramic samples depending on the thermal annealing temperature. The strengthening factors were assessed by comparing data on the hardness and cracking resistance of ceramic samples annealed at temperatures of 1100 – 1500 °C in comparison with the results obtained for ceramic samples annealed at a temperature of 1000 °C. As can be seen from the presented data on the comparison of the hardness and cracking resistance values, changes in these parameters depending on the thermal annealing temperature result in an almost identical trend of changes, which indicates the positive dynamics of the influence of thermal annealing and associated structural changes (ordering and phase transformations caused by the formation of the substitution phase) on the strengthening of ceramics.

The general view of the presented data on changes in hardness and cracking resistance of  $ZrO_2 - Al_2O_3$  ceramic samples depending on the annealing temperature has two characteristic areas, characterized by different trends in changes in strength parameters. For samples annealed at temperatures of 1000 – 1200 °C, the change in hardness and cracking resistance values is insignificant and amounts to no more than 3 – 15 % depending on the annealing temperature (see data on strengthening factors in Figure 5b). At the same time, a small change in hardness and cracking resistance for samples annealed at temperatures of 1000–1200 °C can be explained by effects associated with structural ordering resulting from relaxation processes of deformation distortions caused by mechanochemical solid-phase grinding with increasing thermal annealing (see data on the structural parameters of ceramic samples annealed at temperatures of 1000 – 1200 °C in Table 1). The formation of a substitution phase of the  $AlZrO_2$  type in the composition of ceramics, and a subsequent increase in its content (increase in weight contribution) results in a steep increase in hardness from 1178 HV to 1530 – 1750 HV, which indicates a positive effect of the formation of impurity phases on the strengthening effect (i.e. increase in hardness and resistance to cracking). It is important to highlight that the most significant changes in hardness and resistance to cracking in comparison with samples obtained at a temperature of 1200 °C, at which, according to X-ray phase analysis, the

formation of the  $\text{AlZrO}_2$  phase (the content of which is no more than 6 %) occurs, are observed with an elevation in temperature from 1200 °C to 1300 °C, at which the strengthening is about 30 %, and each subsequent increase in annealing temperature by 100 °C leads to significantly smaller changes in hardness and cracking resistance.

Analyzing the obtained data on alterations in hardness and resistance to cracking depending on the thermal annealing temperature, it can be concluded that two factors can affect the strengthening of ceramics: structural ordering associated with changes in the parameters of the crystal lattice, caused by its compaction at annealing temperatures of 1100 – 1200 °C and the formation of inclusions in the form of an impurity tetragonal  $\text{AlZrO}_2$  phase, an increase in the contribution of which leads to significant changes in strength parameters. The comparative analysis of strengthening factor changes versus structural ordering degree in Figure 6 supports the assumption based on differences in contributions to ceramic strengthening. It should be noted that in the case of sample annealing temperatures above 1200 °C, the main effect on strengthening is the formation of an impurity phase in the ceramic composition, the content of which increases with annealing temperature growth. In this regard, it should be noted that at low temperatures of thermal annealing (1000 – 1200 °C), the main contribution to the change in strength parameters is made by effects associated with crystal lattice ordering, as well as a decrease in deformation distortions of the structure due to their relaxation, and at high annealing temperatures (1300 – 1500 °C), the appearance of the  $\text{AlZrO}_2$  impurity phase leads to more pronounced strengthening effects, which can be explained by the presence of interphase boundaries, as well as dislocation strengthening (change in dislocation density). According to the X-ray diffraction data presented in Figure 1, for samples annealed at temperatures above 1300 °C, the shape of the diffraction reflections indicates a decrease in the size of crystallites, which is characteristic of the processes of recrystallization of the main phases as a result of the formation of an impurity substitution phase. As a result, as the crystallite size decreases, the dislocation density increases, the value of which, as is known, is inversely proportional to the square of the crystallite size. From this, it follows that the

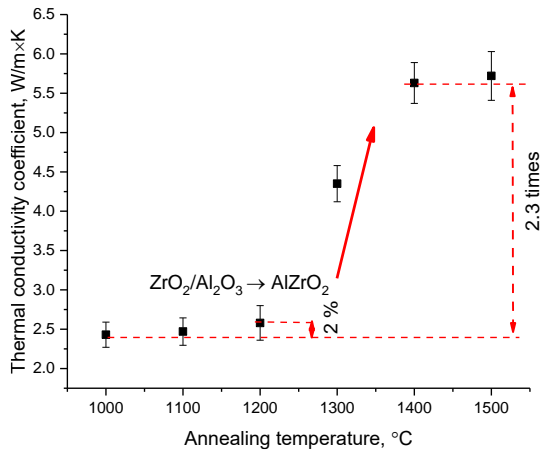
observed increase in strength parameters for samples annealed at temperatures of 1400 – 1500 °C is due not only to the effects of phase transformations but also to dislocation strengthening associated with an elevation in dislocation density.



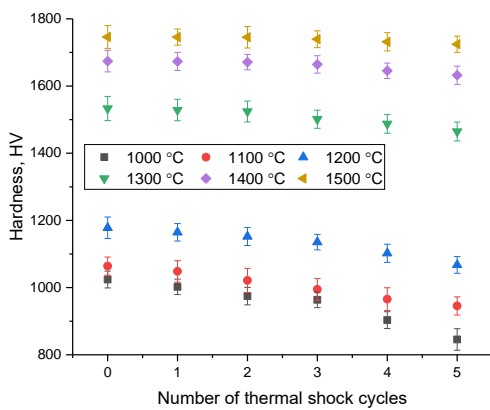
**Figure 6** - Comparative analysis of changes in strengthening factors (changes in hardness and cracking resistance) depending on the degree of structural ordering)

Figure 7 demonstrates the assessment results of the thermal conductivity coefficient of the studied  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  ceramics depending on the thermal annealing temperature, which were obtained using the longitudinal heat flow method. The general appearance of the presented data showed that the main changes in the thermal conductivity of ceramics are observed in the case when the formation of an  $\text{AlZrO}_2$  impurity phase is observed in the composition of the ceramics, the appearance of which results in more than twofold increase in the thermal conductivity coefficient (from 2.5 to 5.5 – 5.6  $\text{W/m}\cdot\text{K}$ ). This behavior of thermophysical parameters may be because these impurity inclusions have higher thermal conductivity than the dominant  $\text{ZrO}_2$  phase, which has a rather low thermal conductivity. It should be noted that the structural ordering that occurs at annealing temperatures of 1000 – 1100 °C does not lead to significant changes in the thermal conductivity of ceramics, which means that the dominant role in changing the thermophysical properties of ceramics is played by the presence of an impurity phase, the contribution of which should exceed more than 15 %.

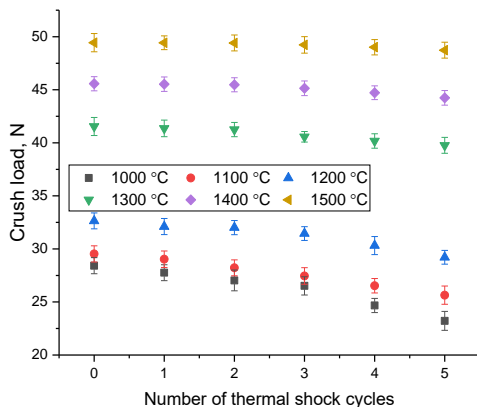




**Figure 7** - Results of changes in the thermal conductivity coefficient in  $ZrO_2 - Al_2O_3$  ceramics depending on the thermal annealing temperature



a)

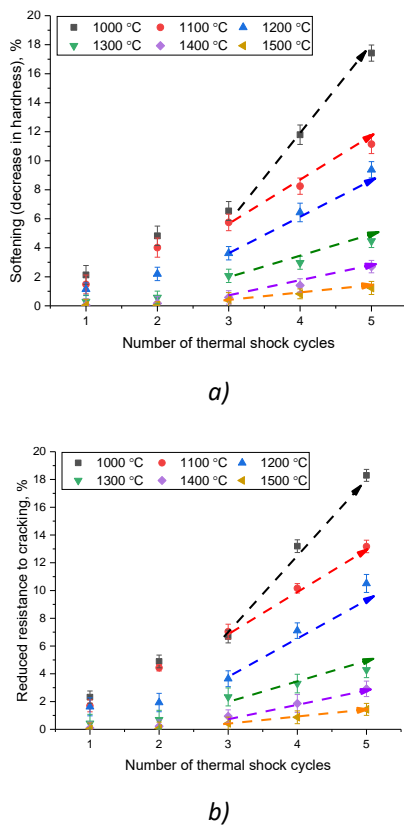


b)

**Figure 8** – Results of experiments to determine the stability of strength parameters to thermal shocks: a) dependence of hardness change; b) dependence of change in resistance to cracking

Figures 8a–b reveal the results of experiments related to determination of the stability of the strength characteristics (hardness and resistance to cracking under single compression) of  $ZrO_2 - Al_2O_3$  ceramic samples to thermal shocks, simulating extreme operating conditions of ceramic materials associated with rapid heating and sudden cooling. The measurements were carried out in the form of serial experiments, after each of which the hardness and cracking resistance of the ceramic samples under study were established in order to determine the kinetics of softening as a result of thermal effects. As can be seen from the presented data, the most pronounced changes in strength characteristics are observed for samples obtained at temperatures of 1000 – 1100 °C, which consist in a decrease in the values of hardness and resistance to cracking under single compression after 2 consecutive cycles. Moreover, this decrease is nonlinear, indicating softening and degradation of materials as a result of thermal shocks. In the case of ceramic samples in which the formation of inclusions in the form of the  $AlZrO_2$  phase was observed, changes in strength parameters depending on the number of cycles have a less pronounced downward trend, indicating a higher resistance of ceramics to thermal shocks and associated degradation processes.

Based on the obtained dependencies of changes in hardness and the maximum pressure that ceramics can withstand during a single compression, softening factors were determined (decrease in hardness and resistance to cracking), which reflect the resistance of materials to external influences that occur under extreme operating conditions. The assessment results of the softening factors, as well as the main trends in their changes depending on the number of test cycles for all studied ceramics, are presented in Figure 9a – b. The presented data indicate that the most pronounced changes in strength parameters associated with softening are observed after 2-3 cycles, during which the softening grows sharply and amounts to about 10 – 18 % for ceramic samples obtained at annealing temperatures of 1000 – 1200 °C. In the case of ceramics obtained at annealing temperatures of 1300 – 1500 °C, the maximum softening is no more than 2 – 4 %, which indicates a fairly high resistance of these ceramics to temperature changes, as well as softening effects associated with sudden changes in operating temperatures and, as a consequence, possible deformation distortions resulting from thermal expansion of the ceramic structure.



**Figure 9** – Results of evaluation of strength properties reduction: a) decrease in hardness depending on the number of cycles; b) decrease in resistance to cracking

Analyzing the combination of the obtained test data for thermal shocks and resistance to them under repeated impacts (as a result of cyclic tests), it can be concluded that the formation of impurity inclusions in the ceramics in the form of the  $\text{AlZrO}_2$  phase results in an elevation in resistance to structural degradation due to the presence of interphase boundaries, which prevent the processes of deformation distortion of the crystal structure under thermal influence. At the same time, the higher thermal conductivity values for these ceramics also ensure that effects associated with local overheating at low thermal conductivity, which can lead to accelerated deformation distortions of the crystal structure, cannot occur in the samples.

## Conclusions

Using solid-phase mechanochemical synthesis methods, samples of  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  ceramics were obtained. Their characterization using methods of X-ray diffraction analysis, scanning electron microscopy, and methods for determining hardness and resistance to cracking, alongside thermal

conductivity, made it possible to establish the dependence of the influence of the phase composition of ceramics on their resistance to external influences. The established temperature dependences of alterations in phase changes, caused by the formation of the  $m - \text{ZrO}_2 \rightarrow t - \text{Zr}(\text{Al})\text{O}_2$  type polymorphic transformations in the structure of  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  ceramics, cause an elevation in the strength and resistance to cracking of ceramics, alongside an increase in resistance to thermal influences resulting in softening due to a reduction in hardness and resistance to cracking.

Analyzing the dependence of the influence of the annealing temperature of  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  ceramics on the structural ordering and phase formation processes, it was found that at a temperature of 1200 °C and above, the formation of impurity inclusions in the form of a tetragonal  $\text{AlZrO}_2$  phase is observed, which in turn results in the formation of three-phase ceramics. Moreover, the formation of the  $\text{AlZrO}_2$  phase occurs due to the partial substitution of zirconium for aluminum in the composition of aluminum oxide, which leads to the displacement of the contribution of the rhombohedral  $\text{Al}_2\text{O}_3$  phase, as well as an increase in the contribution of the  $\text{AlZrO}_2$  phase from 6 to 20 %.

It is important to highlight that according to measurement data of the thermal conductivity coefficient, a change in the phase composition of ceramics due to polymorphic transformations  $m - \text{ZrO}_2 \rightarrow t - \text{Zr}(\text{Al})\text{O}_2$  leads to a more than twofold increase in the thermal conductivity coefficient, which, together with the increased parameters of hardness and crack resistance, indicates a positive effect of the influence of inclusions of the  $t - \text{Zr}(\text{Al})\text{O}_2$  phase in the composition of ceramics, the formation of which occurs at temperatures from 1200 °C and above.

The obtained results of the influence of the phase composition of  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  ceramics on the strength and thermophysical parameters, alongside resistance to thermal influences, open up the possibility of considering these ceramics as candidate materials for inert matrices of dispersed nuclear fuel. At the same time, the proposed method for producing composite ceramics using simple mechanical grinding and subsequent thermal sintering at a given temperature is not resource-intensive compared to other methods for producing composite ceramics (sol-gel method, chemical coprecipitation), and is also quite easily scalable, which will allow obtaining the required amount of composite powders with the specified



parameters. Based on the established phase changes, we can conclude that by controlling the content of the  $t - \text{Zr(Al)O}_2$  phase in the composition of ceramics, by changing the conditions of thermal sintering of powders, it is possible to control the strength and thermophysical parameters. This, in turn, opens up the possibility of creating an alternative to  $\text{ZrO}_2$  ceramics, which are considered one of the promising materials for inert matrices, due to good compatibility with other materials, as well as low thermal expansion and fairly high thermal conductivity among oxide ceramics (except for beryllium oxide). In this case, the resulting composite  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$ , which contains  $t - \text{Zr(Al)O}_2$  inclusions of more than 10 %, has thermal conductivity coefficients above  $5 \text{ W/m}\cdot\text{K}$ , which exceeds the thermal conductivity of  $\text{ZrO}_2$  ceramics by more than 2.0 – 2.5 times (thermal conductivity coefficient for  $\text{ZrO}_2$  ceramics is about 1.7 – 2.0  $\text{W/m}\cdot\text{K}$ ).

In the future, studies of these ceramics will be aimed at investigating their radiation resistance, in particular, the influence of the phase composition of ceramics on resistance to the accumulation of structural damage caused by the interaction of

heavy ions comparable in energy to fission fragments of nuclear fuel.

**Conflicts of interest.** On behalf of all authors, the corresponding author states that there is no conflict of interest.

**CRediT author statement:** **D. Borgekov:** Conceptualization, Writing - Original Draft, Methodology, Formal analysis; **A. Kozlovskiy:** Conceptualization, Writing - Original Draft, Writing - Review & Editing, Funding acquisition, Supervision, Methodology; **D. Shlimas:** Writing - Review & Editing, Supervision, Methodology; **R. Shakirziyanov:** Original Draft, Methodology, Formal analysis, Writing - Review & Editing; **A. Popov:** Conceptualization, Writing - Review & Editing; **M. Konuhova:** Conceptualization, Writing - Review & Editing.

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## Композитті керамика құрамындағы алюминий және цирконий оксидтері компоненттерінің концентрациясының өзгеруінің физика-химиялық және беріктік қасиеттеріне әсерін зерттеу

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### ТҮЙІНДЕМЕ

Мақала композитті керамикалардың бастапқы оксидтерінің қатынасының вариациясымен байланысты механикалық және жылу физикалық сипаттамалардың өзгеруін зерттеуге арналған, бұл өзгерістер керамикалардың фазалық құрамының өзгеруімен байланысты.  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  композитті керамикаларын алу әдісі ретінде механохимиялық қатты фазалық араластыру және кейіннен сынамааларды термиялық күйдіру әдісі таңдалды. Растворлық электронды микроскопия мен рентгенфазалық талдау әдістерін пайдалана отырып алынған композициялық керамика « $\text{ZrO}_2$  түйіршіктері түріндегі қосындылары бар  $\text{Al}_2\text{O}_3$  матрицасы» типті құрылымдар екені анықталды. Ал зерттеу барысында бастапқы құрамдағы алюминий оксидінің мөлшерінің жоғарылауы цирконий диоксиді түйіршіктерінің өсуі мен агломерациясын тежейтіні анықталды. Сондай-ақ, зерттелген  $\text{ZrO}_2 - \text{Al}_2\text{O}_3$  керамикаларының құрылымдық ерекшеліктерін бағалау барысында алюминий оксидінің мөлшерін арттыру нәтижесінде  $\text{AlZrO}_2$  тетрагональды фазасының құрылымда қалыптасатыны және оның салмақтық үлесінің оксидтер компоненттерінің қатынасына байланысты артатыны анықталды. Зерттелген керамикалардың механикалық сипаттамаларын анықтау барысында фазалық құрамның вариациясы керамикалардың беріктігін арттыратыны (қаттылықтың және шытынауға төзімділіктің өсуі) белгілі болды,

Мақала келді: 8 қараша 2024

Сараптамадан өтті: 29 қараша 2024

Қабылданды: 4 желтоқсан 2024

	алайда $Al_2O_3$ көп салмақтық үлесі бар құрамда алюминий оксидінің қаттылығы цирконий диоксидіне қарағанда төмен болғандықтан, механикалық сипаттамалардың төмендеуіне әкелетіні анықталды.
	<b>Түйінді сөздер:</b> $ZrO_2 - Al_2O_3$ керамикалары, композитті конструкциялық материалдар, беріктік қасиеттер, беріктену, фазалық трансформациялар, жылу өткізгіштік.
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## Изучение влияния вариации концентрации компонент оксидов алюминия и циркония в составе композитных керамик на физико-химические и прочностные свойства

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Поступила: 8 ноября 2024 Рецензирование: 29 ноября 2024 Принята в печать: 4 декабря 2024	<b>АННОТАЦИЯ</b> Статья посвящена изучению вариации соотношения исходных оксидов в композитной керамике на изменение прочностных и теплофизических параметров, изменение которых обусловлено изменением фазового состава керамик. В качестве метода получения композитных $ZrO_2 - Al_2O_3$ керамик был выбран метод механохимического твердофазного смешивания с последующим термическим отжигом образцов. С применением методов растровой электронной микроскопии и рентгенофазового анализа установлено, что полученные композитные керамики представляют собой структуры по типу « $Al_2O_3$ матрица с включениями в виде зерен $ZrO_2$ », при этом в ходе исследований было установлено, что увеличение содержания в исходном составе оксида алюминия сдерживает рост и агломерацию зерен диоксида циркония. Также в ходе оценки структурных особенностей исследуемых $ZrO_2 - Al_2O_3$ керамик было установлено, что увеличение содержания оксида алюминия приводит к формированию в структуре тетрагональной фазы $AlZrO_2$ , весомой вклад которой увеличивается в зависимости от соотношения компонент оксидов. В ходе определения прочностных параметров исследуемых керамик было установлено, что вариация фазового состава приводит к упрочнению керамик (увеличению твердости и устойчивости к растрескиванию), однако при большом весовом вкладе $Al_2O_3$ в составе наблюдается снижение прочностных параметров, обусловленное более низкими показателями твердости оксида алюминия в сравнении с диоксидом циркония.
	<b>Ключевые слова:</b> $ZrO_2 - Al_2O_3$ керамики, композитные конструкционные материалы, прочностные свойства, упрочнение, фазовые трансформации, теплопроводность.
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