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DETERMINATION OF THE EFFECT OF SIZE FACTOR AND PHASE COMPOSITION IN LITHIUM-CONTAINING CERAMICS ON RESISTANCE TO EXTERNAL MECHANICAL AND THERMAL INFLUENCES

I. E. Kenzhina[1], **A. U. Tolenova**[1], **A. L. Kozlovskiy**[1,2*]

[1] *Satbayev University, Almaty, Kazakhstan*
[2] *RSE "Institute of Nuclear Physics" ME RK, Almaty, Kazakhstan*

* *E-mail for contacts: kozlovskiy.a@inp.kz*

The paper presents data on the effect of size factors that cause a change in dislocation density, as well as the phase composition of two-phase lithium-containing ceramics based on lithium metacirconate on the strength characteristics of ceramics, as well as resistance to high-temperature tests. The size effect, dislocation density and the presence of interphase boundaries, the change of which is due to the effect of variation in the phase composition of ceramics, were considered as hardening factors during assessment of the strength properties, alongside resistance to temperature influences. During the studies, it was found that alteration of the grinding speed above 400 rpm results in more than twofold decrease in grain size, which in turn elevates the dislocation density, the change in which is a hardening factor for growth of hardness and crack resistance. During determination of the strength characteristics, it was found that a change in the phase composition due to the dominance of the $Li_6Zr_2O_7$ phase in the composition of ceramics leads to an elevation in hardness and resistance to cracking due to an increase in interphase boundaries, which serve as additional barriers to the propagation of microcracks under external influences. During experiments conducted to determine resistance to long-term thermal annealing and heat resistance tests, it was found that grain size reduction to less than 250 nm for all three types of ceramics under study leads to a rise in degradation resistance of strength properties due to dislocation hardening, and the presence of interphase boundaries, which is most pronounced for samples with a predominance of the $Li_6Zr_2O_7$ phase in the ceramic composition.

Keywords: *lithium metazirconate; two-phase ceramics; dislocation hardening; interphase boundaries; hardness; crack resistance.*

INTRODUCTION

Developments in the field of increasing the resistance to external influences of lithium-containing ceramics today occupy a very important place in materials science, due to the great interest in this class of materials as one of the potential candidate materials in alternative energy The development of lithium-containing ceramics to enhance their resistance to external influences is currently very important in materials science, in view of the great interest in this class of materials as one of the potential candidate materials in alternative energy [1–3]. The use of lithium-containing ceramics as anode materials of lithium-ion batteries has proven itself quite well due to its high capacitance characteristics, ensuring good charge stability and performance over a long period of operation [4, 5]. The use of lithium-containing ceramics as a key material for blankets used in thermonuclear energy for tritium propagation is one of the most promising solutions to the problem of tritium fuel [6, 7], the volume of which is one of the limiting factors in thermonuclear installations, the elimination of which requires special attention. At the same time, much attention in this direction is paid to studying not only the processes associated with the production and release of tritium from ceramics, but also determining the prospects of using various methods for increasing the resistance of these ceramics to external influences, both to the accumulation of radiation damage associated with nuclear reaction processes, and to mechanical impacts caused by operating processes, including thermal expansion and the formation of microcracks under mechanical loads [8–11]. One of the ways to change the properties of ceramics while maintaining the productivity of tritium production is to create two-phase ceramics by combining various types of lithium-containing ceramics, including combining lithium titanate with lithium silicate, or to form two-phase ceramics by initializing phase transformation processes during the manufacture of ceramics [12–15]. The underlying hypothesis of this method for enhancing resistance to external influences is that the hardening effect is formed by interphase boundaries, the presence of which creates additional barriers for migrating point and vacancy defects, as well as products of nuclear reactions in the form of helium or hydrogen ions, the agglomeration of which leads to destructive swelling of the near-surface layer, and as a consequence, its embrittlement and softening [14, 15]. Also, in several works [16–18], the size factor, consisting in grain size reduction, and consequently, dislocation density growth, is considered as a method of enhancement of resistance to radiation damage associated with the accumulation of structural distortions and amorphous inclusions due to the accumulation of products of nuclear reactions of lithium with neutrons [19, 20]. The inverse quadratic dependence of grain sizes and dislocation density, in this case, determines a fairly good hardening effect due to the presence of a large number of grain boundaries and dislocations, which are located near grain boundaries and are restraining factors for the propagation of microcracks and deformation distortions caused by both mechanical effects and the radiation damage accumulation in the structure.

The aim of the study is to determine the effect of the phase composition of lithium-containing ceramics based on metazirconate and size factors associated with alterations in the manufacturing conditions of ceramics on the resistance of ceramics to external mechanical and temperature influences characteristic of the operating modes of these ceramics, which are candidate materials for blankets [21, 22]. The working hypothesis taken as the basis for conducting these studies assumes that variation of the synthesis conditions, by changing the mechanical grinding speed, contributes to a change in grain sizes, the reduction of which, while maintaining the ratio of metazirconate phases, will make it possible to initiate the dislocation hardening effect of in ceramics, associated with size factors. At the same time, the presence of interfacial hardening, well known for two-phase ceramics, will also be considered when determining the strength properties of ceramics, especially during high-temperature stability tests, as well as maintaining the stability of strength and thermophysical parameters during life tests.

MATERIALS AND METHODS

The objects of study were lithium-containing ceramics obtained by mixing the initial ZrO_2 and Li_2CO_3 powders in different molar ratios ranging from 0.25 to 0.75 M. Mechanochemical synthesis was chosen to obtain a homogeneous mixture of initial components ground in a planetary mill at a grinding speed from 300 to 500 rpm. Variation of the grinding speed in increments of 50 rpm is due to the possibility of variation of grain sizes due to changes in the intensity of crushing during the interaction of grinding media with powders. The selection of the grinding speed range was based on a priori experimental data, including detailed assessments of the influence of grinding intensity and speed on the change in size factors, as well as the degree of homogeneity during grinding. The grinding speed was controlled by programming the planetary mill in order to establish the identity of the conditions of the experiments, as well as by maintaining the accuracy of the experimental work. The difference in the speed values was no more than 1% deviation from the specified mode.

Previously, in [23], it was shown that the use of ZrO_2 and Li_2CO_3 powders with different variations in the ratio of components in the case of mechanochemical solid-phase synthesis makes it possible to obtain two-phase ceramics with different variations in the weight contributions of the monoclinic phases Li_2ZrO_3 (PDF-00-033-0843) and $Li_6Zr_2O_7$ (PDF-01-081-2375). According to the data obtained, the phase composition of ceramics when changing the ratio of the components of the initial powders is 0.92 Li_2ZrO_3 : 0.08 $Li_6Zr_2O_7$ for a ratio of molar fractions of 0.25 M ZrO_2 and 0.75 M Li_2CO_3. With an equal molar ratio of powders (0.5 M ZrO_2 and 0.5 M Li_2CO_3), the ratio of the weight contributions of the phases is 0.8 Li_2ZrO_3 : 0.2 $Li_6Zr_2O_7$, and with a ratio of powders of 0.75 M ZrO_2 and 0.25 M Li_2CO_3, the weight contributions are 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$, which indicates the dominance of the $Li_6Zr_2O_7$ phase in the composition of the ceramics. The phase ratio in the ceramics was determined using the weight contribution method, by determining the proportion of contributions of each of the identified phases in the composition based on the obtained X-ray diffraction data. At the same time, it was determined that a change in the phase composition of ceramics, caused by an alteration in the phase ratio, leads to an elevation in strength and thermophysical parameters, which indicates a positive effect, which is due to the presence of interphase boundaries, an increase in the number of which results in hardening [23].

In this work, variation in the grinding speed of samples was chosen to determine the possibility of variation in grain sizes, which, together with changes in the phase composition, can lead to the formation of additional hardening effects associated with size factors causing dislocation hardening. This assumption is based on the effect of mechanical crushing of particles at high grinding speeds, leading to the formation of fine grains, the sizes of which can reach nanometer scales. Grinding was carried out for 30 minutes; the grinding time, as well as the mass of the initial components placed in the grinding glass, were chosen considering the elimination of the effect of cold welding of powders on the walls of the glass, which occurs during high-speed long-term grinding. Thermal sintering of the samples was carried out in a muffle furnace SNOL 39/1100 (AB UMEGA-GROUP, Ukmergė, Lithuania) at a temperature of 900 °C. Annealing was carried out for 8 hours at a heating rate of samples placed in corundum crucibles of 20 °C /min. Upon reaching the specified temperature, which was controlled using thermocouples placed in the furnace, the samples were kept for a specified time, after which they were subjected to slow cooling during the day inside the furnace chamber until they reached room temperature. Analysis of the phase composition of the ceramics under study when changing the conditions of mechanical grinding showed the preservation of the phase ratio for all grinding speeds, from which it can be concluded that the phase formation processes are not affected by the speed of mechanical action, and the processes themselves depend on the sintering temperature, the variation of which was not carried out in this experiment.

To conduct experiments to determine the mechanical properties of ceramics, as well as their resistance to mechanical and thermal influences, samples were pressed into a tablet with a diameter of 10 mm and a thickness of about 1 mm under a pressure of 250 MPa for 30 minutes, after which they were subjected to thermal relaxation of mechanically induced structural defects in a muffle furnace for 5 hours at a temperature of 500 °C.

The particle sizes after milling were determined using the laser optical diffraction method, which made it possible to estimate both the average particle size and the homogeneity of grain sizes depending on the weight contribution and production conditions. The effect of variations in grinding speed on the grain sizes of the ceramics under study was determined by measuring the size diagrams using the optical laser diffraction method, implemented on an ANALYSETTE 22 NeXT Nano particle analyzer (Fritsch, Berlin, Germany). Based on the data obtained, the dependences of the average grain size on the ratio of the initial components during grinding, as well as the grinding speed, were established.

Experiments to determine resistance to high-temperature degradation were carried out by simulating long-term thermal exposure at temperatures of the order of 1000 °C, characteristic of the operating temperatures of the core. Tests were carried out by placing samples in muffle furnaces, followed by slow heating (heating rate was 10 °C/min) to a given temperature and subsequent exposure at it for 100, 300 and 500 hours, then the samples cooled down with the furnace for 10–20 hours, depending on the heating temperature. After holding the samples at given temperatures for a certain time, hardness and crack resistance were measured, based on the measurements of which softening factors associated with destructive changes in the crystal structure resulting from thermal exposure were determined.

Determination of the thermal stability of ceramics under sudden changes in the temperature of the samples was carried out by quickly heating the samples in a muffle furnace at a speed of 50 °C/min, holding them at a temperature of 1000 °C for 1 hour, and removing the samples from the furnace into air to simulate thermal shock processes. The number of test cycles was about 5 cycles, after each cycle the hardness of the test samples was measured in order to determine changes caused by thermal effects during a sharp change in temperature.

Determination of the strength parameters of the ceramics under study, as well as determination of resistance to external influences, including long-term temperature exposure and heat resistance tests, was carried out using the following methods.

The hardness of the samples was determined using the indentation method, implemented using a Duroline M1 microhardness tester (Metkon, Bursa, Turkey), where a Vickers pyramid is used as an indenter, and the load on the indenter during testing was about 100 N. All measurements were carried out in the form of series of 15–20 tests, which made it possible to determine the standard deviation, as well as the measurement error.

Tests for resistance to single-compression cracking at a constant speed were carried out on a single-column testing machine LFM-L 10kH (Walter + Bai AG, Löningen, Switzerland), by placing ceramic samples in special clamps while applying external pressure to them at a constant speed.

The hardening parameters were determined by comparative analysis of changes in hardness values depending on the synthesis conditions and phase composition of ceramics. The obtained values reflect how effectively changes in the production conditions influence the degree of hardening and changes in the resistance of the mechanical and strength properties of ceramics to external influences.

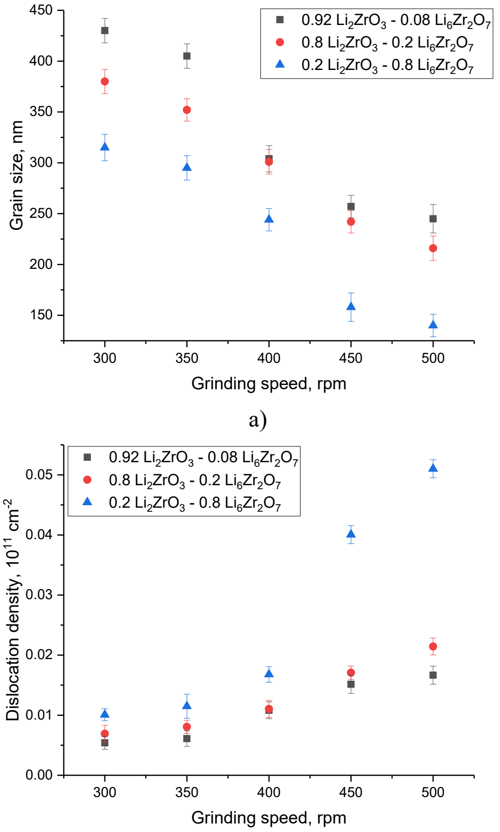
The determination of the thermophysical parameters of the studied ceramics depending on the phase composition, grain sizes, as well as changes caused by thermal effects and high-temperature degradation was carried out using the method of determining longitudinal heat flow. The main purpose of testing ceramics for heat resistance is the need to understand the processes of ceramic resistance to extreme operating conditions, which can lead to the acceleration of destruction processes and weakening due to the instability of the crystalline structure to sudden changes in temperature effects.

The measurements were carried out by placing ceramic samples between thermocouples, after which the samples were heated on one side, and control was carried out considering the temperature difference across the thermocouples. Based on these changes, thermal conductivity coefficients were determined, the change in which for dielectric ceramics is due to changes in the phonon mechanism of heat transfer. The choice of the time of experiments aimed at assessing the resistance of ceramics to thermal aging was based on a priori experimental work, which made it possible to establish a relationship between the rate of destruction and the resistance of ceramics to external influences.

RESULTS AND DISCUSSION

Figure 1a presents the results of a comparative analysis of changes in the average grain size of the ceramics under study, determined using the optical laser diffraction method. The data are presented as a dependence of the change in grain size on the grinding speed, which was varied during the ceramic manufacturing process. According to the data presented, variation of the initial component ratio during grinding under the same grinding conditions leads to a change in grain sizes, which consists in the fact that a rise in the ZrO_2 content in the ceramic composition results in more intense crushing of grains. However, this effect is most pronounced at low grinding speeds (300–350 rpm), but the grinding speed growth to 400 rpm and higher leads to the fact that the most significant differences in grain sizes are observed at ZrO_2 concentrations equal to 0.75 M. In this case, the difference between the sizes is about 80–100 nm compared to the grain sizes of ceramics obtained at ZrO_2 concentrations of 0.25 M and 0.5 M.

Analyzing the data presented in Figure 1, it can be concluded that the most significant changes in grain sizes are observed when the grinding speed rises above 400 rpm, at which a more pronounced reduction in grain sizes is observed during mechanical crushing, due to the effect of grinding balls on the initial powders. The grinding speed elevation from 300 to 350 rpm leads to a decrease in grain size by 5–7%, which is within the permissible measurement errors, and at speeds above 400 rpm the reduction in grain size is more than 2–2.5 times. It should be noted that among the three types of ceramics, more pronounced changes in grain sizes are observed for ceramic samples in which the $Li_6Zr_2O_7$ phase dominates. Such alterations in the dynamics of grain fragmentation can be explained by the presence of a high concentration of zirconium dioxide, the presence of which contributes to the formation of metastable states under mechanical action, which leads to increased grain fragmentation and, therefore, the formation of a smaller dispersed fraction.

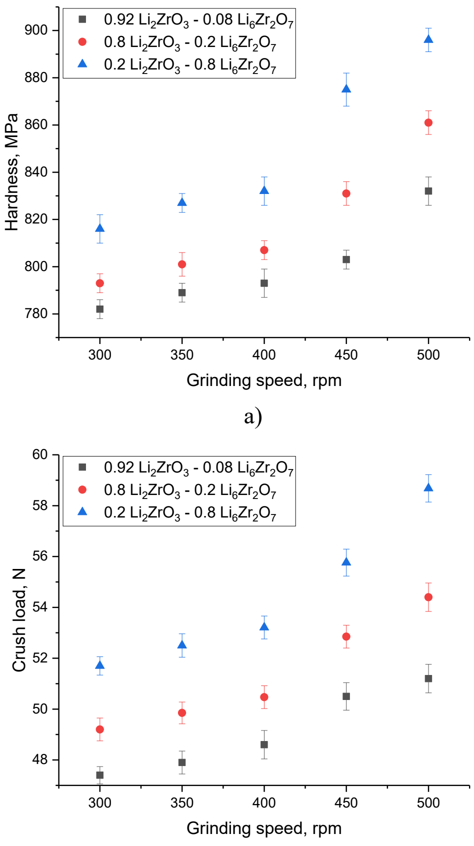


b)

Figure 1. a) Data on changes in the average grain size of the studied lithium-containing ceramics with variations in the grinding speed of the initial components in a planetary mill; b) Assessment results of changes in the dislocation density of the ceramics under study depending on the grinding speed

Based on the obtained grain size data, the dislocation density of the ceramics under study was determined, the results of changes in which are presented in Figure 1b. The dislocation density was calculated based on a standard evaluation technique based on the determination of grain size parameters and their changes depending on the variation of synthesis conditions. Obtaining grain sizes was carried out by estimating crystallite sizes from X-ray diffraction. The data are presented as the dependence of the change in dislocation density on the grinding speed of the initial powders. The dislocation density was assessed considering the relationship between the dislocation density (δ) and grain size (D), which can be expressed by the formula $\delta = 1/D^2$. As is evident from the data presented, the most significant changes in dislocation density are observed for ceramic samples containing the $Li_6Zr_2O_7$ phase content of about 80%, which were obtained at grinding speeds above 400 rpm. In this case, the dislocation density is on the order of $0.04–0.05\times10^{11}$ cm^{-2}, while for samples obtained at lower grinding speeds, the dislocation density values are on the order of $0.005–0.01\times10^{11}$ cm^{-2}. At the same time, it important to highlight that for 0.92 Li_2ZrO_3 : 0.08 $Li_6Zr_2O_7$ and 0.8 Li_2ZrO_3 : 0.2 $Li_6Zr_2O_7$ samples the change in dislocation density depending on the grinding speed is less pronounced in contrast to 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ samples, and the maximum value of the dislocation density of these samples at a grinding speed of 450–500 rpm is $0.015–0.02\times10^{11}$ cm^{-2}, which is half the same value determined for 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ samples. An increase in dislocation density in ceramics due to a decrease in grain size can contribute to the emergence of the so-called dislocation hardening effect [24, 25], the formation of which causes an increase in hardness and resistance to cracking or wear. This effect is based on the size factor associated with the fact that when grain sizes decrease, a large number of grain boundaries are formed (the so-called dispersion hardening effect), which serve as restraining barriers for the propagation of cracks under external pressure, as well as sinks for defects, the formation of which occurs as a result of external influences on the structure of ceramics. At the same time, the grain sizes decrease. Therefore, it results in the dislocation density growth, which in this case also serve as barriers to defects during their migration and diffusion as a result of external influences, especially during thermal influences.

The small grain sizes in ceramics, as well as the presence of two phases, can lead to a synergistic hardening effect, resulting in higher hardness and crack resistance, and in the case of thermal effects, these effects can play a key role in curbing high-temperature degradation due to thermal expansion. Moreover, as was shown in [23], an alteration in the phase composition of ceramics leads to the formation of a hardening effect, i.e., a growth in hardness and resistance to cracking due to a change in the ratio of phases in the composition of ceramics, obtained by variation of the ratio of components in the composition of ceramics during their grinding and subsequent thermal annealing. It is important to highlight that the ceramics' phase composition alteration by variation of the types of lithium-containing components is one of the most promising ways to enhance resistance to external influences [26–28], and the use of the size effect caused by the ceramics' grain size reduction was considered in [29] as one of the factors determining the radiation damage resistance growth. Also, the influence of size factors on the properties of lithium-containing ceramics was considered in [30], in which the authors, using the hydrothermal synthesis method and nanostructured powders, obtained the dependences of changes in microstructural properties, alongside the phase composition of lithium ceramics.



a)

b)

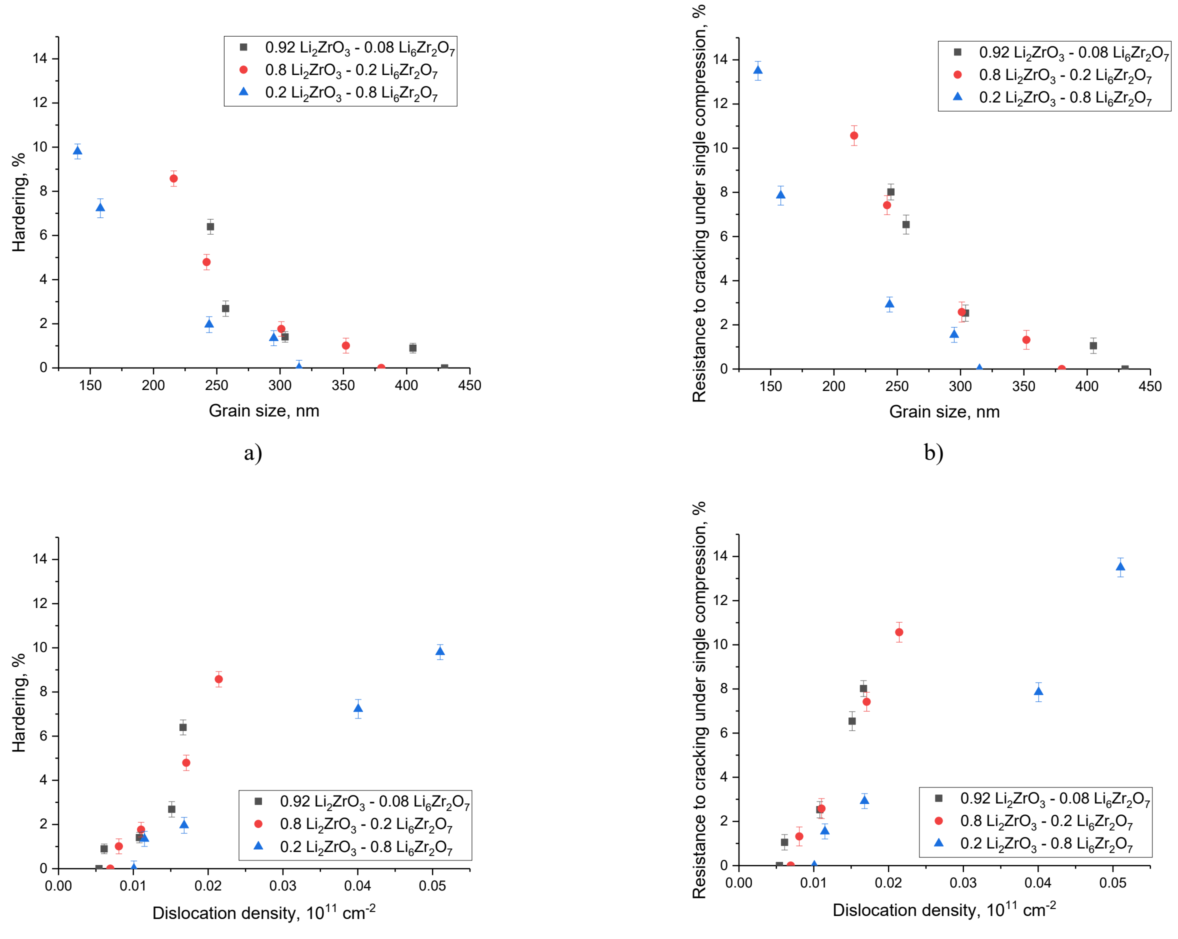
Figure 2. a) Assessment results of alterations in the hardness values of the ceramics under study contingent upon the phase ratio, alongside at the grinding speed alteration; b) Assessment results of the change in the maximum pressure that ceramics can withstand during a single compression at a constant speed for samples obtained at different grinding speeds, causing changes in grain sizes

Figure 2a reveals the hardness values of ceramic samples contingent upon the phase composition, as well as grain size, the change of which is due to variations in grinding conditions. As is evident from the data presented, variation in the phase composition of ceramics obtained at a grinding speed of 300 rpm (this speed was chosen as the starting point relative to which further comparison and calculation of hardening factors was carried out) results in hardness growth. Moreover, for 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ samples the hardness value exceeds 810 MPa, while for the other two samples the hardness values are less than 800 MPa, which indicates a positive hardening effect due to a change in the phase ratio in the ceramic composition. At the same time, it should be noted that the absence of changes in the phase ratio at different grinding speeds indicates that changes in hardness and cracking resistance for samples obtained at higher grinding speeds are due to size effects, as well as dislocation hardening. As can be seen from the presented data on the dependences of changes in hardness values on the grinding speed, and consequently, changes in grain sizes, in view of the established inverse relationship between grinding speed and grain sizes, it can be concluded that grain size reduction due to grinding speed growth leads to an elevation in hardness values. At the same time, the most significant alterations in hardness are observed at grinding speeds above 400 rpm, for which, according to the data presented in Figure 1a, the grain sizes are less than 250 nm, and in the case of 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics, the decrease in size is less than 200 nm. Moreover, according to the data obtained, a decline in grain size leads to an increase in hardness by an amount of about 6–10%, depending on the ratio of phases in the composition of the ceramics. From the data presented it can be concluded that with an elevation in the contribution of the $Li_6Zr_2O_7$ phase in the composition of ceramics, more pronounced changes in hardness are observed, due to both dimensional factors and the presence of interphase boundaries, the density of which is determined by the phase ratio. It is important to highlight that the observed growth in the hardness of ceramics depending on size factors is in good agreement with the results of [16, 31], in which the grain sizes were varied by addition of various additives, as well as by variation of the synthesis conditions. At the same time, in [32] it was shown that the use of lithium carbonate (Li_2CO_3) as an initial component makes it possible to increase the density of ceramics, alongside resistance to cracking, by more than 4 times, while maintaining the fine fraction in ceramics.

Figure 2b illustrates the assessment results of changes in the maximum pressure that ceramics can withstand during a single compression at a constant compression rate, reflecting the resistance of ceramics to cracking under external load. The data was obtained on a testing machine by determining the pressure at which the formation of cracks in the sample was recorded, the fixation of which was carried out using an extensometer, as well as determining the pressure drop (a sharp decrease at a constant compression rate). The results of tests for resistance to cracking have similar trends with changes in hardness values, which characterize a positive effect on increasing resistance to cracking under external mechanical influences, which is due to size effects associated with a decrease in grain size, and consequently, an increase in dislocation density. At the same time, the change in the maximum pressure that ceramics can withstand during a single compression is more pronounced for samples of 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics, which confirms the influence of the size effect and phase composition on the hardening and increase in the resistance of ceramics to external influences. It should also be noted that the trend of changes for all three types of ceramics depending on the grinding speed is preserved, which indicates the preservation of the effect of interphase boundaries, caused by a change in the phase ratio in the composition on the strengthening of ceramics. Moreover, in the case of high grinding speeds (above 400 rpm) for samples of 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics, more pronounced changes in the parameters of hardness and resistance to cracking are observed, which indicates that at small grain sizes, the presence of a large number of interphase boundaries has a positive effect on growth of resistance to external influences, which results in higher measured values.

The results of a comparative analysis of the effects of hardening (changes in hardness and the maximum pressure that characterizes resistance to cracking) in the form of dependences on grain sizes and dislocation density are shown in Figures 3a-d. The hardening factor was assessed by comparative analysis of the hardness values of ceramic samples obtained at a grinding speed of 300 rpm, which were chosen as the initial value, and samples obtained at higher grinding speeds. Similar calculations were carried out for the factor reflecting resistance to cracking under single compression, calculated by comparing the values of the maximum pressure at which crack formation is observed.

Analysis of these changes in hardening (increase in hardness) and resistance to cracking (changes in the maximum pressure that ceramics can withstand during a single compression) contingent upon the grain size shows the relationship that with a decrease in grain size, the effects of hardening become more pronounced. It should be noted that by comparing the presented values, it can be concluded that the size factor has a greater influence on resistance to cracking, since these values presented in Figure 3b have larger values than the hardening values presented in Figure 3a. This difference can be explained by the fact that during compression, the presence of interphase boundaries, as well as small grain sizes, lead to the appearance of the effect of dispersion hardening, which is caused by size effects. It should also be noted that for all the studied samples, the size effect of hardening is most pronounced when the grain size decreases to less than 250–270 nm, and in the case of larger grain sizes, small changes in the measured characteristics are due to the phase composition and the presence of interphase boundaries.



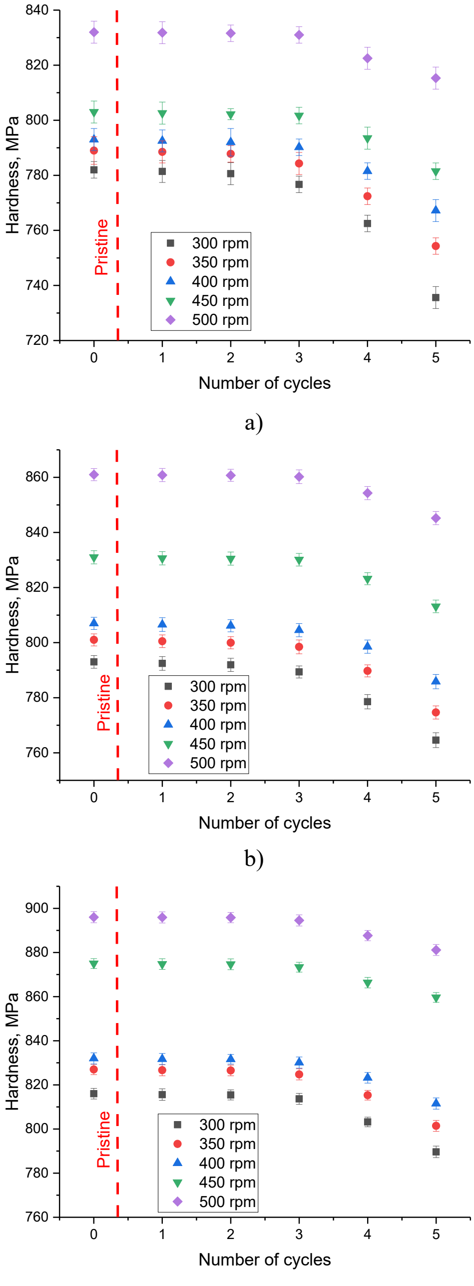
a) b) c) d)

Figure 3. Results of a comparative analysis of the observed strengthening effects associated with changes in the phase composition of the ceramics under study, alongside size factors caused by alterations in the grinding speed, and, as a consequence, grain sizes and dislocation density: a) results of changes in hardness depending on grain size; b) results of changes in resistance to cracking under single compression depending on grain sizes; c) results of changes in hardness depending on dislocation density; d) results of changes in resistance to cracking under single compression depending on the dislocation density

The general appearance of the presented dependences of alterations in hardening factors (changes in hardness and resistance to cracking under single compression) indicates a direct dependence of these values on the dislocation density, alongside the phase composition of ceramics. For samples with a low $Li_6Zr_2O_7$ phase content, the main changes are due to a reduction in grain sizes below 250 nm, which leads to an elevation in hardness and resistance to cracking by more than 5–10%, which indicates a fairly effective growth in strength parameters determined by dimensional factors, as well as changes in dislocation density. It should be noted that in the case of 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics, according to the data presented in Figure 3c-d, the most pronounced contribution to hardening is made by the phase composition of the ceramics, which dominates at large grain sizes (more than 250 nm). Moreover, for ceramic samples with similar grain sizes, the hardening effect is more pronounced (the values of ΔHV and resistance to cracking under single compression) are greater at lower dislocation density values than for 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics. As is known, the hardening mechanisms for two-phase ceramics are mainly due to effects associated with interphase boundaries and their features, which in turn are caused by size effects. In this case, the observed hardening effects for 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics are due to the presence of interphase boundaries, as well as a more pronounced reduction in grain size at grinding speed growth during mechanochemical solid-phase synthesis. In turn, the same type of crystal lattices of the Li_2ZrO_3 and $Li_6Zr_2O_7$ phases (both phases are characterized by a monoclinic type of crystal lattice) determines complete conjugation between particles of one phase, which are located in the matrix of the other phase, the content of which dominates in the composition of the ceramics. In this case, the observed effect of dispersion hardening with a decrease in particle size is most pronounced for samples of 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics, for which a change in grinding conditions (elevation in grinding speed) results in more pronounced grain size reduction (see data in Figure 1a).

Figures 4a-c and 5a-c present the results of changes in hardness and crack resistance (as a function of changes in the maximum compression pressure) during thermal cyclic tests simulating the effects of sudden temperature changes. Such tests are used to evaluate the resistance of ceramics to external influences during critical or emergency situations during operation, as well as thermal expansion processes resulting from sudden temperature changes.

The general appearance of the presented dependencies indicates that the most significant changes in strength parameters associated with a reduction in hardness and resistance to cracking are observed after three successive cycles of heat resistance tests, which indicates a fairly high stability of ceramics to sudden temperature changes, which are accompanied by the occurrence of thermal shocks in the structure, as well as destabilization of the crystal structure due to sudden changes in the amplitude of thermal vibrations. At the same time, from the presented dependences it is clear that a change in the phase composition due to the formation of $Li_6Zr_2O_7$ in the composition and a rise in its contribution leads to an elevation in resistance to a decrease in hardness and resistance to cracking, which is most pronounced when the $Li_6Zr_2O_7$ phase dominates in the composition of ceramics.

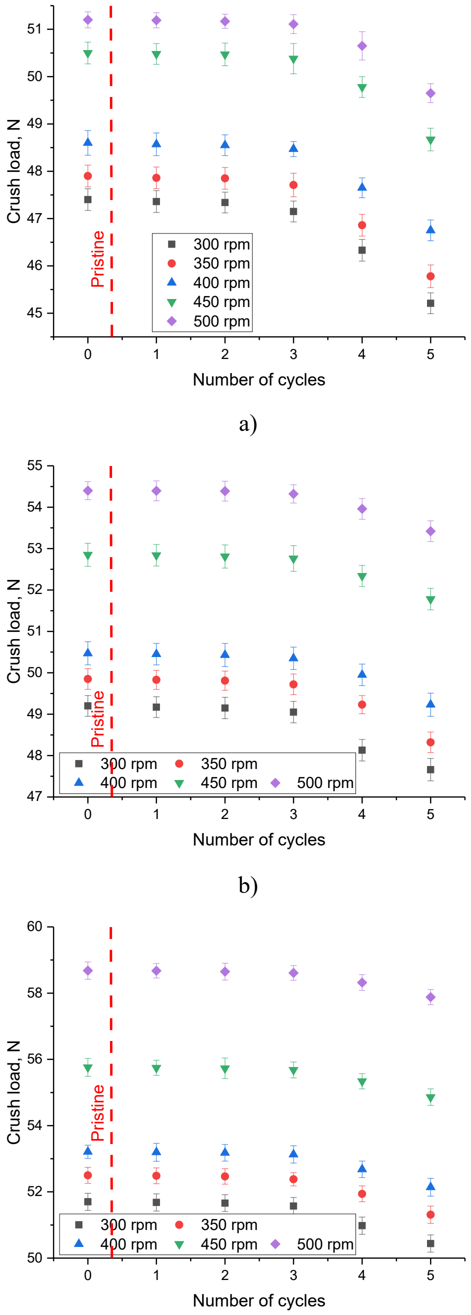


a)

b)

c)

Figure 4. Results of changes in the hardness of ceramics during cyclic tests for heat resistance (rapid heating and rapid cooling): a) 0.92 Li_2ZrO_3 : 0.08 $Li_6Zr_2O_7$ ceramics; b) 0.8 Li_2ZrO_3 : 0.2 $Li_6Zr_2O_7$ ceramics; c) 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics



a)

b)

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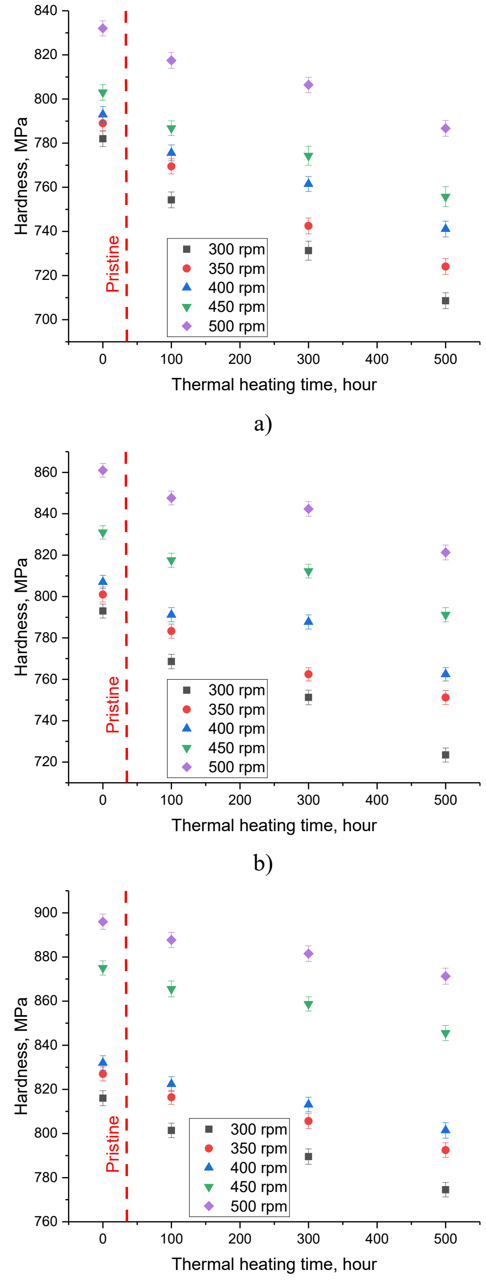
Figure 5. Results of changes in resistance to cracking (in the form of a dependence of changes in the maximum compression pressure) of ceramics during cyclic test tests for heat resistance (rapid heating and rapid cooling): a) 0.92 Li_2ZrO_3 *: 0.08* $Li_6Zr_2O_7$ *ceramics; b) 0.8* Li_2ZrO_3 *: 0.2* $Li_6Zr_2O_7$ *ceramics; c) 0.2* Li_2ZrO_3 *: 0.8* $Li_6Zr_2O_7$ *ceramics*

It should also be noted that the change in grain size, which is determined, as was previously shown, by the grinding speed, leads to an elevation in degradation resistance of strength characteristics, which consists in less pronounced trends in the decline in hardness values and resistance to cracking after 3 consecutive cycles of heat resistance tests. Small alterations for samples of 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics, especially for particle sizes less than 250 nm, are due to a combination of two factors influencing hardening: the presence of interphase boundaries and the size factor, a change in which results in the dislocation density growth. The presence of a high dislocation density, in combination with the presence of interphase boundaries, leads to an increase in resistance to thermal effects of the crystalline structure, which in turn is expressed in less pronounced changes in hardness and resistance to cracking with a large number of cyclic heat resistance tests. It is important to note that the presence of a large contribution of the $Li_6Zr_2O_7$ phase in this case determines not only higher hardness and crack resistance in the initial state, but also higher resistance to external influences, which is expressed in changes in the degradation trends of strength parameters presented in Figures 4c and 5c.

Figures 6a-c and 7a-c present the results of alterations in hardness and resistance to cracking during tests aimed at simulation of thermal aging processes. The general appearance of the presented dependencies reflects the change in the strength parameters of the ceramics under study, measured after 100, 300 and 500 hours of thermal exposure, and the reduction in values is due to high-temperature degradation of ceramics during prolonged thermal exposure.

As can be seen from the presented dependencies, changes in strength parameters (hardness and resistance to cracking) are most pronounced after 300 hours of sequential thermal exposure, while the decreasing trends have a clear dependence on both the phase composition of the ceramics and dimensional factors caused by variations in the grinding speed. The least pronounced changes associated with a decrease in the difference between hardness values and the maximum pressure that ceramics can withstand during a single compression are observed for samples whose grain sizes are less than 250 nm. In this case, changes in trends of the reduction of strength parameters are primarily due to size factors resulting in dispersion and dislocation hardening through the creation of barrier defects for the migration of point and vacancy defects, as well as processes of deformation expansion of the crystal structure as a result of prolonged thermal exposure. At the same time, it should also be noted that the smallest changes in the trends of the reduction of strength parameters are observed for samples of 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics, for which, in addition to dislocation hardening, the presence of interphase boundaries plays an important role in the growth of resistance to external influences, as well as the large contribution of the $Li_6Zr_2O_7$ phase in the composition of the ceramics.

Figure 8a-b demonstrates the assessment results of the relationship between changes in dislocation density in ceramics and softening factors associated with a decrease in hardness (see Figure 8a) and resistance to stress cracking (see Figure 8b) for ceramic samples subjected to heat resistance tests. The data are given for samples subjected to five heat resistance tests of the studied samples, at which the maximum reduction in strength parameters was observed.



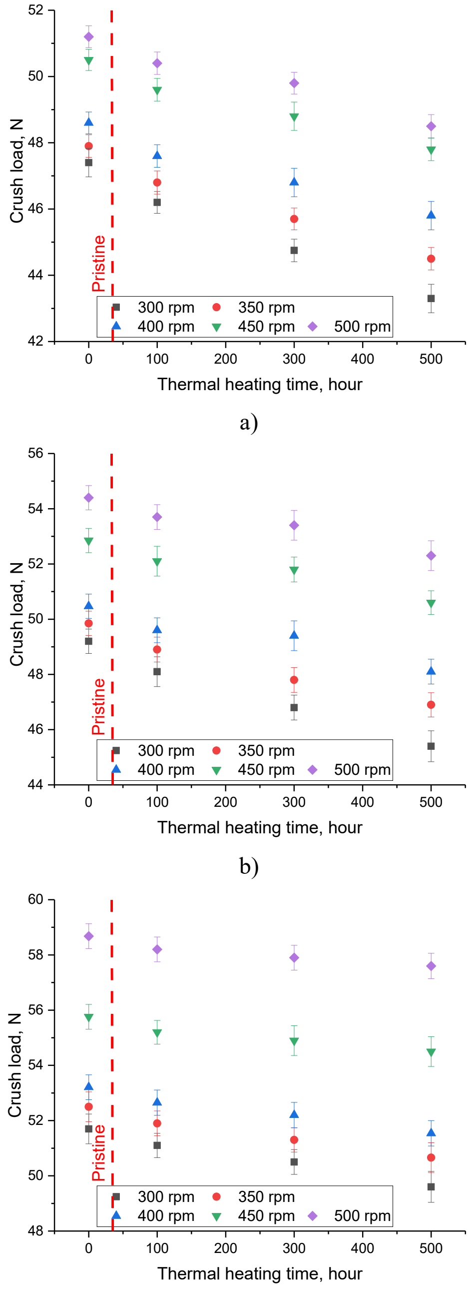
a)

b)

c)

Figure 6. Results of hardness changes during long-term thermal exposure tests simulating thermal aging processes:
a) 0.92 $Li_2ZrO_3 : 0.08\ Li_6Zr_2O_7$ *ceramics;*
b) 0.8 $Li_2ZrO_3 : 0.2\ Li_6Zr_2O_7$ *ceramics;*
c) 0.2 $Li_2ZrO_3 : 0.8\ Li_6Zr_2O_7$ *ceramics*

The general appearance of the presented dependences of changes in the values of degradation of strength properties, expressed in a reduction in hardness and resistance to cracking after five successive heat resistance tests, indicates the positive effect of an increase in dislocation density on growth of the resistance of ceramics to destructive embrittlement resulting from destabilization of the crystal structure as a result of sudden temperature changes. At the same time, the most pronounced changes in stability are characteristic of a dislocation density of 0.01–0.025×10^{11} cm^{-2}, which is typical for grain sizes less than 250 nm.

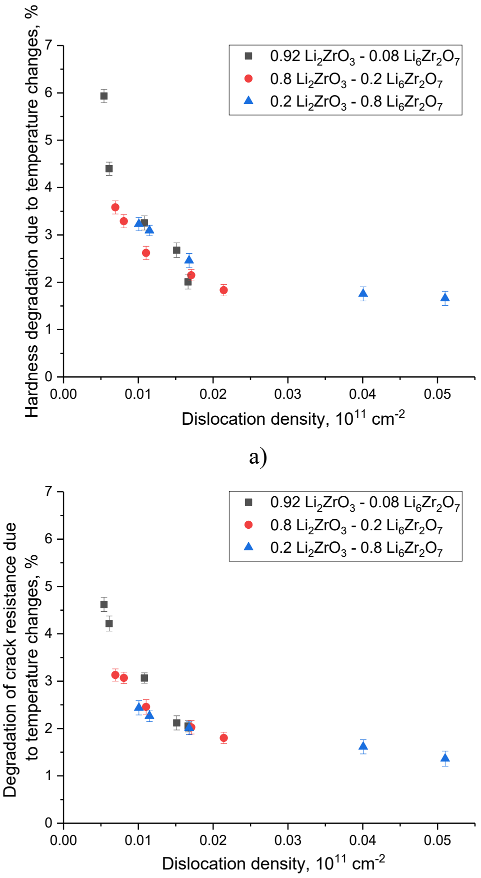


a)

b)

c)

Figure 7. Assessment results of changes in the values of the maximum pressure that ceramics can withstand during a single compression, subjected to thermal effects simulating thermal aging processes:
a) 0.92 $Li_2ZrO_3 : 0.08\ Li_6Zr_2O_7$ *ceramics;*
b) 0.8 $Li_2ZrO_3 : 0.2\ Li_6Zr_2O_7$ *ceramics;*
c) 0.2 $Li_2ZrO_3 : 0.8\ Li_6Zr_2O_7$ *ceramics*



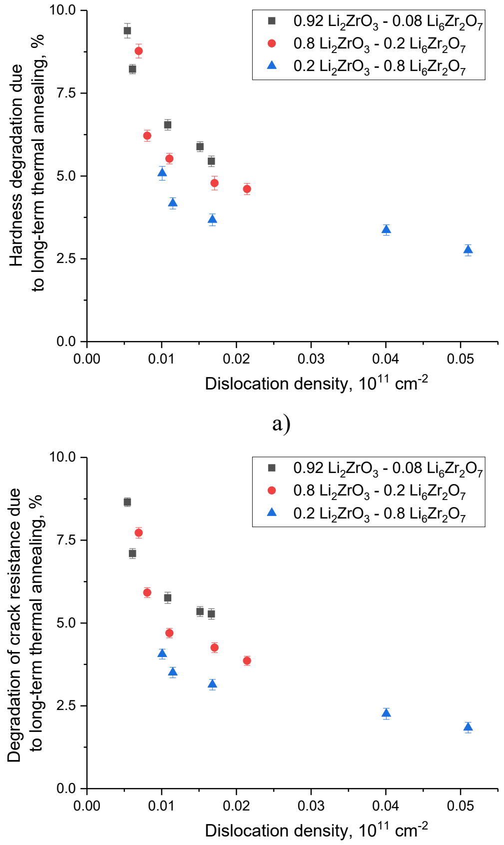
a)

b)

Figure 8. Results of a comparative analysis of experimental data to determine the thermal stability of the ceramics under study: a) relationship between changes in dislocation density and the degree of softening, which characterizes the decrease in the hardness of samples after heat resistance tests; b) relationship between changes in dislocation density and a decrease in resistance to cracking during single compression of samples after heat resistance tests

Figure 9a-b illustrates the results of a comparative analysis of the influence of dislocation density on the stability of strength parameters (hardness and resistance to cracking under single compression) during test tests simulating thermal aging during long-term thermal heating of samples. Data are given for samples kept at a temperature of 1000 °C for 500 hours.

It should be noted that the most pronounced alterations in strength parameters are observed when the dislocation density changes from 0.005 to 0.02×10^{11} cm^{-2}, which corresponds to a grain size reduction from 450–500 nm to 250–270 nm. In this case, a decrease in grain size leads to a more than 1.5–2-fold increase in degradation resistance of strength parameters caused by thermal effects on the crystal structure. At the same time, for samples of 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics, the reduction in size is less than 250 nm, for which the dislocation density is on the order of 0.04–0.05×10^{11} cm^{-2}, the increase in the stability of strength parameters is less pronounced, which may be due to the saturation effect, i.e., a less pronounced effect on growth of resistance to high-temperature degradation of a high dislocation density, the presence of which in turn has a positive effect on growth of hardness and resistance to cracking under external influences in the initial state.



a)

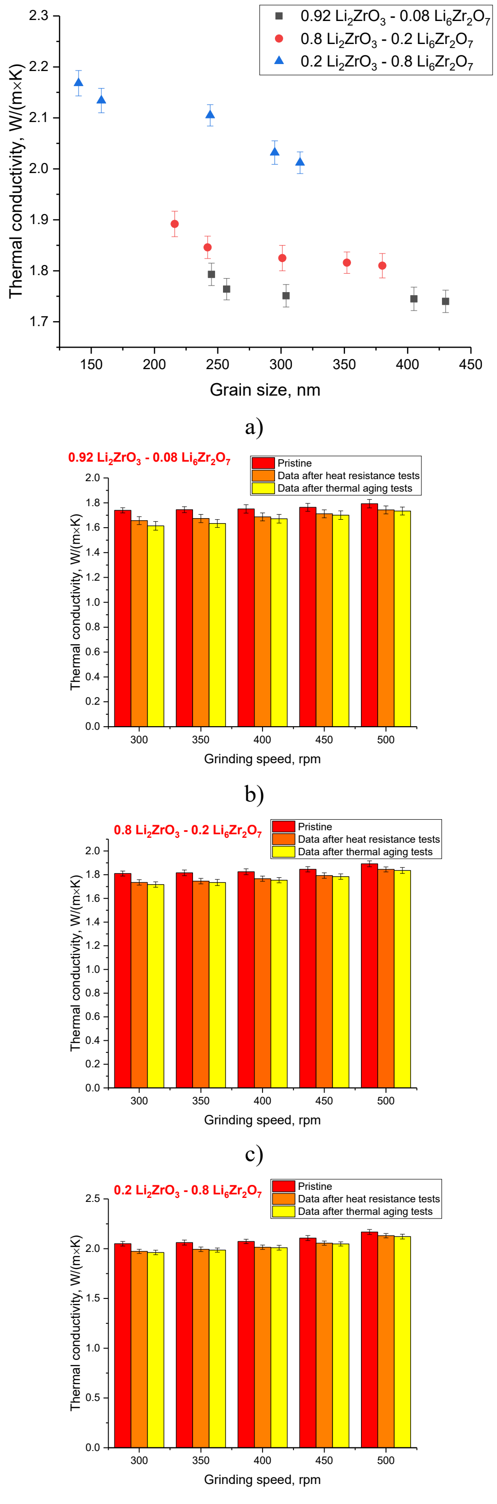
b)

Figure 9. Results of a comparative analysis of experimental data to determine resistance to long-term thermal heating, simulating thermal aging processes: a) relationship between changes in dislocation density and the degree of softening, which characterizes the decrease in the hardness of samples after thermal aging tests; b) relationship between changes in dislocation density and a decrease in resistance to cracking under single compression of samples after thermal aging tests

The obtained dependencies allow us to conclude that changing the phase composition of ceramics due to an increase in the contribution of the $Li_6Zr_2O_7$ phase in the composition, as well as a decrease in grain sizes, makes it possible to elevate resistance to external temperature influences, including sudden temperature changes, as well as long-term thermal exposure. Moreover, in the case of heat resistance tests, the presence of interphase boundaries, as well as dislocation density, leads to a growth in resistance to destructive embrittlement, characteristic of sudden temperature changes associated with changes in the amplitude of thermal vibrations, which cause deformation distortion of the crystal structure due to rapid heating and cooling. In this case, the high dislocation density, as well as interphase boundaries, inhibit the embrittlement effect due to barrier effects that inhibit the migration of defects and vacancies. With prolonged thermal exposure to the structure of ceramics, deformation distortions are associated with the effect of thermal expansion on the crystal lattice, as well as an increase in the migration of point and vacancy defects due to thermal exposure. In the case of a high dislocation density and the presence of interphase boundaries, migration processes are restrained, which leads to a decrease in the rate of structure degradation, and consequently, embrittlement and softening.

Figure 10a illustrates the results of a comparative analysis of changes in the thermal conductivity coefficient of the ceramics under study depending on the variation in grain sizes due to changes in the grinding speed, as well as the phase composition of the ceramics, changes in which are due to variations in the ratio of components during grinding. As is evident from the data presented, a change in the phase composition of ceramics, caused by an elevation in the contribution of the $Li_6Zr_2O_7$ phase in the composition of ceramics, leads to an increase in the thermal conductivity coefficient, which causes higher values associated with the thermophysical properties of this phase. Moreover, a general analysis of the presented changes depending on the grain size indicates that the most significant changes are observed at grain sizes below 250 nm. The absence of significant changes for ceramic samples with larger grain sizes indicates a small influence of size factors on changes in thermophysical parameters, since for these ceramics, due to their dielectric nature, the main mechanism of heat transfer is the phonon mechanism, based on heat transfer due to phonon scattering.

Figures 10b-d reveal the results of a comparative analysis of alterations in the thermal conductivity coefficient of the ceramics under study in the initial state and after testing for heat resistance (after 5 cycles) and thermal aging (after 500 hours), reflecting the influence of dimensional factors and phase composition of ceramics on maintaining the stability of thermal conductivity, the change of which occurs as a result of structural degradation. As is evident from the presented dependences, the most significant changes in the thermal conductivity coefficient, indicating degradation caused by structural changes resulting from thermal effects, are observed for samples of 0.92 Li_2ZrO_3 : 0.08 $Li_6Zr_2O_7$ ceramics. At the same time, the degradation degree has a clear dependence on the grain size, which consists in the fact that a reduction in grain size results in less degradation of the thermal conductivity coefficient, which indicates a positive effect of size factors on maintaining the stability of the thermophysical properties of ceramics. So, for example, in the case of 0.92 Li_2ZrO_3 : 0.08 $Li_6Zr_2O_7$ ceramics, with grain sizes of the order of 400 nm, the degradation of the thermal conductivity coefficient in the case of heat resistance tests is about 4.7%, and when tested for thermal aging for 500 hours at a temperature of 1000 °C, the degradation of the thermal conductivity coefficient is about 7.2%.



a)

b)

c)

d)

Figure 10. a) Results of a comparative analysis of changes in the thermal conductivity coefficient of ceramics depending on grain sizes; Results of a comparative analysis of changes in the thermal conductivity coefficient of the ceramics under study in the initial state and after heat resistance tests and thermal aging tests:
b) 0.92 Li_2ZrO_3 : 0.08 $Li_6Zr_2O_7$ ceramics;
c) 0.8 Li_2ZrO_3 : 0.2 $Li_6Zr_2O_7$ ceramics;
d) 0.2 Li_2ZrO_3 : 0.8 $Li_6Zr_2O_7$ ceramics

Moreover, for ceramics with grain sizes less than 250 nm, similar changes in the thermal conductivity coefficient are no more than 2.8% and 3.3%, respectively. It is important to highlight that in the case of the dominance of the $Li_6Zr_2O_7$ phase in the composition of ceramics, with small grain sizes, the decrease in the thermal conductivity coefficient during heat resistance and thermal aging tests is no more than 2% of the initial value, which indicates fairly high stability of the thermophysical properties of ceramics, which are determined both by the phase composition and by size and dislocation effects, which consist in growth of resistance to external influences due to dispersion and dislocation hardening and elevation in the resistance of ceramics to high-temperature degradation.

CONCLUSION

During studies of the influence of grinding speed on changes in grain sizes and dislocation density, it was found that the most significant changes are observed at speeds above 400 rpm, for which a more than twofold decrease in grain size is observed, due to an increase in the grinding intensity, as well as the formation of metastable states as a result of mechanical action. At the same time, the most pronounced effects are observed for samples in which the $Li_6Zr_2O_7$ phase dominates, the formation of which occurs due to a large amount of zirconium dioxide during the manufacture of ceramics. It has been established that a change in the phase composition of ceramics due to the $Li_6Zr_2O_7$ phase dominance, at grinding speeds of 450–500 rpm, results in reduction in grain size to 140–150 nm, which determines the dislocation density of the order of $0.04–0.05\times10^{11}$ cm^{-2}.

During tests for heat resistance and resistance to high-temperature aging as a result of long-term thermal exposure, it was found that a growth in dislocation density due to a grain size reduction leads to an increase in the stability of strength properties (changes in hardness and resistance to cracking under single compression), which results in smaller changes in hardness and crack resistance. At the same time, an important role in the stability of the strength properties of ceramics is played by the phase composition, the change in which is caused by an elevation in the contribution of the $Li_6Zr_2O_7$ phase in the composition, the dominance of which leads both to an increase in the values of hardness and resistance to cracking in the initial state, and to less pronounced trends in the degradation of these values as a result of thermal influences.

An analysis of changes in the thermal conductivity coefficient of the studied ceramics depending on the phase composition and grain sizes showed that in the case of initial values, the greatest contribution to the increase in the thermal conductivity coefficient is made by a change in the phase composition associated with an increase in the contribution of the $Li_6Zr_2O_7$ phase in the composition of the ceramics, while the size effect appears only for grain sizes less than 250 nm. It should be noted that a change in grain size for the ceramics under study in the case of thermal tests leads to an increase in stability to degradation of the thermal conductivity of the ceramic samples under study due to increased resistance to destruction of the crystalline structure of ceramics under thermal influence, which is due to the presence of dislocation and dispersion hardening.

Authors' contributions

I. E. Kenzhina *– conducting experiments, working out the modes of obtaining ceramics, characterizing structural changes.*

A. U. Tolenova *– conducting experiments, interpreting the obtained data, analyzing the state of the problem, processing the obtained results.*

A. L. Kozlovskiy *– conducting experiments, general analysis of the relationship between structural changes and strength parameters, determining the kinetics of material degradation.*

Acknowledgments

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ЛИТИЙ ҚҰРАМДАС КЕРАМИКАЛАРДАҒЫ ӨЛШЕМДІК ФАКТОРЛАР МЕН ФАЗАЛЫҚ ҚҰРАМНЫҢ СЫРТҚЫ МЕХАНИКАЛЫҚ ЖӘНЕ ТЕРМИЯЛЫҚ ӘСЕРЛЕРГЕ ТӨЗІМДІЛІГІНЕ ӘСЕРІН АНЫҚТАУ

И. Е. Кенжина[1,2], **А. У. Толенова**[1], **А. Л. Козловский**[1,2*]

[1] Қ.И. Сәтбаев атындағы ҚазҰТЗУ, Алматы, Қазақстан
[2] ҚР ЭМ «Ядролық физика институты» РМК, Алматы, Қазақстан

* *Байланыс үшін E-mail: kozlovskiy.a@inp.kz*

Бұл жұмыста дислокация тығыздығының өзгеруіне әкелетін өлшемдік факторлардың және литий метацирконаты негізіндегі екіфазалы литий құрамдас керамикалардың фазалық құрамының беріктік сипаттамалары мен жоғары температуралық сынақтарға төзімділігіне әсері зерттелген. Беріктік қасиеттерін және температуралық әсерлерге төзімділікті бағалау барысында күшейту факторлары ретінде өлшемдік эффект, дислокация тығыздығы және фазалар аралық шекаралардың болуы қарастырылды, олардың өзгерісі керамикалардың фазалық құрамының әртүрлілігі әсерінен туындайды. Зерттеулер барысында, ұнтақтау жылдамдығының 400 айн./мин-тан жоғары болуы дәндердің өлшемін екі еседен астамға азайтатыны анықталды, бұл өз кезегінде дислокация тығыздығын арттырып, қаттылық пен жарықшақтарға төзімділікті күшейтетін фактор болып табылады. Беріктік сипаттамаларын анықтау барысында керамика құрамында $Li_6Zr_2O_7$ фазасының басым болуымен фазалық құрамның өзгерісі микрожарықшақтардың таралуына тосқауыл болатын қосымша фазалар аралық шекаралардың көбеюі арқылы қаттылық пен жарықшақтарға төзімділікті арттыратыны анықталды. Ұзақ мерзімді термиялық күйдіру мен термиялық төзімділікке сынақ жүргізу нәтижесінде барлық үш түрдегі зерттелген керамикалар үшін дәндердің өлшемі 250 нм-ден аз болған жағдайда, дислокациялық күшейту мен фазалар аралық шекаралардың болуы есебінен беріктік қасиеттерінің нашарлауына төзімділіктің артатыны белгілі болды. Бұл әсер әсіресе құрамында $Li_6Zr_2O_7$ фазасы басым үлгілерде айқын көрінді.

***Түйін сөздер**: литий метацирконаты, екіфазалы керамика, дислокациялық күшейту, фазалар аралық шекаралар, қаттылық, жарықшақтарға төзімділік.*

ОПРЕДЕЛЕНИЕ ВЛИЯНИЯ РАЗМЕРНОГО ФАКТОРА И ФАЗОВОГО СОСТАВА В ЛИТИЙСОДЕРЖАЩИХ КЕРАМИКАХ НА УСТОЙЧИВОСТЬ К ВНЕШНИМ МЕХАНИЧЕСКИМ И ТЕРМИЧЕСКИМ ВОЗДЕЙСТВИЯМ

И. Е. Кенжина[1,2], **А. У. Толенова**[1], **А. Л. Козловский**[1,2*]

[1] КазНИТУ им. К.И. Сатпаева, Алматы, Казахстан
[2] РГП «Институт ядерной физики» МЭ РК, Алматы, Казахстан

* *E-mail для контактов: kozlovskiy.a@inp.kz*

В работе представлены данные исследования влияния размерных факторов, обуславливающих изменение дислокационной плотности, а также фазового состава двухфазных литийсодержащих керамик на основе метацирконата лития на прочностные характеристики керамик, а также устойчивость к высокотемпературным испытаниям. В качестве факторов упрочнения при оценке прочностных свойств, а также устойчивости к температурным воздействиям рассматривались размерный эффект, дислокационная плотность и наличие межфазных границ, изменение которых обусловлено эффектом вариации фазового состава керамик. В ходе проведенных исследований было установлено, что изменение скорости перемалывания выше 400 об./мин приводит к более чем двукратному уменьшению размеров зерен, что в свою очередь увеличивает дислокационную плотность, изменение которой является упрочняющим фактором для повышения твердости и трещиностойкости. При определении прочностных характеристик было установлено, что изменение фазового состава за счет доминирования фазы $Li_6Zr_2O_7$ в составе керамик приводит к увеличению значений твердости и устойчивости к растрескиванию за счет увеличения межфазных границ, которые служат дополнительными барьерами для распространения микротрещин при внешних воздействиях. В ходе проведенных экспериментов по определению устойчивости к длительному термическому отжигу и тестов на термостойкость было установлено, что уменьшение размеров зерен менее 250 нм для всех трех типов исследуемых керамик приводит к увеличению устойчивости к деградации прочностных свойств за счет дислокационного упрочнения, а также наличия межфазных границ, которое наиболее проявлено для образцов с доминированием фазы $Li_6Zr_2O_7$ в составе керамик.

Ключевые слова: *метацирконат лития, двухфазные керамики, дислокационное упрочнение, межфазные границы, твердость, устойчивость к растрескиванию.*