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Study of phase formation mechanisms in composite $xSi_3N_4 – (1-x)ZrO_2$ ceramics and their role in hardening of ceramics

Abstract. The article presents the results of studies of phase transformation dynamics in composite $xSi_3N_4 – (1-x)ZrO_2$ ceramics obtained using the mechanical activation method during thermal annealing of the obtained mixtures of components with different component ratios, leading to the initialization of phase formation processes. Using the X-ray phase analysis method, dynamics of phase transformations in $xSi_3N_4 – (1-x)ZrO_2$ ceramics, the general appearance of which may be written as $ZrO_2/ZrSiO_4 \rightarrow ZrSiO_4$/finely dispersed fraction of SiO_2, was established. It was found that addition of Si_3N_4 to ZrO_2 ceramics allows for the initiation of polymorphic transformations of the type $m-ZrO_2 \rightarrow t-ZrSiO_4$, the formation of which in combination with the finely dispersed fraction of SiO_2 leads to hardening of the ceramics and a resistance elevation thereof to external influences. During the conducted experimental work, aimed at study of the effect of the phase polymorphic transformation processes in composite ceramics, caused by the component ratio alteration, on resistance to mechanical loads, It was established that the formation of a finely dispersed fraction of SiO_2 in ceramics' structure increases resistance to cracking by more than 1.5 times compared to single-component ceramics, the stability of which decreases in the case of the compression rate growth.
Key words: composite ceramics, phase transformations, dispersion hardening, nanosized grains, finely dispersed fraction.

Introduction

The annual increase in energy consumption in the world requires a solution to the problem of obtaining cheap and environmentally friendly energy through the use of alternative energy sources, one of which is nuclear energy, which is based on the principle of obtaining energy as a result of nuclear reactions [1, 2]. At the same time, compliance with the standards of accepted global concepts of gradual abandonment of hydrocarbon fossil fuels for energy production, as well as the transition to alternative energy sources, requires an annual growth in the percentage of alternative energy sources in the energy industry [3,4]. It is important to mention that there is a need to comply with safety and environmental standards when using alternative energy sources, especially in terms of creating new generation nuclear reactors, which are currently considered as one of the most promising ways to solve problems in the energy sector, combining the elimination of shortages in energy production, as well as reducing the share of fossil fuel use in the world. One way to increase energy production from nuclear power is to use new generation reactors, including fast neutron reactors and high temperature reactors, the development of which requires new types of structural materials that have high resistance to external influences and are also capable of operating in extreme conditions associated with both high temperatures and high mechanical loads [5-8]. Among the technologies being developed for creating new structural materials for nuclear reactors, the main focus is on composite ceramic materials based on refractory compounds in the form of oxides, nitrides or carbides, the use of which allows not only to enhance the efficiency of nuclear reactors when using these materials as a basis for creating new generation fuel elements [9-12], capable of withstanding large doses of radiation exposure in the form of fission fragments, but also to increase

the safety of operating nuclear installations, due to the high strength and radiation resistance of composite ceramics [13,14].

Interest in researching the processes of phase formation in composite ceramics based on refractory compounds is due, above all, to expansion of fundamental knowledge about phase formation processes, including the effect of changes in the ratio of components on the course of crystallization processes under thermal influence [15,16]. Secondly, as is known, the processes of phase formation in refractory compounds can be accompanied by the metastable phase formation, the appearance of which can have an adverse impact on the strength characteristics of ceramics during their operation, the modes of which typically involve high-temperature heating, substantial mechanical stress, and, when used as radiation-resistant materials, exposure to radiation. [17,18].

The purpose of this work is to study the phase formation processes in composite ceramics based on $xSi_3N_4 – (1-x)ZrO_2$ compounds, the variation of which makes it possible to obtain ceramics with different phase compositions. Selecting $xSi_3N_4 – (1-x)ZrO_2$ composite ceramics as the focus of the study is due to the combination of their strength, thermal and anticorrosive properties, which allows them to be considered as candidate materials for the creation of inert matrices of dispersed nuclear fuel or as materials for storing and holding spent nuclear fuel from destruction. The methods of the study included scanning electron microscopy used to determine morphological features and their relationship with changes in phase composition, as well as the method of X-ray phase analysis used to clarify the kinetics of phase transformations in the structure of ceramics when changing the ratio of components. Much attention in the work is paid to detailing the structural transformations in the composition of ceramics caused by thermal sintering processes, which in turn allow the initiation of recrystallization processes, which results in formation of phase transformations of the $ZrO_2/ZrSiO_4 \rightarrow ZrSiO_4$/finely dispersed fraction of SiO_2 type.

Materials and methods

The $xSi_3N_4 – (1-x)ZrO_2$ ceramics were synthesized using solid-phase mechanochemical grinding by mixing silicon nitride (Si_3N_4) and zirconium dioxide (ZrO_2) powders in different stoichiometric ratios, the step of which was 0.05 M. In this case, the use of components with a high content of Si_3N_4 leads to uncontrolled processes of phase transformations associated with the accumulation of inclusions in the structure in the form of SiO_2. Solid-phase mixing was performed using a PULVERISETTE 6 planetary mill (Fritsch, Berlin, Germany) at a speed of 600 rpm for 30 minutes. The samples were then thermally sintered at a temperature of 1500°C for 5 hours in a muffle furnace. The choice of thermal annealing conditions is determined by the required time for initialization of phase transformation processes, excluding uncontrolled high-temperature oxidation processes during prolonged thermal exposure of samples during their synthesis. According to previously conducted studies [19,20], it was found that these conditions are the most optimal for obtaining ceramics with high strength properties. Using these conditions for obtaining ceramics, a series of samples with different component ratios were obtained, the variation in which as a thermal sintering result in the formation of ceramics with different phase compositions.

In this case, variation of synthesis conditions in the case of mechanochemical solid-phase synthesis can lead, as was shown in [19, 20], to a change in grain sizes, which in turn causes the effect of dislocation strengthening, caused by a change in dislocation density, which restrains the propagation of microcracks under external mechanical influences. However, in this case, resistance to external influences can be influenced not only by dimensional factors but as well as the phase composition of the ceramics, which changes when the ratio of components in the sample's changes.

The morphological features of the synthesized ceramics, depending on the change in the ratio of the initial components in the composition, were determined by scanning electron microscopy, implemented using a Phenom™ ProX microscope (Thermo Fisher Scientific, Eindhoven, the Netherlands). Measurements were carried out using special holders, onto which powders were applied by spraying. Spraying was carried out using a Nebula particle disperser (Thermo Fisher Scientific, Eindhoven, the Netherlands). Dispersion of particles was achieved by spraying, resulting in a distribution of particles on the holder.

Diffractograms of ceramic samples were obtained on a D8 Advance ECO powder diffractometer

(Bruker, Karlsruhe, Germany). Diffractograms were recorded in the Bragg-Brentano geometry, in the angular range of $2\theta = 20\text{-}100°$, the recording step was $0.03°$, the time of obtaining the spectrum at a point was 1 s. To evaluate the structural parameters, the DiffracEVA v.4.2 software was used, which is based on the Rietveld method used to refine the parameters of each established phase, alongside to determine the structural ordering degree of the studied ceramics. The phase composition was established by comparison of the position of diffraction reflections with the reference values from the PDF-2(2016) database, considering deformation distortions, as well as possible effects of partial substitution.

The structural ordering degree was calculated by analyzing the data on the change in the diffraction maxima areas and the background radiation area, which characterizes the amount of amorphous inclusions in the composition of ceramics. Calculating the ratio of these two areas allowed determination of the structural ordering degree parameter in the sample's contingent upon the concentration of the composition. In the case of determining the degree of structural ordering, the emphasis was placed on the effect of thermal sintering of ceramics, leading to compaction due to the burning out of structural defects and oxygen vacancies, which in turn leads to an increase in the t2h2e density of the ceramics, and, therefore, the formation of a more perfect crystalline structure. The sintering effect was taken into account in combination with changes resulting from thermal expansion due to a shift in the component ratio within the composition.

The impact of modifications in the phase composition of ceramics on resistance to external influences, which is one of the key criteria determining the potential for using ceramics as heat-resistant structural materials, was determined using the method of resistance to cracking under single compression in the case of variation in the rate of loading on the samples. The tests were conducted using a universal single-column electromechanical testing machine LFM-L 10kH (Walter + Bai AG, Löningen, Switzerland). The loading rate was varied in order to establish the dependence of the ceramics' resistance to cracking upon changes in compressive loads, an increase in which leads to the initialization of microcrack growth in the structure, the presence of which accelerates the destruction process. The range of loading rates was from 0.1 to 0.5 mm/min. The application of the single compression method enabled us to assess the resistance of ceramics to deformation-induced embrittlement caused by external mechanical loads and to establish the maximum allowable load on samples, which is a key criterion in determining the strength properties of ceramics. Deformation and subsequent cracking were recorded using the extensometry method, the use of which allowed us to determine the degradation rate, as well as to record the onset of cracking of samples with high accuracy.

Results and discussion

A key parameter influencing the potential use of composite ceramics as structural materials, especially for applications involving extreme operating conditions, is the ratio of the phase composition properties, strength and thermal parameters, the totality of which determines the scope of application of ceramics. Moreover, in the case of composite ceramics, the determining role in changing the strength and thermal properties is played by the ratio of phases, the alteration of which occurs with a variation in the composition of the initial components used in synthesis, as well as the conditions for obtaining ceramics.

Figure 1 shows the morphological characteristics of the obtained $x\mathrm{Si_3N_4} - (1\text{-}x)\mathrm{ZrO_2}$ ceramics as a function of the variation in component ratios within the composition, the alteration of which causes the formation of ceramics with different grain geometries. All images were obtained at the same scales, and the observed changes are related to size effects arising from phase transformations in the ceramic composition. The results presented in Figure 1 indicate phase transformation processes associated with changes in grain sizes, as well as compaction effects that occur with variations in the components in the composition.

The overall presentation of the data of the studied samples of $x\mathrm{Si_3N_4} - (1\text{-}x)\mathrm{ZrO_2}$ ceramics indicates that when $\mathrm{Si_3N_4}$ is added to the composition of the ceramics, the formation of two-component ceramics, consisting of a $\mathrm{ZrO_2}$ matrix having larger grain sizes with inclusions in the form of spherical or sphere-like grains, which, according to the assessment of morphological features, have a structure and phase composition different from $\mathrm{ZrO_2}$, is observed. Moreover, an elevation in the $\mathrm{Si_3N_4}$ concentration in the composition above 0.25 M results in formation of

a dendrite-like structure of the obtained grains, having inclusions different from those previously established, which indicates stages in the formation of the ceramic samples. In the case of Si_3N_4 concentrations above 0.35 M, the morphology of the ceramics is represented by a matrix of heavier elements with inclusions of lighter fine particles, elemental analysis of which suggests that these particles are SiO_2 grains, which can be attributed

to thermal effects linked to the decomposition of Si_3N_4 during thermal annealing. This process involves interaction with oxygen, resulting in the formation of a finely dispersed SiO_2 phase. The process of thermal decomposition $Si_3N_4 \rightarrow SiO_2$ during thermal annealing at high temperatures is well known and occurs under thermal influence when sintering of samples occurs in an air atmosphere.
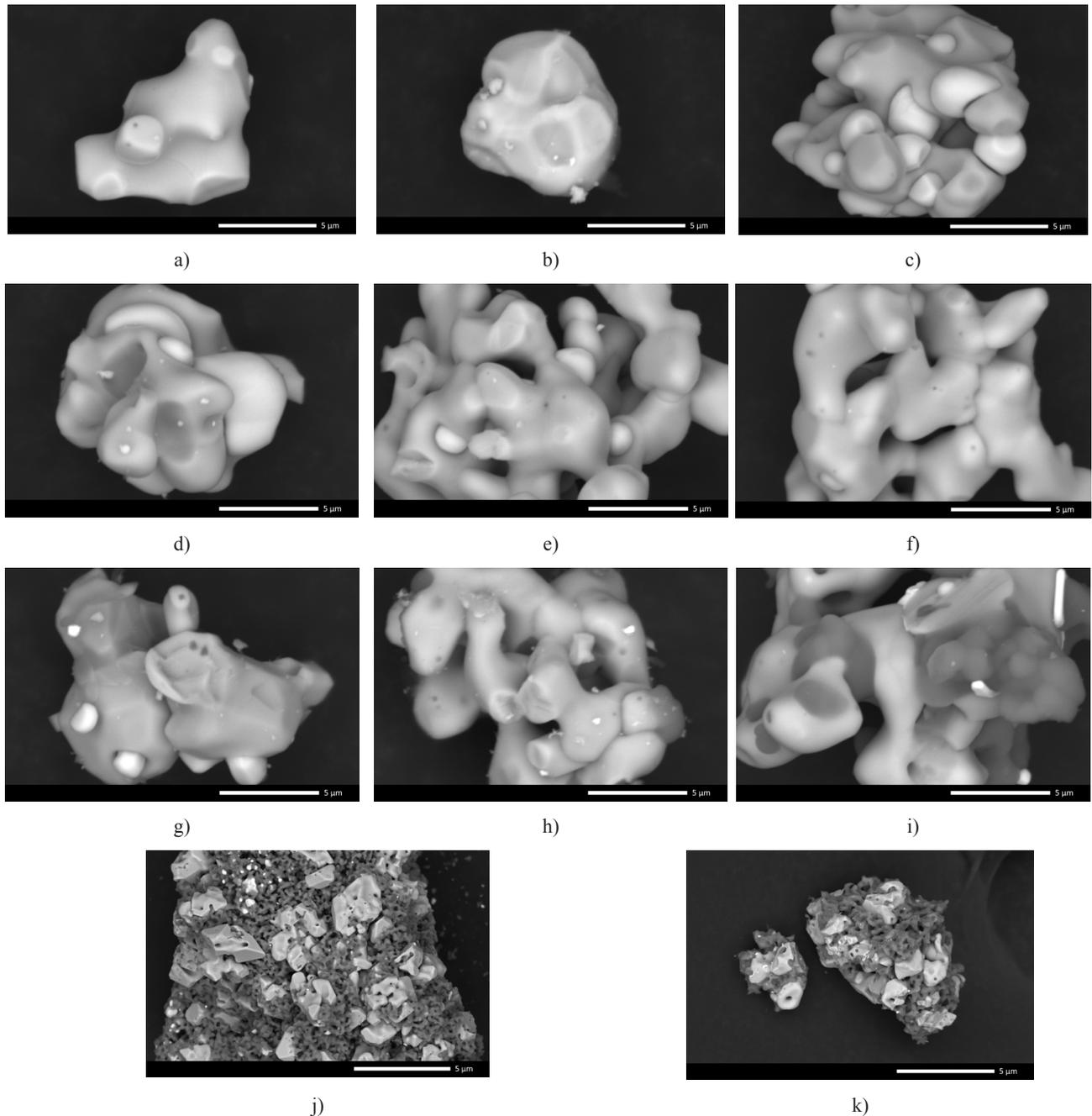

Figure 1 – Morphological analysis results of the examined $xSi_3N_4 – (1-x)ZrO_2$ ceramics based on the component ratio in the composition: a) x=0.0 M; b) x=0.05 M; c) x=0.10 M; d) x=0.15 M; e) x=0.20 M; f) x=0.25 M; g) x=0.30 M; h) x=0.35 M; i) x=0.40 M; j) x=0.45 M; k) x=0.50 M

Figure 2 shows the results of the X-ray diffraction analysis of the studied $xSi_3N_4 - (1-x)ZrO_2$ ceramics in the form of a set of X-ray diffraction patterns, the general appearance of which reflects the alteration in the phase composition and the structural ordering degree in the samples at the component ratio alteration in the composition during mechanochemical synthesis and subsequent thermal annealing. The results are presented as a set of X-ray diffraction patterns reflecting variations in the component ratios and weight contributions of the identified phases within the composition.

The overall appearance of the presented X-ray diffraction patterns suggests a fairly high structural ordering degree, the value of which, according to estimates, is about $92 - 94$ %, while small changes in this value (see the data presented in Table 1) are due to processes of changing the phase composition, the kinetics which is linked to a variation in the ratio of the initial components in the composition. The degree of structural ordering (degree of crystallinity) was determined on the basis of a comprehensive analysis of X-ray diffraction patterns, which consisted of determining the ratio of the areas of diffraction reflections and the area of background radiation associated with the concentration of defective inclusions in the composition of ceramics. When the Si_3N_4 concentration is low in the ceramic composition, according to the data presented, the monoclinic ZrO_2 phase (PDF-01-070-02491) plays a dominant role in the composition, the diffraction reflections of which are quite well manifested in the diffraction patterns and have a weakly expressed asymmetry due to the presence of deformation distortions induced by mechanochemical grinding, and the influence of the Si_3N_4 dopant, the addition of which, based on the X-ray phase analysis data, leads to the formation of the $ZrSiO_4$ phase (PDF-00-006-0266) with a tetragonal type of crystal lattice in the structure. The formation of the $ZrSiO_4$ phase, along with the absence of diffraction reflections characteristic of the Si_3N_4 phase, is due to the fact that during thermal annealing at a temperature of 1500 °C in the case of annealing in an air atmosphere, decomposition processes of the $Si_3N_4 \rightarrow SiO_2$ type are initiated, the formation of which in low concentrations results in formation of zirconium silicate in the composition. Comparison of the morphological features of the obtained samples with the X-ray phase analysis data, leads to the conclusion that the formed spherical grains in the

composition of samples with a Si_3N_4 concentration of $0.15 - 0.25$ M are zirconium silicate grains embedded in a ZrO_2 matrix. At the same time, the shape of these inclusions indicates a strong deformation of these formations, which is also indicated by the shapes of the diffraction lines recorded for the $ZrSiO_4$ phase. Moreover, comparing the ratios of the intensities of reflections for the ZrO_2 and $ZrSiO_4$ phases that develop as the concentration of Si_3N_4 increases in the composition of ceramics, the observed change in the weight contributions indicates the ZrO_2 phase displacement from the composition and the $ZrSiO_4$ phase dominance. Under conditions where the Si_3N_4 component content in the ceramics is about 0.3 M, the dominant phase is $ZrSiO_4$, and no reflections of the monoclinic ZrO_2 phase are recorded in the diffraction patterns, which indicates a complete transformation of ZrO_2 into $ZrSiO_4$, which can also be caused by the initialization of polymorphic transformation processes of the $m-ZrO_2 \rightarrow t-Zr(SiO_2)O_2/ZrSiO_4$ type, arising due to the thermal decomposition $Si_3N_4 \rightarrow SiO_2$ and subsequent transformation. Thus, the formation of the tetragonal phase of $ZrSiO_4$ at dopant concentrations of $0.1 - 0.25$ M Si_3N_4 may indicate the possibility of initialization of the Processes of polymorphic transformation in ceramic compositions, resulting not only in structural parameter change, but also in size effects. It should be noted that at Si_3N_4 concentrations in the ceramics above 0.3 M, X-ray diffraction patterns show reflections that can be compared with the hexagonal phase of SiO_2 (PDF-01-074-9378), the formation of which in this case can be explained by the effect of supersaturation with silicon dioxide, which, according to the images obtained using the scanning electron microscopy method, are finely dispersed particles embedded in a matrix of $ZrSiO_4$. It should also be noted that at concentrations of $0.45 - 0.5$ M Si_3N_4, the shape of the $ZrSiO_4$ grains is prismatic crystals, which indicates the ordering of this phase and the end of its formation in the composition of ceramics. Generation of the $ZrSiO4$ phase in the composition of ceramics leads to their compaction, as well as the formation of a composition of the $ZrSiO_4$ matrix surrounded by a finely dispersed fraction of SiO_2 grains.

At the same time, the analysis of the structural parameters given in Table 1 illustrated that the component ratio alteration in the composition of ceramics results in changes in the parameters, which can be caused by both the effects of structural ordering,

the alteration of which is caused by the processes of variation of the type of deformation distortions that arise in the structure of ceramics during thermal annealing, and by substitution processes associated with the partial substitution of zirconium ions by silicon ions, for which differences in ionic radii can lead to a alteration in the parameters and volume of the crystal lattice. The structural ordering degree alteration during the ZrO_2 phase displacement, caused by the $ZrO_2 \rightarrow ZrSiO_4$ type polymorphic transformations, in turn, indicates that the main contribution to the changes is made by impurity inclusions and changes in their concentration in the ceramics' composition.
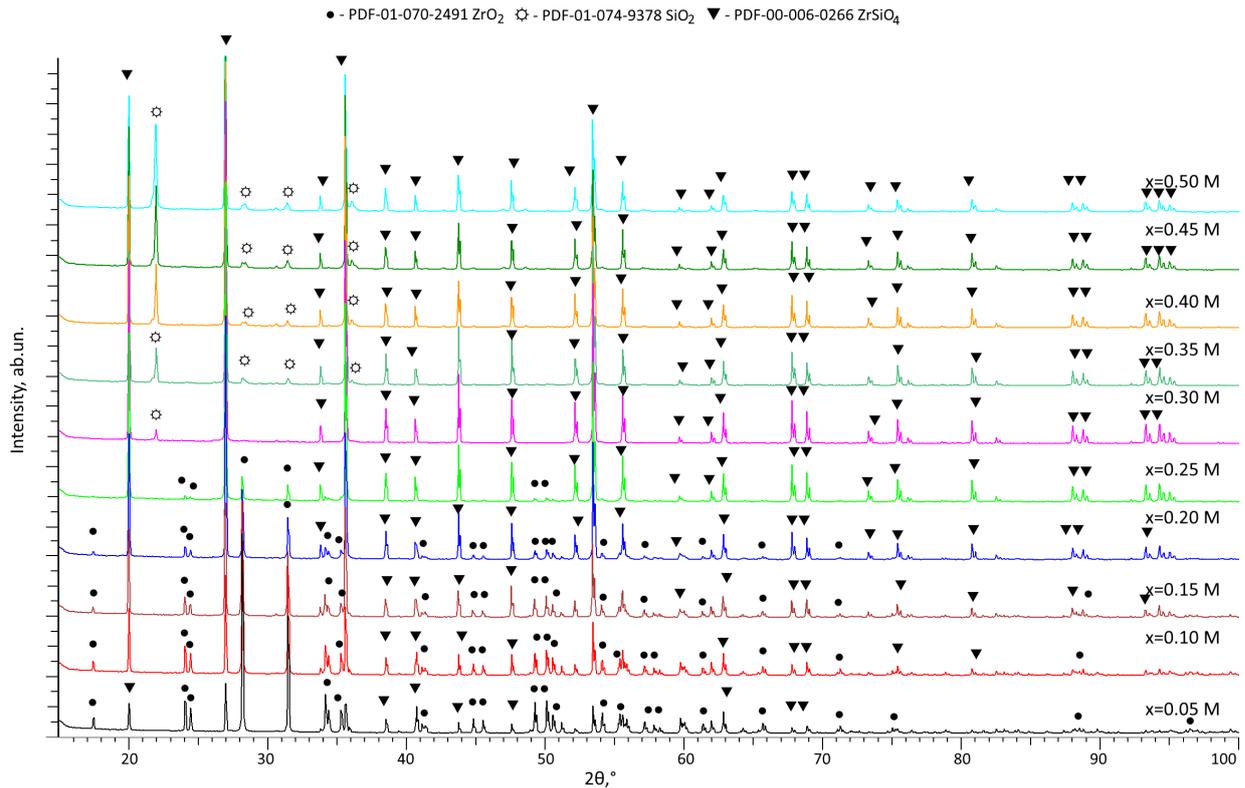
Figure 2 – X-ray diffraction patterns of $xSi_3N_4 - (1-x)ZrO_2$ ceramics dependent on the component ratio in the composition

Figure 3 presents the results of the weight contributions of the established phases in the composition of $xSi_3N_4 - (1-x)ZrO_2$ ceramics, with variation in the component ratio used in the synthesis. The phase composition of the ceramics, as well as the weight of each specific phase depending on the ratio of the components, was determined using expression (1):

$$V_{\text{admixture}} = \frac{RI_{\text{phase}}}{I_{\text{admixture}} + RI_{phase}} \qquad (1)$$

where I_{phase} is the intensity of the main phase, $I_{admixture}$ is the intensity of the impurity phase, the presence of which is linked to phase transformations, R=1.45. The use of formula (1) made it possible to determine the weight contributions of all established phases, as well as to determine the kinetics of changes in phase formation processes in ceramics when changing the concentration of components. For each ceramic sample, the weight contributions were estimated taking into account the corundum numbers, as well as a priori information about the samples and the ratios of the components used. The change in the concentration of components was also taken into

account when determining the structural parameters, the change of which determines the degree of structural ordering and phase transformations.

As is evident from the data presented, a low concentration of Si_3N_4 results in formation of inclusions in the structure in the form of $ZrSiO_4$, the contribution of which varies from 20 to 36 wt. %. At the same time, the addition of 0.15 – 0.20 M Si_3N_4 to the composition of ceramics results in the dominance of the $ZrSiO_4$ phase in the composition, and at a Si_3N_4 concentration of 0.25 M to an almost complete displacement of the monoclinic phase, due to transformations of the $ZrO_2 \rightarrow ZrSiO_4$ type. Moreover, in the case of Si_3N_4 concentrations above 0.25 M, the formation of inclusions in the form of SiO_2 is observed in the composition, the weight contribution of which varies from 3 wt. % to 30 wt. % depending on the ratio of components. The occurrence of polymorphism processes, characteristic of structural changes of the $ZrO_2 \rightarrow ZrSiO_4$ type, causes a change in the phase composition in almost the entire measured range of ceramic component concentrations. The formation of inclusions in the form of a finely dispersed fraction consisting of SiO_2 grains is accompanied by changes in morphological features, leading to compaction of ceramics, as well as changes in strength parameters, thereby increasing resistance to external influences. In turn, the increase in the contribution of the finely dispersed fraction in the samples is due to the displacement of SiO_2 inclusions during the decomposition of silicon nitride during high-temperature annealing, most of which interacts with zirconium dioxide, thereby forming a stable tetragonal phase of $ZrSiO_4$.
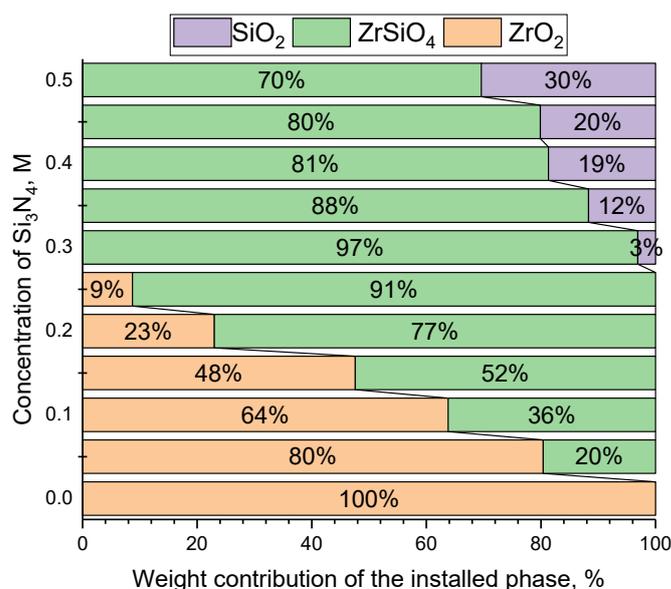

Figure 3 – Assessment results of the weight contributions of the phases determined
in the composition of $xSi_3N_4 – (1-x)ZrO_2$ ceramics

Table 1 – Data of structural parameters of the studied $xSi_3N_4 – (1-x)ZrO_2$ ceramics.

Si_3N_4 concentration, M	ZrO_2 – Monoclinic, PDF-01-070-02491	$ZrSiO_4$ – Tetragonal, PDF-00-006-0266	SiO_2 – Hexagonal, PDF-01-074-9378	Degree of structural ordering, %
0.05	a=5.1337±0.0015 Å, b=5.2118±0.0012 Å, c=5.3075±0.0016 Å, β=99.124°, V=140.21 Å³	a=6.6026±0.0022 Å, c=5.9718±0.0013 Å, V=260.34 Å³		92.5±1.4

Continuation of the table

Si$_3$N$_4$ concentration, M	ZrO$_2$ – Monoclinic, PDF-01-070-02491	ZrSiO$_4$ – Tetragonal, PDF-00-006-0266	SiO$_2$ – Hexagonal, PDF-01-074-9378	Degree of structural ordering, %
0.10	a=5.1448±0.0017 Å, b=5.2092±0.0013 Å, c=5.3083±0.0017 Å, β=99.243°, V=140.43 Å^3	a=6.6066±0.0013 Å, c=5.9728±0.0016 Å, V=260.66 Å^3		93.5±1.7
0.15	a=5.1499±0.0019 Å, b=5.2171±0.0011 Å, c=5.3211±0.0015 Å, β=99.243°, V=141.11 Å^3	a=6.6092±0.0016 Å, c=5.9862±0.0021 Å, V=261.49 Å^3		93.7±1.2
0.20	a=5.1475±0.0012 Å, b=5.2076±0.0015 Å, c=5.3138±0.0013 Å, β=99.322°, V=140.43 Å^3	a=6.6066±0.0012 Å, c=5.9766±0.0017 Å, V=260.87 Å^3		93.1±1.6
0.25	a=5.1489±0.0015 Å, b=5.2118±0.0011 Å, c=5.3147±0.0013 Å, β=99.203°, V=140.78 Å^3	a=6.6065±0.0011 Å, c=5.9862±0.0026 Å, V=261.28 Å^3		93.8±1.5
0.30	-	a=6.6093±0.0018 Å, c=5.9766±0.0013 Å, V=261.07 Å^3	a=4.9723±0.0013 Å, c=6.9291±0.0016 Å, V=171.31 Å^3	94.2±1.8
0.35	-	a=6.6040±0.0011 Å, c=5.9790±0.0017 Å, V=260.76 Å^3	a=4.9752±0.0015 Å, c=6.9181±0.0013 Å, V=171.24 Å^3	93.4±1.2
0.40	-	a=6.6106±0.0012 Å, c=5.9838±0.0013 Å, V=261.49 Å^3	a=4.9772±0.0015 Å, c=6.9291±0.0022 Å, V=171.65 Å^3	92.5±1.3
0.45	-	a=6.6106±0.0022 Å, c=5.9718±0.0021 Å, V=260.97 Å^3	a=4.9772±0.0019 Å, c=6.9291±0.0012 Å, V=171.65 Å^3	92.4±1.7
0.50	-	a=6.6119±0.0012 Å, c=5.9892±0.0018 Å, V=261.70 Å^3	a=4.9811±0.0022 Å, c=6.9319±0.0015 Å, V=171.99 Å^3	92.6±1.4

Thus, summarizing the observed changes in the phase ratio in the composition of xSi$_3$N$_4$ – (1-x) ZrO$_2$ ceramics, it can be concluded that at Si$_3$N$_4$ concentrations equal to $0.2 - 0.25$ M, the polymorphic transformation processes of the ZrO$_2$ → ZrSiO$_4$ type are completed in the structure of the ceramics, and with a further growth of the Si$_3$N$_4$ concentration in the ceramics' composition, it is represented by a mixture of two phases ZrSiO$_4$/SiO$_2$, the structure of which, according to scanning electron microscopy data, is represented by a matrix of ZrSiO$_4$ with inclusions in the form of SiO$_2$ grains surrounding larger grains of prismatic or pyramidal shape.

Figure 4 reveals the assessment results of the resistance of ceramics to external mechanical loads associated with a single compression of ceramics. The use of the single compression method makes it possible to establish the relationship between changes in the structural properties of ceramics caused by phase transformation processes and the resistance of ceramics to mechanical effects leading to the formation of microcracks and subsequent destruction. The general appearance of the presented dependence in Figure 4a indicates positive dynamics of changes in the resistance of synthesized ceramics to external influences, including a growth in resistance to cracking due to a rise in the strength and compaction of ceramics. Moreover, the most pronounced trend of changes in resistance to single compression is observed in the case when the ZrSiO$_4$/SiO$_2$ phase ratio dominates in the structure of ceramics, associated with the completion of the ZrO$_2$ → ZrSiO$_4$ type polymorphic transformation processes, as well as the formation of a finely dispersed SiO$_2$

fraction, the presence of which was established using the scanning electron microscopy method. The appearance of inclusions of a finely dispersed fraction leads to compaction of ceramics due to an increase in interphase boundaries, the presence of which causes a dispersion effect of strengthening, the presence of which leads to an increase in the stability of ceramics to external mechanical influences.
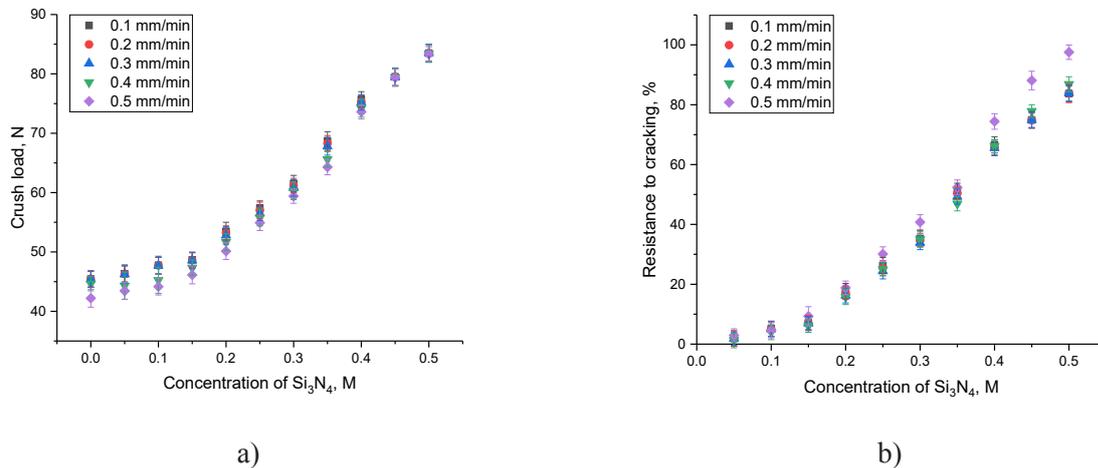

a)   b)

Figure 4 – Evaluation of the strength parameters of the studied $xSi_3N_4 – (1-x)ZrO_2$ ceramics depending on the variation of the ratio of components in the composition: a) Assessment results of the maximum load pressure under single compression that a sample can withstand before the cracking stage; b) Evaluation results of the determination of the increase in crack resistance under single compression of samples depending on the phase composition of ceramics, calculated for different compression rates during testing.

Alteration of the compression conditions of the samples, as can be seen from the presented dependencies, leads to the most pronounced changes in samples in which the monoclinic ZrO_2 phase dominates, while an elevation in the $ZrSiO_4$ proportion in the composition of ceramics results in growth in resistance to cracking, as well as a decrease in the influence of the compression rate on the value of pressure at which destructive damage of the samples occurs. This behavior of ceramics, especially for samples of the $ZrSiO_4/SiO_2$ composition, is due to the effects of dispersion hardening associated with the filling of the pore space with a finely dispersed fraction of SiO_2, which in turn leads to the formation of the effect of buffer barriers preventing the propagation of microcracks during compression of samples due to an elevation in the resistance to the mobility of grains of the main phase under mechanical exposure.

The observed strengthening effects associated with changes in the phase composition of ceramics in this case can contribute to the promotion of their potential for use as structural heat-resistant ceramics with high crack resistance under external influences.

Conclusion

The phase composition and mechanical properties of $xSi_3N_4 – (1-x)ZrO_2$ ceramics were studied contingent upon the alteration of the ratio of components in the composition of the ceramics. During the research, emphasis was placed on studying the variation of the component ratio and their role in determining the kinetics of the phase composition, as well as their influence on strength characteristics, including resistance to mechanical compression.

According to the X-ray phase analysis results, phase transformations were established in the composition of $xSi_3N_4 – (1-x)ZrO_2$ ceramics with variations in the ratio of components, according to which the addition of small concentrations of Si_3N_4 leads to the formation of two-phase ceramics in which the monoclinic ZrO_2 phase with inclusions in the form of grains of the tetragonal $ZrSiO_4$ phase dominates.

Analysis of the phase composition showed that the formation of the tetragonal phase $ZrSiO_4$ leads to

compaction of ceramics due to a change in structural parameters, as well as a change in resistance to external influences. At the Si_3N_4 dopant concentrations above 0.25 M, the composition of the ceramics is dominated by the $ZrSiO_4$ phase with inclusions in the form of a finely dispersed SiO_2 fraction with a hexagonal crystal lattice type.

As a result of the measurements of crack resistance under single compression of ceramic samples, it was established that a variation in the phase composition of ceramics due to the formation of the $ZrO_2 \rightarrow ZrSiO_4$ type polymorphic transformation processes results in enhancement of the resistance of ceramics to external influences, alongside maintenance of the crack resistance stability with an increase in the compression rate, which indicates a positive effect of dispersion hardening associated with the formation of a finely dispersed fraction of SiO_2 in the structure, acting as buffer inclusions that restrain the propagation of microcracks caused by compression of samples, which also makes it possible to enhance resistance to destruction in the case of mechanical impacts.

Further plans in this direction are related to determining the resistance of these types of ceramics to high-temperature degradation caused by external influences, as well as determining the influence of variations in the phase composition of ceramics on the resistance to the accumulation of radiation damage, as well as the associated mechanisms of softening of the surface layers.

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