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Research Article

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STUDY OF THE EFFECT OF THE COMPONENT RATIO VARIATION IN TWO-PHASE CERAMICS ON THE RESISTANCE TO HIGH-DOSE PROTON IRRADIATION SIMULATING THE EFFECTS OF HYDROGEN SWELLING

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Abstract. *The paper presents the evaluation results of the destruction processes of the strength and thermal parameters two-phase lithium-containing ceramics subjected to high-dose irradiation with protons, the impact of which simulates the processes of hydrogen swelling. Interest in this research topic is primarily due to the possibilities of determining the influence of variation in the ratio of two components of lithium meta zirconate and lithium orthosilicate on maintaining stability and resistance to radiation damage, and diffusion processes associated with post-radiation isothermal annealing of samples, typical for simulation of desorption processes. During the conducted studies of the effect of the component ratio variation in two-phase ceramics on resistance to radiation-induced softening processes and reduction in crack resistance, it was determined that, unlike single-component ceramics, the combination of two phases in the composition leads not only to an elevation in the initial strength parameters, but also to a softening resistance growth due to the presence of interphase boundaries. In the case of testing the studied ceramics to thermal impact processes (thermal resistance tests), it was found that in the case of two-phase ceramics, a rise in the stability of maintaining strength properties to long-term temperature changes is observed.*

Keywords: hydrogen swelling; breeders; two-phase ceramics; high-dose irradiation; lithium meta zirconate; lithium orthosilicate.

1. Introduction

The use of alternative energy sources, including nuclear and thermonuclear energy, is the most promising way to solve global problems associated with the increase in global demand for energy consumption, as well as reducing the negative impact on the environment associated with the depletion of fossil resources, as well as the need to reduce the amount of harmful emissions that lead to the threat of global warming [1]. In the case of using nuclear energy to solve these problems, great emphasis is placed on the development of concepts for the use of new types of nuclear reactors, which consist of increasing the power and service life by changing the concept of nuclear fuel, as well as the use of materials capable of withstanding high temperatures [2]. When considering thermonuclear energy as an alternative energy source, much attention is paid to the use of the D-T fuel cycle, which includes the use of deuterium and tritium as the basis of thermonuclear fuel, the use of which allows for the production of large amounts of energy, as well as the almost complete absence of nuclear waste.

The concept of obtaining tritium to maintain the fuel D-T cycle in thermonuclear reactors is to produce tritium in a blanket containing lithium, the use of which is due to the possibility of obtaining tritium as a result of nuclear reactions of lithium with neutrons, the fission products of which are tritium and helium [3]. At the same time, for stable maintenance of the D-T cycle in a thermonuclear reactor, it is necessary that the tritium production coefficient in the blanket be greater than 1, which imposes a definition of the condition for ceramic materials of lithium-containing ceramics, the key one of which is a high lithium content in the composition. One of the most suitable types of ceramics containing a large amount of tritium are lithium orthosilicate ceramics (Li_4SiO_4), which, due to their structure, contain much more lithium than other types of ceramics, such as lithium titanate (Li_2TiO_3), lithium aluminate ($LiAlO_2$) or lithium metazirconate (Li_2ZrO_3). Also, an important role in the selection of blanket materials is played by their thermophysical properties, which determine the mechanisms for transforming the energy of incident fast neutrons into thermal energy, thereby reducing the risk of overheating effects, as well as reducing energy costs for plasma containment using electromagnetic forces [4-6]. It is important to highlight that the ceramic materials of the blanket, in addition to the above properties, must have sufficiently high indicators of resistance to destruction during the radiation damage accumulation, which is caused by both the impact of neutrons and fission products of nuclear reactions in the form of helium and hydrogen, the accumulation of which occurs in the near-surface layers of the blanket, due to the high mobility of these elements, alongside an increase in their diffusion at high temperatures, the maintenance of which is required by operating conditions, as well as the need to initialize the desorption processes of the formed tritium in the ceramics.

In view of this, in recent years, much attention has been paid to developments in the field of creating ceramic materials used as tritium breeders for blankets of thermonuclear reactors, the use of which will solve the problem of producing tritium, which is necessary to maintain thermonuclear reactions [7,8]. At the same time, the most intensive research in this area is aimed at finding optimal compositions of lithium-containing ceramics with high rates of chemical inertness and stability to mechanical impacts, high density of lithium in the composition, radiation resistance and resistance to the radiation damage accumulation caused by neutron irradiation, as well as the influence of nuclear reaction products in the form of helium and hydrogen. The most promising types of lithium-containing ceramics are considered to be two-phase ceramics with different phase contents [8], core-shell structures [9,10] or composite ceramics, which are substitution or interstitial solid solutions [11]. Among these types of lithium-containing ceramics, the most promising are two-phase ceramics obtained by various synthesis methods, such as sol-gel or hydrothermal methods [12], rolling methods [13], mechanochemical solid-phase synthesis combined with thermal annealing of samples [14,15]. Interest in them is due to the possibility of combining the properties of various components of lithium-containing ceramics, as well as the formation of interphase or dispersion strengthening effects arising due to size effects [16], as well as variations in the ratio of phases in the composition [17]. At the same time, despite a fairly large number of existing works in this area, interest in such studies does not subside, and the annual number of scientific publications on the topic of research related to the development of technology for obtaining lithium-containing ceramics, as well as the study of the processes of their interaction with ionizing radiation, including neutron, proton and alpha particles, only increases, which indicates the high significance of such studies due to the need to solve the problem of tritium production.

The main idea of this study is to determine the influence of variation in the ratio of lithium meta zirconate and orthosilicate components on the resistance to radiation damage associated with hydrogenation processes in the near-surface layer.

At the same time, the effect of the component ratio variation on resistance to hydrogenation processes was assessed by measuring the trends of hardness reduction, crack resistance and cracking under mechanical action, as well as the degradation kinetics of ceramics subjected to hydrogenation and subsequent thermal action, simulating thermal aging processes. In this case, long-term high-temperature heating initiates the processes of implanted hydrogen diffusion, which leads to its agglomeration in voids, thereby increasing the deformation distortion of the crystalline structure, which has a negative effect on the strength properties of ceramics. Also, the presented results of experimental work related to determining the influence of irradiation temperature on the degree of change in strength parameters caused by thermal expansion of the crystalline structure and more pronounced diffusion made it possible to establish the influence of variation in the ratio of components in two-phase ceramics on resistance to degradation.

The novelty of this study lies in determining the prospects for using two-component lithium-containing ceramics as blanket materials for tritium breeding, with the main emphasis in the study being placed on assessing the influence of hydrogenation processes on changes in the strength characteristics of ceramics.

2. Material and methods of research

Five types of ceramics were selected as objects for conducting studies related to determining the effect of varying the ratio of lithium orthosilicate and lithium metazirconate components on the resistance to hydrogen swelling and destruction of the surface layer under high-dose irradiation. Two of them are single-phase ceramics based on lithium metazirconate (Li_2ZrO_3) and lithium orthosilicate (Li_4SiO_4), as well as three types of two-phase ceramics obtained by varying the ratio of xLi_2ZrO_3 – $(1\text{-}x)Li_4SiO_4$ components at x equal to 0.75, 0.5 and 0.25 M. Moreover, in the work [18], published earlier by our research group, a detailed analysis and characterization of the strength and thermal physical parameters of these types of ceramics in the initial state with variations in the ratio of powder components was carried out, according to which it was determined that the most optimal compositions with the highest indicators of hardness, resistance to cracking under single compression, and crack resistance are two-phase ceramics with an equal ratio of components in the composition. At the same time, test trials of the radiation resistance of these ceramics to the accumulation of structural damage associated with high-temperature irradiation with He^{2+} ions showed that two-phase ceramics are more resistant to radiation damage caused by the accumulation of implanted helium in the surface layers, while single-phase ceramics have fairly low stability indicators of strength and thermal physical parameters to radiation damage [18]. Table 1 reveals the parameters of the strength and thermal characteristics of the studied ceramics obtained in [18], which were used as reference data for a comparative analysis of changes associated with the accumulation of radiation damage with variations in irradiation fluence. According to the data presented, an alteration in the ratio of components $(1\text{-}x)Li_2ZrO_3$ – xLi_4SiO_4 in the composition of ceramics leads to a change in the strength parameters, up to an equal ratio of components. At the same time, the dominance of Li_4SiO_4 in the composition of ceramics at concentrations above 0.5 M leads to a decrease in the strength parameters relative to the maximum values obtained for ceramics with an equal ratio of components in the composition. It is important to note that in the case of single-component ceramics, the strength indicators for Li_2ZrO_3 ceramics are higher than for Li_4SiO_4, which in turn indicates a higher resistance to external influences of lithium metazirconate in comparison with lithium orthosilicate, which was also confirmed by irradiating samples with He^{2+} ions [18]. According to the studies cited, the highest resistance to external influences under single compression and three-point bending are found in ceramics with an equal ratio of components in the composition, for which the increase in resistance is about 10 %. Such alterations in this case can be explained both by the effect of the presence of interphase boundaries and by dispersion strengthening, the presence of which is due to changes in the size of grains and the density of their packing, as shown in Figure 1. The morphological characteristics of the studied ceramics were measured using the scanning electron microscopy method, performed using a Phenom™ ProX microscope (Thermo Fisher Scientific, Eindhoven, Netherlands).

Table 1. Parameters of hardness, resistance to single compression, crack resistance, thermal conductivity coefficient

Paramater	**(1-x) Li_2ZrO_3 – xLi_4SiO_4 ceramics**				
	0	**0.25**	**0.5**	**0.75**	**1**
Hardness, HV	752±7	761±6	795±8	775±6	685±7
Crush load, N	44.5±1.4	48.7±1.8	51.6±1.7	47.2±1.3	34.5±1.6
Crack resistance, $MPa\times m^{1/2}$	1.65±0.14	1.71±0.09	1.94±0.11	1.82±0.12	1.67±0.13
Thermal conductivity, W/(m×K)	1.75±0.13	1.81±0.11	1.97±0.08	1.94±0.14	1.73±0.12

The influence of variation in the ratio of components in two-phase ceramics on resistance to hydrogen embrittlement and related processes of degradation of strength and thermal parameters was determined by simulation of the processes of implanted hydrogen accumulation due to irradiation with protons with an energy of 1 MeV and various irradiation fluences from 10^{15} to 10^{18} cm^{-2}. These fluences, according to the presented method of converting fluence into the value of atomic displacements (dpa) [19, 20], which is a universal parameter used to compare the values of radiation damage caused by different types of ionizing radiation, correspond to the range of 0.04 – 40 dpa, which, when converted to neutron flux, is about 10^{18} – 10^{22} neutron/cm^2 (for neutrons with an energy of more than 0.1 MeV).

The study of the mechanisms responsible for the reduction of the strength parameters (hardness, resistance to cracking, crack resistance) was carried out using standard methods for determining hardness by the indentation method, single compression of samples to determine resistance to crack formation, and determination of resistance to three-point bending to determine the value of crack resistance. Methods for assessing changes in strength characteristics used for lithium-containing ceramics are presented in [5].

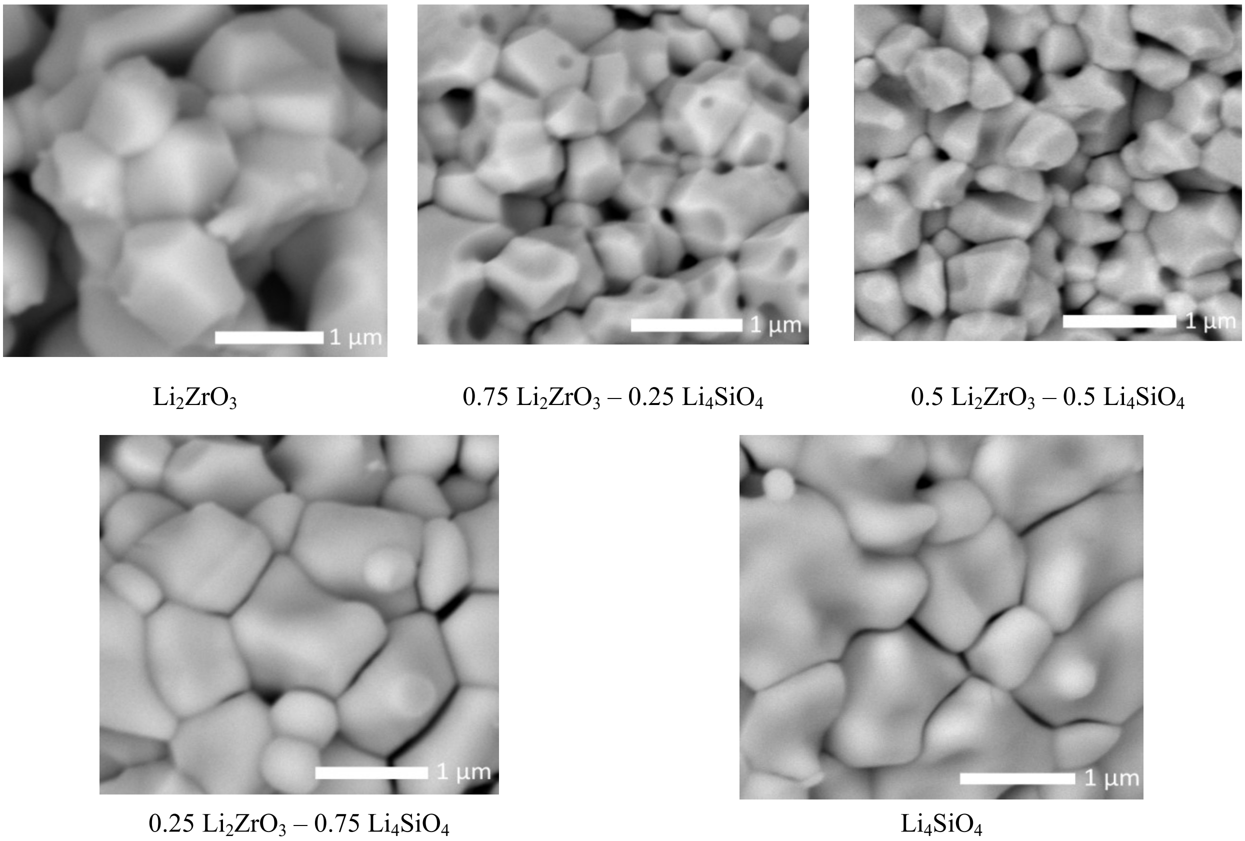


Fig. 1. Assessment results of the morphological features of the studied ceramics contingent upon the ratio of components in the composition, reflecting the influence of their variation on dimensional factors, as well as the possibility of forming the effect of dispersion hardening

In this case, the change in the ratio of components in the composition of two-phase ceramics leads to the formation of a structure containing both rhomboid grains of Li_2ZrO_3 and spherical grains characteristic of Li_4SiO_4, which have larger sizes. The observed strengthening effects in this case are due to the influence of the presence of interphase boundaries, which arise due to differences in grain sizes, as well as the formation of a structure of the type of larger grains of Li_4SiO_4, surrounded by a finely dispersed fraction of Li_2ZrO_3.

The thermal conductivity coefficient was measured by determining changes in the stationary heat flow using a universal thermal conductivity meter KIT-800 (KB Teplofon, Moscow, Russia).

The influence of the accumulated dose of proton irradiation on resistance to high-temperature effects (non-thermal resistance tests) was determined by rapidly heating the samples to a temperature of 1000 °C (heating rate 50 °C/min), holding for 1 hour at this temperature and abrupt cooling by removing the samples from the muffle furnace into the air. As a result of these manipulations with the samples, the effect of sharp temperature changes typical of emergency situations arising in critical situations during the operation of ceramic samples during abnormal situations is simulated. The number of tests was about 10 consecutive cycles, which made it possible to evaluate the degradation resistance of samples in the initial state and irradiated with fluences of 10^{16} and 10^{18} proton/cm^2. The results of these experiments made it possible to establish not only the kinetics of sample destruction under conditions characteristic of extreme situations during operation, but also to establish the effect of variation in the component ratio on the resistance of ceramics to thermal effects. All experimental work was carried out in several parallels in order to determine measurement errors and standard deviation, as well as the convergence of results. The experiments carried out allowed us to exclude factors that could have a negative impact on the project results, as well as to exclude inaccuracies in the data presented.

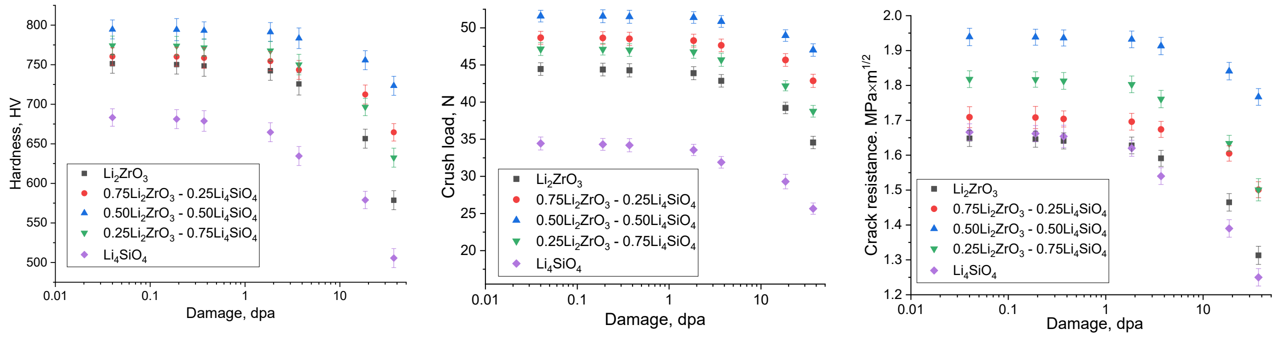
3. Results and discussion

The key parameters for using lithium-containing ceramics for tritium multiplication, in addition to the efficiency of multiplication and subsequent desorption of tritium, are their resistance to degradation of strength properties, the change of which can make significant adjustments to the service life. In this case, deterioration of resistance to external influences due to the accumulation of structural damage and defective inclusions, which in most cases are agglomerations of point defects and oxygen vacancies in the damaged layer, can lead to deterioration of tritium desorption processes, as well as their destruction due to loss of stability to external mechanical effects associated with compression of samples during thermal expansion. Also, an important role in determining the potential of application is played by the thermophysical parameters of the studied ceramics, the deterioration of which is caused, as a rule, by the processes of accumulation of disordered areas, creating additional barriers for phonon heat exchange mechanisms. In some cases, one of the factors that allows increasing the resistance of ceramics to external influences, as well as radiation damage, is the creation of interphase boundaries, due to the variation of the phase ratio, as well as the effect of dispersion strengthening, which occurs when the grain sizes decrease, and, as a consequence, the dislocation density increases. The combination of these factors allows not only to increase the mechanical properties of ceramics, as shown in Table 1, but also to increase resistance to external influences associated with the accumulation of structural damage resulting from the accumulation of the damage dose during irradiation.

Figure 2 demonstrates the assessment results of the change in the strength characteristics (hardness, resistance to cracking and crack resistance) of the studied ceramics depending on the irradiation fluence (recalculated for the value of atomic displacements). The general form of the presented dependencies reflects the degradation of the strength properties of the studied ceramics, as well as the influence of the variation in the ratio of components in the composition of two-phase ceramics on resistance to softening associated with the accumulation of structural damage. It should be noted that the measurements were carried out on a series of samples, which made it possible to establish the measurement error, as well as the values of the standard deviation, the values of which indicate the repeatability of the changes observed during irradiation, which also confirms the fact of the stability of the technological process for manufacturing ceramics according to the proposed production method.

As can be seen from the presented dependences of the change in strength properties on the magnitude of atomic displacements, the observed trends of changes indicate a difference in the trends of degradation of strength properties caused by the effect of accumulation of structural damage caused by proton irradiation and, as a consequence, a change in the magnitude of atomic displacements in the damaged layer. At irradiation fluences corresponding to the value of atomic displacements up to 1 dpa, the changes in the strength parameters are minimal and are within the permissible measurement errors, which indicates a high resistance of ceramics to softening at low irradiation doses (less than 1 dpa corresponds to a fluence range from 10^{15} to 5×10^{16} proton/cm^2). In this case, small changes in the strength parameters are due to the cumulative effect of structural distortions that appear during high-dose irradiation. While at low fluences, the resulting point and vacancy defects are able to relax, which leads to the formation of isolated structurally distorted areas in the damaged layer, the dimensions (in particular, the diameter and length), as shown in [21,22], directly depend on the type of interacting particles, as well as their energy. In the case of protons used for these experiments, due to their nature, the damaged areas have a large extended shape (more than 20 μm in size) and a diameter of less than 1 nm, which leads to their isolation from each other even in the case of sufficiently high irradiation fluences.

At the same time, according to a number of studies [23], the main structural defects in lithium-containing ceramics are E-centers associated with the formation of oxygen vacancies, while at high irradiation fluences (in atomic displacement values above 1-5 dpa), the accumulation of radiolysis products, i.e. complex defects associated with physicochemical processes, begins in the structure. In this regard, small changes in strength parameters at irradiation fluences below 5×10^{16} proton/cm^2 may be due to the effects of small structural changes caused by the formation of vacancy defects, the accumulation of which, together with the products of physicochemical radiolysis processes, leads to the formation of complex defects, the presence of which has a more significant negative effect on the change in strength parameters, expressed in a change in the trends of hardness reduction, the value of maximum pressure under single compression and crack resistance determined in three-point bending tests. In this case, it can be noted that the critical irradiation fluences, upon reaching which a change in the trends of changes in strength parameters is observed, is a value of about 10^{17} proton/cm^2. It is also important to reflect the fact that changes in the ratio of components in the composition of ceramics lead to a change in the trends of degradation of strength properties, which in turn indicates a positive dynamic of the effect of variation in the phase composition of ceramics on strengthening and an increase in resistance to radiation-induced destruction processes in comparison with single-phase ceramics.



a) b) c)

Fig. 2. Assessment results of changes in the strength parameters of (1-x)Li_2ZrO_3 – xLi_4SiO_4 ceramics subjected to proton irradiation: a) results of changes in the hardness of ceramics depending on the value of atomic displacements; b) results of the maximum pressure that ceramics can withstand during a single compression depending on the value of atomic displacements; c) results of changes in the crack resistance value determined by the three-point bending method depending on the value of atomic displacements

It is noteworthy that the critical irradiation fluence of the order of 10^{17} proton/cm^2, at which a nearly exponential nature of the decrease in the trends of strength parameters is observed, is in good agreement with a number of works related to the study of the processes of swelling of the near-surface layer of ceramics subjected to helium irradiation [24,25]. The similarity of the observed changes in this case can be explained by the fact that in both cases, at high irradiation fluences, agglomeration of implanted helium and hydrogen occurs in pores and voids due to diffusion processes and weak solubility of these types of ions, which in turn leads to the formation of gas-filled bubbles in the near-surface damaged layer, the deformation expansion of which leads to the destruction of the near-surface layer. In this case, as was shown in the work [26], the evolution of the processes of accumulation of products of nuclear reactions in the form of tritium, helium, hydrogen and their isotopes is accompanied by filling of voids in lithium-containing ceramics, with subsequent release of gas from these voids, which can be accompanied by deformation opening of these voids, as well as partial embrittlement of the surface layer. In this case, it can be concluded that the main observed changes in the reduction of strength parameters, as in the case of helium accumulation in the surface layer, are associated with the processes of deformation embrittlement caused by the effects of diffusion and agglomeration of hydrogen in voids with a subsequent increase in the deformation of the crystalline structure. It should also be noted that the observed differences in the trends of reduction in strength properties are primarily associated with a change in the ratio of components in the composition of ceramics, from which it follows that the formation of two-phase ceramics, especially in which the Li_4SiO_4 content is 0.25 and 0.5 M, leads to an elevation in resistance to softening caused by high-dose irradiation. In this case, the observed effect of growth in resistance to softening caused by the accumulation of structural distortions, and in the case of high doses of irradiation of the products of physical and chemical processes of radiolysis, is due to the presence of interphase boundaries, as well as dispersion hardening associated with changes in grain sizes (and, as a consequence, dislocation density). The observed effect of dislocation hardening associated with an increase in the resistance of ceramics to radiation damage caused by high-dose irradiation is in good agreement with the results of works [27, 28].

Figure 3 illustrates the dependences of the change in the softening factors of the parameters under study, caused by the influence of the destruction of the crystal structure, as well as the accumulation of structural damage caused by proton irradiation. The data presented in Figures 3a-c were obtained by comparative analysis of the values of the strength parameters of the irradiated samples with the values obtained for the samples in the initial state. In this case, the values of the softening factors are given in percentage terms, reflecting the dependence of the degradation of strength properties with the accumulation of structural damage in the samples under study. The general form of the observed changes in the softening factors indicates a two-factor effect of both the irradiation fluence (in this case, the magnitude of atomic displacements caused by irradiation) and the ratio of components on the stability of two-phase ceramics. In the case of a change in the irradiation fluence, and as a consequence, the magnitude of atomic displacements in the damaged layer, an exponential growth of the softening factors is observed, indicating a negative effect of accumulated structural damage on the strength parameters, which are most pronounced when the magnitude of atomic displacements exceeds 5 dpa. When this threshold value of atomic displacements is reached, in the case of single-phase (Li_2ZrO_3 and Li_4SiO_4) ceramics, a sharp increase in changes in the softening factors is observed. At the same time, comparing the observed changes, it can be concluded that the degradation of strength properties has a similar order of magnitude (the differences are less than 1 %), from which it follows that the accumulation of deformation distortions affects both the degree of resistance to external influences and a decrease in crack resistance, due to the formation of defective inclusions that create additional deformation stresses in the structure of the damaged layer. It should be noted that in the case of two-phase ceramics, the use of an equal ratio of Li_2ZrO_3 and Li_4SiO_4 components in the composition results in more than twofold increase in the resistance of strength parameters to degradation, according to the dependences presented in Figures 2 and 3. Such changes associated with the increase in the resistance of two-phase ceramics to the softening effect under high-dose irradiation can be explained by the presence of interphase boundaries, the change in the concentration of which, together with dispersion hardening (caused by size effects) leads to the creation of additional obstacles in the form of dislocations at grain boundaries, restraining diffusion processes. The observed effects of increasing resistance to high-dose irradiation, causing an increase in resistance to external influences due to the presence of interphase boundaries, are in good agreement with the results of [29,30]. It should also be noted that an increase in the concentration of the Li_4SiO_4 component to more than 0.5 M in the composition results in the hardening efficiency reduction, as in the case of lower concentrations of Li_4SiO_4 (less than 0.5 M), from which it follows that the optimal ratio of the components is 0.5 M Li_4SiO_4 and 0.5 M Li_2ZrO_3. According to the presented data for this type of ceramics, the maximum decrease in the strength parameters at an irradiation fluence of 10^{18} protons/cm^2 is no more than 10% of the initial value, while for single-phase ceramics the degree of softening at the maximum fluence is more than 20 %. At the same time, the general analysis of strength parameters indicates that the key role in determining the strength characteristics is played by the content of the Li_2ZrO_3 phase, a change in the concentration of which causes deterioration in strength properties due to lower strength indicators of Li_4SiO_4.

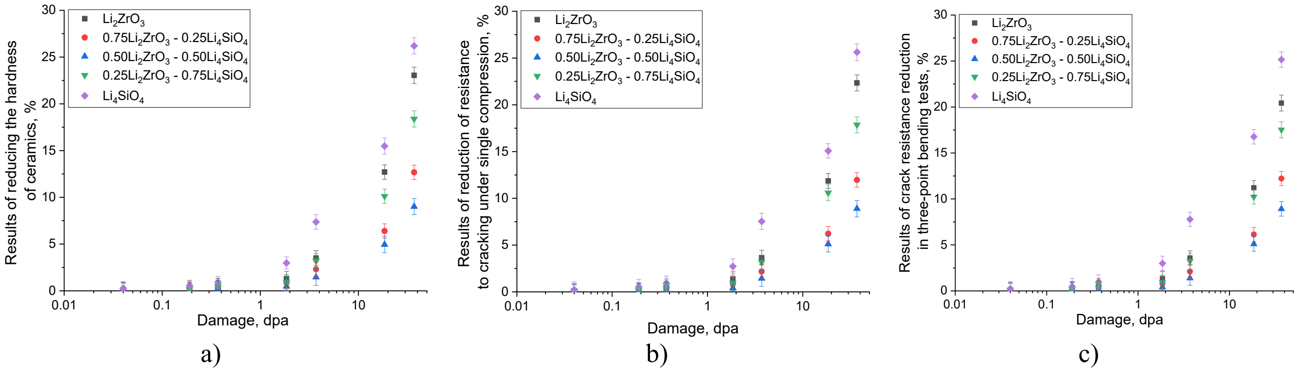


Fig. 3. Results of alterations in the softening factors of the main strength parameters: a) results of changes in the hardness value of ceramics, characterizing the softening of the near-surface layer; b) results of changes in the value of resistance of ceramics to single compression of ceramic samples; c) results of changes in the value of crack resistance of ceramics during three-point bending tests.

It should be noted that Li_4SiO_4 has a higher percentage of tritium yield among all lithium-containing ceramics under consideration [31,32], which makes it possible to conclude that the use of an equal ratio of components in two-phase ceramics makes it possible to establish a balance between the tritium production efficiency, as well as resistance to destructive changes in strength parameters as a result of high-dose irradiation. Figure 4 reveals the assessment results of changes in the thermal conductivity coefficient of the studied ceramics depending on the value of atomic displacements, obtained for different types of ceramics, in the case of variation in the ratio of components. The general form of the observed changes in the thermal conductivity coefficient contingent upon the value of atomic displacements has a similar trend, which is the case of the observed changes in the strength parameters, however, the nature of the changes, especially with high-dose irradiation, has a smaller order of magnitude (approximately, the changes in the thermal conductivity coefficient are two times lower than the changes in the strength parameters, see the comparison of the results presented in Figures 3a-c and 4b).

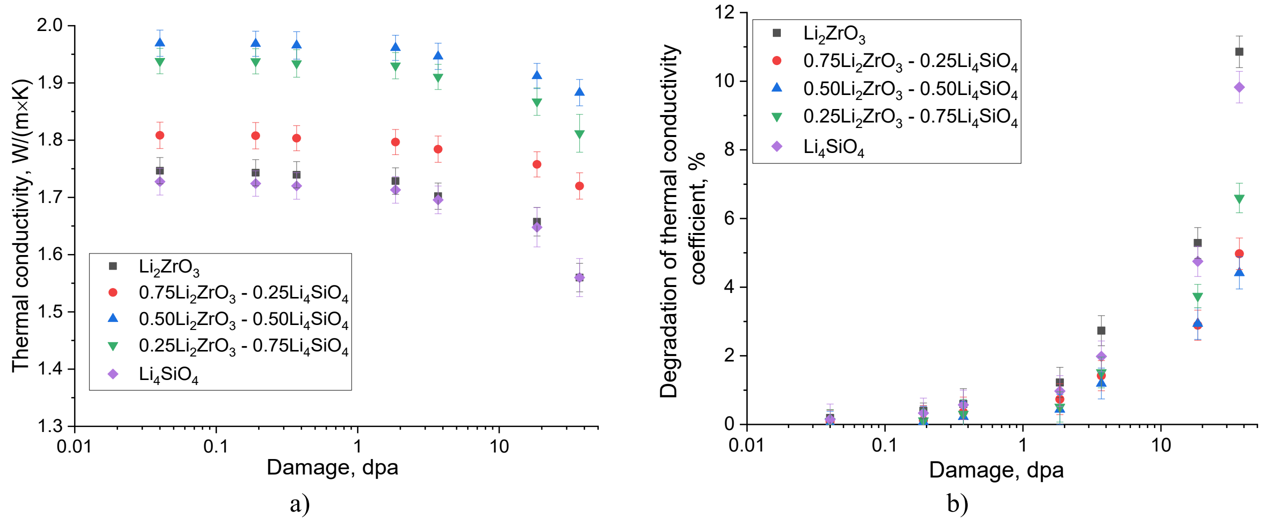
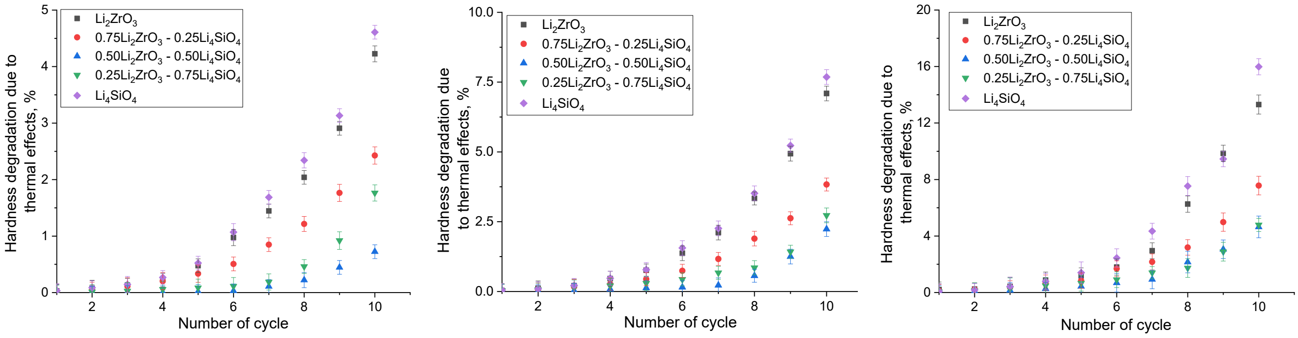


Fig. 4. a) Results of changes in the thermal conductivity coefficient of the studied ceramics depending on the value of atomic displacements; b) Evaluation of changes in thermal conductivity reflecting thermal conductivity degradation associated with disordering.

Moreover, as in the case of strength parameters, a change in the ratio of components in the composition of two-phase ceramics leads to an elevation in resistance to degradation of the thermal conductivity coefficient. Analysis of the observed changes in the thermal conductivity coefficient in comparison with the value of atomic displacements indicates that the most significant changes are observed when the value of atomic displacements exceeds 1 dpa, which corresponds to the effect of the emergence of complex defects in the structure of the products of physicochemical radiolysis processes. From which it follows that the formation of disordered regions and the accumulation of complex defects greatly affect the decrease in the rate of heat transfer due to phonon mechanisms, while an increase in the concentration of point and vacancy defects at low irradiation fluences does not seriously affect the change in thermophysical parameters. It should also be noted that the highest resistance to a decrease in thermal physical parameters is exhibited by 0.5 M Li_4SiO_4 - 0.5 M Li_2ZrO_3 ceramics, for which the decrease in the thermal conductivity coefficient at maximum irradiation fluence is less than 4 %, while for single-phase ceramics the degradation of the thermal conductivity coefficient is more than 10 % compared to the initial value. Such a difference in degradation values, as in the case of a change in strength parameters, is due to the effects of increasing radiation resistance due to the presence of two phases in the composition, which in turn restrain the processes of radiation embrittlement and softening due to the presence of a large number of grain boundaries that restrain the diffusion of structural defects, thereby preventing them from agglomerating into larger clusters or filling voids. Accordingly, interphase boundaries and increased dislocation density caused by fine grain sizes positively influence not only the strengthening mechanisms, but also the stability of thermophysical properties under degrading conditions.

Figure 5 illustrates the results of changes in the strength parameters of the studied ceramics contingent upon the number of heat resistance test cycles, which reflect the resistance of the samples to temperature changes, as well as the effect of the accumulated radiation dose (in units of atomic displacements) on the stability to softening caused by thermal effects. The data are presented for three series of samples in the initial (non-irradiated) state, as well as those irradiated with fluences of 10^{16} and 10^{18} proton/cm^2. The choice of these samples as objects of study for assessment of their resistance to thermal effects (sudden temperature changes) was based on the need to determine the influence of the value of structural damage at which the onset of a decrease in strength parameters is observed (at a fluence of 10^{16} proton/cm^2) and in the case when the degradation of strength properties is maximum in a given experiment (at a fluence of 10^{18} proton/cm^2).

The general appearance of the observed changes in hardness values (the graphs show the values of hardness changes after thermal testing with the initial values) indicates a destructive nature associated with thermal exposure, initiating the formation of metastable states in the composition of the samples, associated both with oxidation processes due to thermal exposure and with diffusion processes of implanted hydrogen and oxygen vacancies, the presence of which is due to the destructive effect of irradiation (in the case of irradiated samples), and in the case of initial samples, thermal expansion of the crystal lattice, initiating processes of migration of defects and vacancies in the structure.



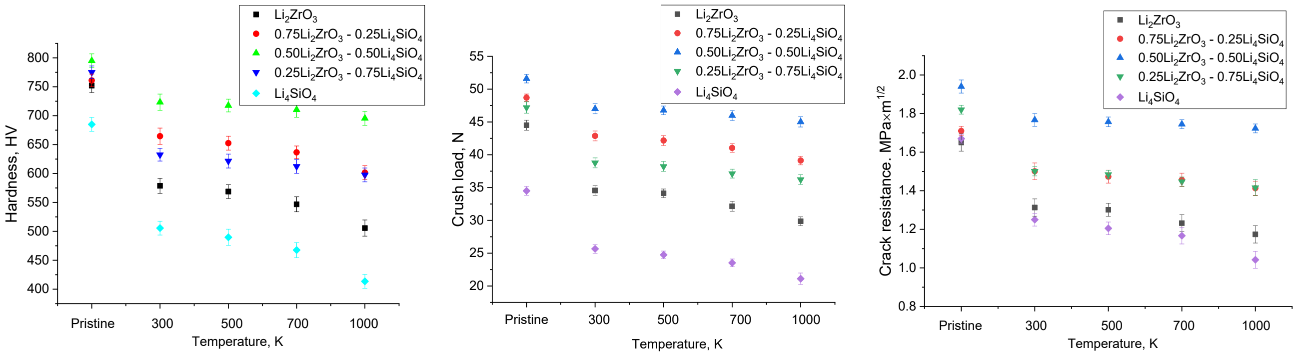
a) b) c)

Fig. 5. Test results of ceramics for heat resistance of the studied ceramics, reflecting the change in the hardness of the samples depending on the number of test cycles: a) test results of ceramics in the initial state; b) test results of ceramics irradiated with a fluence of 10^{16} ion/cm^2; c) test results of ceramics irradiated with a fluence of 10^{18} ion/cm^2

At the same time, the general analysis of the observed changes indicates that the thermal effect affects both the initial samples (non-irradiated) for which the maximum reduction after 20 cycles is about 4 – 5 % in the case of single-component ceramics, and 0.5 – 2 % in the case of two-phase ceramics, and the irradiated samples. Moreover, a change in the concentration of defects in the structure (in the case of a change in the irradiation fluence) results in more pronounced changes, indicating an intensification of the destruction processes due to temperature differences during thermal exposure. It should be noted that for two-phase ceramics, especially for samples with an equal ratio of components, the value of hardness changes after 10 test cycles is more than 3.5 – 4 times lower than for single-component ceramics, which indicates high resistance of these ceramics to external influences, including thermal expansion and oxidation, which causes a significant decrease in the rate of destruction. At the same time, in contrast to single-component ceramics, for which an intensive decrease in hardness is observed after 5 – 6 cycles, for two-component ceramics the most significant changes are observed after 7 – 8 cycles, which indicates not only higher resistance to external influences, but also a slowdown in degradation processes with long-term temperature changes.

One of the key factors influencing the assessment of the applicability of two-phase lithium-containing ceramics for tritium multiplication is their resistance not only to radiation damage, but also to temperature effects during irradiation. To test the studied ceramics for the resistance of strength characteristics to irradiation at various temperatures, the range of which was selected relative to the proposed operating regulations, the studied samples were irradiated with a fluence of 10^{18} proton/cm^2. In this case, irradiation was carried out at various temperatures, the range of which was from 300 to 1000 K. The results of the comparative analysis of the trends in the reduction of strength parameters depending on the irradiation temperature are presented in Figure 6 in the form of dependencies of the change in hardness parameters, the value of the maximum pressure under single compression and crack resistance of the studied samples depending on the irradiation temperature.

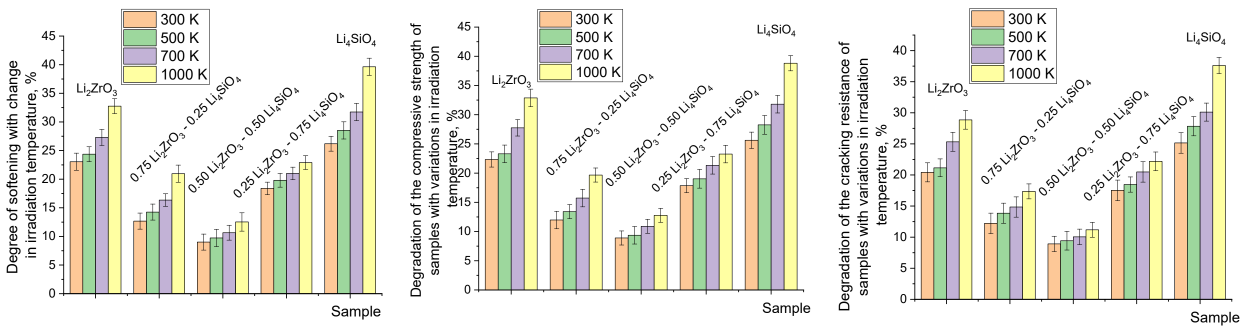
The general form of the presented dependencies indicates a negative effect of increasing the irradiation temperature on the stability of strength parameters in comparison with the initial values of strength indicators. At the same time, the downward trend is observed for all the studied types of ceramics, however, the dynamics of the decrease depending on the irradiation temperature at the same irradiation fluence for the studied single-phase ceramics in comparison with two-phase ones is more pronounced. Similar changes, as in the case of the presented dependences of the degradation of strength and thermal parameters under irradiation with fluence variation, indicate a positive effect of the influence of the presence of interphase boundaries and dispersion hardening caused by a change in grain size on the degradation resistance growth of ceramics exposed to irradiation.



a) b) c)

Fig. 6. Results of changes in the values of hardness (a), the value of the maximum pressure under single compression (b), crack resistance (c) of the studied ceramics subjected to proton irradiation with a fluence of 10^{18} proton/cm^2, with variations in the irradiation temperature (the graphs also show the values of the strength parameters in the initial state for the purpose of a visual comparison of changes with variations in the irradiation temperature)

Figure 7 illustrates the results of a comparative analysis of changes in softening factors (changes in hardness, resistance to cracking under single compression, and crack resistance) depending on the irradiation temperature for all the samples under study. The data are presented to identify the influence of temperature exposure on the degree of softening, as well as to determine the most stable ceramics to high-temperature irradiation. The analysis of strength parameter variations across different types of ceramics indicates that two-phase ceramics, especially those with an equal component ratio, demonstrate greater resistance to strength degradation compared to single-phase ceramics.



a) b) c)

Fig. 7. Results of changes in the softening factors of the main strength parameters of the samples depending on the irradiation temperature: a) results of changes in the hardness of ceramics, characterizing the softening of the surface layer; b) results of changes in the resistance of ceramics to single compression of ceramic samples; c) results of changes in the crack resistance of ceramics during three-point bending tests

As can be seen from the presented data on changes in the strength parameters of the studied ceramics, an increase in the irradiation temperature at one value of the accumulated fluence leads to an increase in the degradation of the strength parameters, with the most significant changes observed at high irradiation temperatures of about 700 – 1000 K. Such observed effects are caused by several factors, the combination of which leads to an acceleration of the degradation of the near-surface damaged layer, thereby reducing the strength indicators. Firstly, when the irradiation temperature varies, effects arise related to the temperature impact both on the crystal structure of the target and on the defects formed as a result of the interaction of incident particles with the electron and nuclear subsystems of the target. In this case, the thermal impact on the crystal structure of the target leads to the occurrence of effects related to the thermal expansion of the crystal structure (a rise in the volumetric and linear coefficients of thermal expansion), changes in the amplitude of thermal vibrations of atoms, which together results in greater mobility of atoms in the crystal structure of the ceramics.

The result of such changes may be effects associated with the migration of point and vacancy defects caused by thermal exposure, as well as lower resistance to external effects, which, during collisions of incident particles, due to the transfer of kinetic energy and its subsequent transformation into thermal energy, may lead to the formation of a greater number of defects than in the case of irradiation at room temperature. These results are confirmed by a direct dependence of the change in the values of degradation of strength parameters with an increase in the irradiation temperature, in the case of the same fluence values. In this case, the observed changes have an identical trend for all the studied types of ceramics with variations in the irradiation temperature with a difference only in the order of magnitude of the degree of degradation.

An elevation in the concentration of defective inclusions in the composition of the damaged layer initiates the growth of metastable highly deformed areas, which in turn leads to a decrease in resistance to mechanical impacts and a more pronounced decrease in crack resistance. Secondly, changing the irradiation temperature helps to accelerate the migration of implanted hydrogen, which, together with the formed oxygen vacancies, can lead to more intensive diffusion processes deep into the damaged layer, thereby increasing the thickness of the damaged layer, which has lower strength parameters, which also helps to accelerate the destruction processes and reduce strength properties.

It should also be noted that at high temperatures the process of agglomeration of small gas-filled cavities into larger ones is initiated due to migration and diffusion processes, which leads to an increase in the volume of these cavities due to their unification [33,34], and as a consequence, the initiation of processes of deformation distortion of the surface layer due to the creation of tensile deformation stresses caused by the pressure of gas-filled cavities on the crystalline structure of ceramics. It should be noted that for two-phase ceramics, the presence of interphase boundaries leads to the inhibition of these processes, which is clearly demonstrated in less pronounced changes in strength parameters, the difference of which, in comparison with single-component samples, is more than a two-fold growth in resistance to destruction at high irradiation temperatures. In the case of single-component ceramics, an increase in the irradiation temperature above 700 K results in more than 1.5-fold increase in the degree of destructive reduction in strength parameters in comparison with similar changes observed during irradiation of samples at room temperature (300 K), which indicates a negative impact of temperature exposure on the resistance of ceramics to radiation damage, and also imposes restrictions on the possibilities of using these ceramics in the case of high-temperature radiation exposure with high doses of damage.

4. Conclusion

Analyzing the obtained results of the dependences of the change in the strength and thermal physical parameters of the studied (1-x)Li_2ZrO_3 – xLi_4SiO_4 ceramics depending on the fluence of proton irradiation, the use of which is due to the processes of modeling the effects of hydrogenation, alongside the accumulation of products of the physicochemical processes of radiolysis that occur during high-dose irradiation, the following conclusions can be made.

The use of proton irradiation for modeling hydrogenation processes in the case of lithium-containing ceramics allows us to estimate the kinetics of changes in strength and thermal parameters depending on the dose of accumulated structural damage, which have different character of changes caused by variations in irradiation fluence. At low irradiation fluences, structural changes are caused by the formation of point defects and oxygen vacancies, to which, according to the presented data, the studied ceramics have fairly good resistance indicators, especially two-phase ceramics. At fluences above 10^{17} proton/cm^2, at which the initialization of physical and chemical processes of radiolysis occurs, an exponential decrease in strength parameters is observed, which is most pronounced for single-component ceramics.

According to the data presented, it was established that the formation of two-phase ceramics leads to a rise in radiation damage accumulation resistance during high-dose irradiation with protons, the accumulation of which results in acceleration of destructive embrittlement and softening processes (reduction of strength parameters). In the case of two-phase ceramics in which the Li_2ZrO_3 content is 0.75 and 0.5 M, the growth in resistance to destructive embrittlement and softening processes is more than two times compared to single-component ceramics. The results of heat resistance tests revealed that in the case of two-phase ceramics, an elevation in the number of test cycles has a lesser destructive effect on the reduction in hardness, the change of which is caused by oxidation processes that occur as a result of sudden temperature changes, as well as emerging metastable states, most pronounced for samples irradiated with fluences of 10^{18} proton/cm^2.

Analysis of the irradiation temperature effect of the studied samples of (1-x)Li_2ZrO_3 – xLi_4SiO_4 ceramics revealed that the presence of two phases in the samples results in suppression of the softening effects caused by the combination of thermal expansion of the crystal structure, as well as accelerated migration of defects in the samples. The increase in resistance in this case is due to higher resistance values of lithium metazirconate to thermal expansion, which, together with the presence of interphase boundaries, creates additional obstacles to softening of the samples due to the suppression of migration processes at the grain boundaries.

Conflict of interest statement.
The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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