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Using ion modification methods for targeted change of strength properties of near-surface layers of composite ceramics

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ABSTRACT
The use of ionic modification methods is one of the promising methods of directed change of strength properties of near-surface layers of materials along with such methods as magnetron sputtering and mechanically induced deformation. Interest in this area of research is primarily due to the possibility of enhanced resistance of materials to external mechanical and thermal influences, as well as improved wear resistance of refractory ceramics, which have great prospects in industrial use and metallurgy and reactor building. This paper presents the assessment results of the possibility of using the ion modification method by irradiating the near-surface layer of ZrO_2 – Al_2O_3 ceramics with low-energy Kr^{15+} and Xe^{22+} ions with energies of 300 and 440 keV to create a radiation-modified layer in the surface layer that is highly resistant to external influences. During the studies, it was found that irradiation with fluences of 10^{14} - 5×10^{14} ion/cm^2 for Xe^{22+} ions and 10^{15} ion/cm^2 for Kr^{15+} ions are optimal conditions for modifying the surface layer, as a result of which growth in wear resistance by 2.0 – 2.5 times and hardening by more than 15 – 20 % is observed compared to non-irradiated ceramics.

Keywords: hardening, ion modification, hardness and wear resistance enhancement, ZrO_2 – Al_2O_3 ceramics, low-energy ions.

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Introduction

Modern technological processes in metallurgy are accompanied by the operation of materials at high temperatures (1000 – 1300 °C), as well as thermal cycling processes (rapid heating and cooling), which can lead to thermal shocks, as well as accelerated degradation of strength properties, including due to temperature changes and exposure to aggressive environments [[1], [2]]. In this regard, the materials used in these technological processes must withstand heavy mechanical loads, and thermal shocks, and also be resistant to high-temperature corrosion and degradation processes that occur during long-term operation [[3], [4]]. To improve the productivity of technological processes, the use of composite materials, including high-entropy alloys based on refractory compounds or ceramic materials, has recently been proposed [[5], [6], [7]]. Interest in composite ceramics based on oxide or nitride compounds in the field of metallurgy and modern mechanical engineering is due to the possibility of creating materials that have a combination of properties such as a high melting point, allowing them to be used in extreme conditions (at high temperatures), high strength and wear resistance, increasing resistance to external influences, as well as insulating properties, including dielectric characteristics and thermal insulation (low thermal conductivity) [[8], [9], [10]]. At the same time, the combination of these properties allows to expand the capabilities of technological lines, as well as to increase the productivity of technological processes, which allows to reduce the cost of manufactured products. In addition to replacing traditional steels and alloys with refractory alloys and ceramics, various options are offered to increase the resistance of materials to external influences.

Thus, among the currently known methods for improving resistance to external influences, including mechanical damage caused by impacts or friction, one can distinguish methods based on the creation of highly deformed near-surface layers that have higher resistance to external influences [[11], [12], [13]]. The main hardening mechanism, in this case, is an increase in dislocation density in a small near-surface layer, the presence of which, together with small grain sizes, results in the creation of barrier boundaries that prevent the propagation of cracks and chips under external influence, and also increases resistance to corrosion and degradation. The mechanisms for creating such layers are different; for example, for steels and alloys, as a rule, they use deformation rolling methods, which, by acting on the near-surface layer, create additional structural defects in it that prevent the propagation of cracks or corrosion [[14], [15]]. Also, one of the promising methods for increasing stability is the method of laser processing of near-surface layers, which consists of surfacing protective coatings on the surface of materials by direct exposure of the surface to laser radiation [[16], [17]]. This method is based on sintering the surface with the applied material, thereby creating a protective layer with higher resistance to external influences. When using the method of magnetron sputtering of protective coatings, much attention is paid to the materials applied to the surface used as protective coatings or layers, due to the need to create good adhesive properties between the applied coating and the surface of the protected material, since the loss of adhesion of the protective coating to the surface of the samples can lead to their peeling or rapid destruction [[18], [19], [20]].

However, in the last few years, the use of ion irradiation methods for targeted modification of near-surface layers has been actively discussed. The method of ion modification or ion implantation itself has been known for quite a long time since it is based on the possibility of introducing impurity atoms into the near-surface layer of a material, the technology of introducing which is actively used to create semiconductor materials [[21], [22], [23], [24], [25]]. The main goal of ion implantation in this direction is to determine the possibilities of increasing the optical, conductive or luminescent properties of modified materials, which have great potential for use in modern materials science. At the same time, the use of ion modification methods, including irradiation with low-energy heavy ions (O, Ar, Kr, Xe with energies of the order of 200 – 500 keV) has recently been actively used to increase the resistance of materials to external influences, due to the creation of dislocation strengthening effects in the near-surface layer of the irradiated material, associated with the processes of deformation distortion and recrystallization (grain crushing) [[26], [27], [28]]. At the same time, the selection of irradiation conditions is important for carrying out such studies, since high-dose irradiation can initiate processes not only of hardening while maintaining a certain balance of deformation distortions but also in the case of accumulation of a large concentration of deformation stresses and distortions in the near-surface layer, it can initiate processes of surface peeling or partial sputtering. Similar effects are usually observed with high-dose irradiation and high concentrations of implanted atoms [[29], [30]].

The purpose of this study is to conduct experiments aimed at determining the possibilities of increasing the resistance to external influences of the surface layer of ZrO_2 – Al_2O_3 ceramics due to ionic modification by creating deformation distortions and recrystallization in the surface layer, leading to the initialization of dislocation hardening effects. Interest in this type of ceramics is primarily due to the possibility of combining high strength indicators and low thermal expansion of zirconium dioxide, as well as good thermophysical parameters of aluminum oxide. Moreover, the use of an equal stoichiometric ratio of these oxides during mechanochemical solid-phase synthesis makes it possible to obtain ceramics of the «Al_2O_3 matrix with embedded ZrO_2 grains» type [31], which creates additional strengthening due to the presence of interphase boundary effects [32].

The difference between this work and previously conducted studies is the possibility of using low-energy irradiation with heavy ions for targeted modification of composite ceramics in order to increase their resistance to external influences. At the same time, the emphasis in the study is on determining the effect of irradiation on changes in the strength characteristics of ceramics.

Experimental part

To assess the prospects of using the method of ion modification of the near-surface layer in order to increase the strength parameters, as well as resistance to external influences, including mechanical friction, pressure, and thermal effects, the following experiments were carried out, described below.

The objects of study were ZrO_2 – Al_2O_3 ceramics samples obtained by mechanochemical solid-phase mixing of initial oxides in an equal weight ratio (50: 50) followed by high-temperature sintering in a muffle furnace. Mechanochemical grinding of the initial zirconium and aluminum oxides was carried out in a planetary mill PULVERISETTE 6 (Fritsch, Berlin, Germany) at a grinding speed of 250 rpm and a time of 30 minutes. The choice of mixing conditions is determined by the need to obtain a homogeneous composition of ceramics that is isotropic by volume, without initializing processes associated with phase transformations as a result of the deformation mechanical action of the grinding media. The samples were sintered in a PM-1700 muffle furnace (Rusuniverstal, Chelyabinsk, Russia) at a heating rate of 10 °C/min. Upon reaching the set temperature of 1500 °C, the samples were kept for 8 hours, after which the samples cooled along with the furnace for 24 hours until they cooled completely and reached room temperature. After thermal annealing, the resulting powders were pressed into tablets with a diameter of about 10 mm and a thickness of 1 mm. The tablets were pressed in a special cylindrical mold under a pressure of 250 MPa for 30 minutes. After pressing, the resulting tablets were annealed at a temperature of 700 °C for 5 hours to remove the deformation distortions in the structure resulting from pressing.

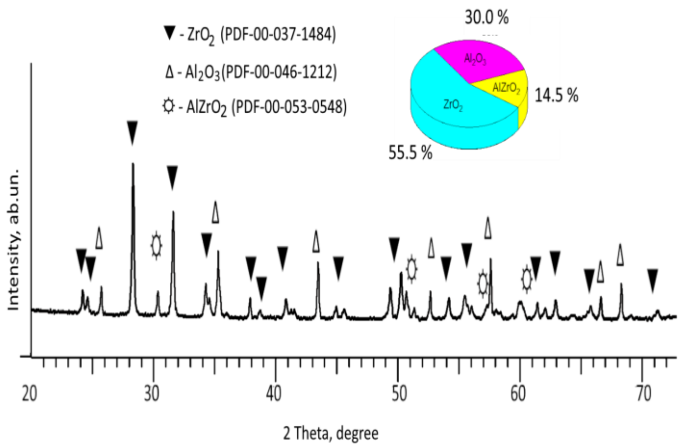
Characterization of the initial samples was carried out using X-ray phase analysis and scanning electron microscopy. X-ray phase analysis was used to determine the degree of structural ordering, the change in which as a result of ionic modification indicates the proportion of the defective fraction in the surface layer, as well as to determine the phase composition of ceramics synthesized using the thermal sintering method. A D8 ADVANCE ECO powder diffractometer (Bruker, Karlsruhe, Germany) was used to take X-ray diffraction patterns. The survey was carried out in the Bragg – Brentano geometry, in the angular range 2θ=20-75°. The determination of the phase composition of ceramics was carried out using the method of determining the weight contributions of diffraction reflections of each established phase with subsequent calculation of their share in the total diffraction pattern. To determine the phases, the PDF-2 (2016) database was used, from which the reference values of each phase and the positions of their main diffraction lines were taken.

The morphological features of the synthesized ZrO_2 – Al_2O_3 ceramics, in order to determine the grain distribution features or the mechanisms by which the ceramic structure is formed, were studied by obtaining images and element distribution maps, which were made using a Phenom™ ProX scanning electron microscope (Thermo Fisher Scientific, Eindhoven, the Netherlands).

Figure 1 reveals the results of characterization of the studied samples using X-ray phase analysis and scanning electron microscopy combined with mapping results. As can be seen from the presented X-ray diffraction pattern of the sample under study, the phase composition of ceramics is represented by a combination of three phases: the monoclinic ZrO_2 phase, the weight contribution of which is more than 55 %, the rhombohedral Al_2O_3 phase, the content of which is no more than 30 %, and the tetragonal $AlZrO_2$ phase, the weight contribution of which is about 15 %. The formation of the $AlZrO_2$ phase is associated with the initialization of polymorphic transformation processes in zirconium dioxide, the result of which is the formation of the tetragonal phase t-ZrO_2 with partial replacement of zirconium with aluminum. Moreover, a general analysis of the presented X-ray diffraction pattern indicates a fairly good structural ordering degree (more than 89%), and the presence of a tetragonal phase indicates that during thermal annealing in a given mode, the process of partial replacement of aluminum with zirconium is initiated, resulting in the formation of a new phase near grain boundaries.

As can be seen from the data presented in Figures 1c-d, which reflect the morphological features of the resulting ceramics, the choice of an equal weight ratio of ZrO_2 and Al_2O_3 oxides during their mechanochemical grinding and subsequent thermal annealing leads to the formation of ceramics of the «Al_2O_3 matrix with embedded ZrO_2 grains» type. It should be noted that ZrO_2 has a fairly large spread in size (the size range varies from 200 – 300 nm to 1.2 – 1.5 µm), and these grains form agglomerates consisting of three to four ZrO_2 grains embedded in an aluminum oxide matrix.

a)



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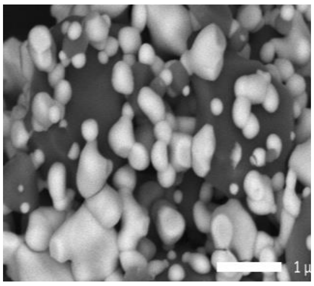

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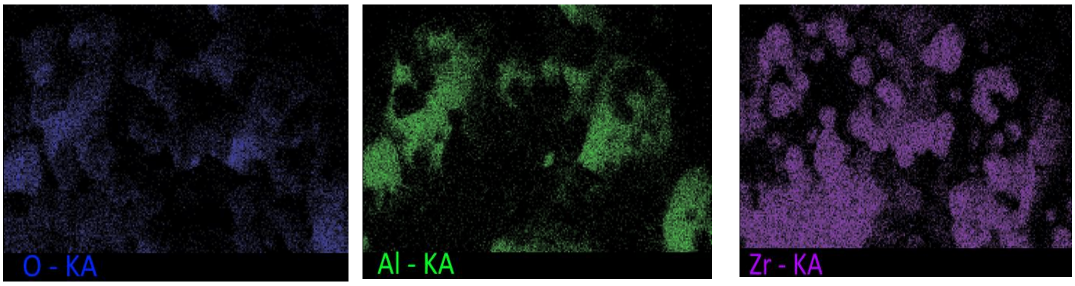
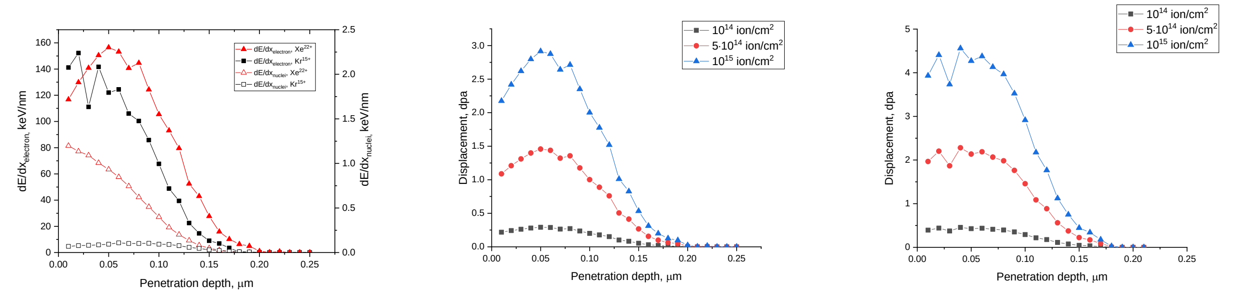


d)

Figure 1 - a) Appearance of samples after thermal annealing in the form of powder and in the form of tablets after pressing; b) The results of X-ray phase analysis of the studied ZrO_2 – Al_2O_3 ceramics, presented in the form of a diffraction pattern and a diagram of the relationship of the established phases; c) SEM image of ZrO_2 – Al_2O_3 ceramics, indicating the formation of a structure of the «Al_2O_3 matrix with embedded ZrO_2 grains» type; d) Mapping results reflecting the distribution of elements in ceramics

The ionic modification was carried out by irradiating the studied samples of ZrO_2 – Al_2O_3 ceramics with low-energy Kr^{15+} and Xe^{22+} ions with energies of 300 and 440 keV. The choice of ions for directional modification is determined by their sizes (ionic radii), as well as the magnitude of ionization losses (see data in Figure 2). Irradiation was carried out at three fluences: 10^{14}, $5×10^{14}$ and 10^{15} ion/cm^2. Irradiation fluences were selected to simulate the processes of deformation distortion of a near-surface layer with a thickness of about 200 – 250 nm, while the selection of irradiation fluences was chosen in such a way as to avoid the effect of sputtering of the near-surface layer as a result of the accumulation of structural changes in it during high-dose irradiation. Irradiation was carried out at the DC-60 heavy ion accelerator (Institute of Nuclear Physics of the Ministry of Energy of the Republic of Kazakhstan, Almaty, Kazakhstan). As can be seen from the presented data, the results of modeling the magnitudes of ionization losses of incident ions along the trajectory of motion, presented in Figure 2, the main contribution to the change in structural features in the surface layer is made by the ionization losses of ions during interaction with electron shells, thereby initiating ionization processes (changes in the distribution of electron density), and as a consequence the occurrence of athermal processes associated with deformation distortion of the structure. At the same time, the differences in the ionization losses of ions in interaction with electron shells are of the order of 15 – 20 keV/nm, while the difference in ionization losses in interaction with nuclei is about 1 order of magnitude, which indicates that during irradiation with Kr^{15+} ions, the main contribution to the changes is made by the interaction of ions with electron shells, while during irradiation with Xe^{22+} ions, the effects due to the interaction of ions with nuclei, especially near the surface, should be taken into account.



a) b) c)

Figure 2 – a) Simulation results of ionization loss values of Kr^{15+} and Xe^{22+} ions in the near-surface layer of ZrO_2 – Al_2O_3 ceramics based on data from the SRIM Pro 2013 calculation code;
b) Simulation results of the values of atomic displacement along the trajectory of ion movement in the near-surface layer of ceramic at irradiation with Kr^{15+} ions; c) Simulation results of the values of atomic displacement along the ion trajectory in the near-surface ceramic layer at Xe^{22+}

Figure 2b-c presents the results of calculations of the magnitudes of atomic displacements caused by the interaction of incident ions with the crystal structure of the near-surface layer and reflects the degree of structural disorder associated with knocking atoms out of positions, as well as deformation distortions arising from athermal effects. The calculation of the magnitude of atomic displacements was performed according to the method specified in [33]. As can be seen from the data presented, the most pronounced changes in the values of atomic displacements are observed upon irradiation with Xe^{22+} ions, the value of which is approximately 1.5 times higher than the similar values of atomic displacements arising during irradiation with Kr^{15+} ions. This difference can be explained not only by differences in the initial energy of the incident ions (for Xe^{22+} ions the initial energy is 440 keV), but also by the fact that during irradiation with Xe^{22+} ions, rather large values of ionization losses associated with interactions with nuclei, resulting in atomic displacement effects, as well as the formation of vacancy defects, are observed. For further description of the observed effects of changes in strength parameters, the maximum values of atomic displacements arising during irradiation with heavy ions will be used.

The study of the effect of ionic modification on the strengthening of the near-surface layer of ceramics was carried out using the method of nanoindentation in depth, to establish changes in the hardness values of the samples along the trajectory of ion movement with variations in the irradiation fluence. To carry out the research, a technique was used to determine the hardness of samples at different loads on the indenter, which makes it possible to carry out measurements at different depths of the sample. The load value was selected a priori in the range from 1 to 100 N. Measurements were carried out in several parallels to determine the isotropy of the strength characteristics, as well as determine the standard deviation and measurement error. Transverse sections were made by pre-pressing the samples in a mold, followed by cutting off the edges of the sample and polishing them.

Tribological tests to determine wear resistance under mechanical friction were carried out using a Unitest framework SKU UT-750 (Unitest, USA). As a method for determining the coefficient of dry friction, the “ball on disk” method was used, the load on the ball was 20 N, the sliding speed was 0.25 m/s, the number of cycles in the tests was about 15000 and was chosen to take into account the tests of the original sample, for which, after 10000 cycles, a sharp deterioration in wear resistance was observed (an increase in the dry friction coefficient was recorded). The silicon carbide ball was used as a counterweight during wear tests, and no wear of the ball was observed. The wear value was determined by measuring the wear profile obtained using the visualization method and then measuring the profile with a profilometer to determine the length of the path travelled. These alterations in the dry friction coefficient were recorded during each test, and the graphs show points after every 1000 tests, clearly demonstrating the change in wear resistance. The growth in wear resistance was assessed by comparing the values of the wear rate determined based on changes in the values of the dry friction coefficient at the beginning and at the end of the tests, and the resulting values were compared with each other.

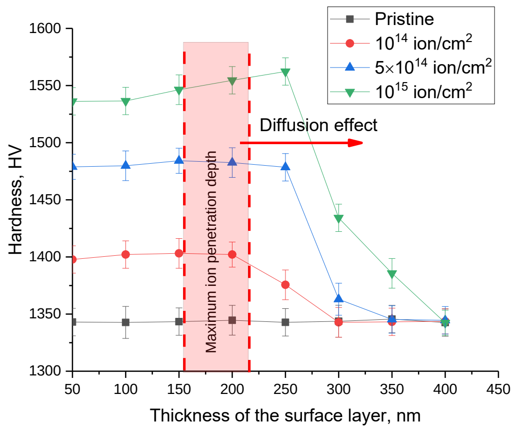
Determination of the resistance of modified ZrO_2 – Al_2O_3 ceramics to thermal cycling, which includes rapid heating of samples to high temperatures and subsequent sharp cooling, was carried out by conducting the following experiments. Samples of $ZrO_2 – Al_2O_3$ ceramics in the initial (non-irradiated) and irradiated state were subjected to rapid heating (heating rate 50 °C/min) to temperatures of 700, 1000 and 1200 °C, after which the samples were kept at a given test temperature for 1 hour, then the samples were removed from the muffle furnace into the air to initiate thermal shock processes. This procedure was carried out with the samples in the form of a sequence of tests (5 cycles); after each cycle, the hardness values of the surface layer were measured to determine resistance to thermal effects.

Results and Discussion

The most indicative parameters reflecting the influence of ionic modification on the strengthening of the near-surface layer are the values of hardness and wear resistance of ceramics, measured depending on the irradiation fluence. Moreover, in the case of hardness measurements, it is important to understand not only the general trend of changes in hardness but also the thickness of the modified layer, in which the hardness parameters differ from the base material.

Figure 3 shows the results of hardness measurements (Vickers) along the ion penetration depth (with a step of 50 nm), reflecting changes in the strength characteristics of ceramics depending on the irradiation fluence. Also, for comparison, the results of hardness measurements for the original (non-irradiated sample) are given, which reflect the isotropy of the strength parameters in depth.

The general appearance of the presented dependences of the change in hardness with depth indicates several effects associated with irradiation with heavy ions, which depend on both the type of ions and the irradiation fluence. The observed hardening (rise in sample hardness depending on the irradiation fluence) is in good agreement with the results of [[33], [34], [35]], in which the observed strengthening is explained by an elevation in dislocation density and the formation of dislocation loops, as well as, as a consequence, the formation of deformation distortions in the damaged layer caused by the accumulation of implanted ions. In this case, the observed strengthening can be explained by the fact that during the interaction of incident ions with the structure of the near-surface layer, due to the high values of ionization losses in the damaged layer, recrystallization processes can be initiated, accompanied by a change in crystallite sizes or orientation, which, as a consequence, result in an alteration in the dislocation density (its increase in the case of observed decreases in crystallite sizes, due to the inverse square dependence of the dislocation density on the crystallite sizes).



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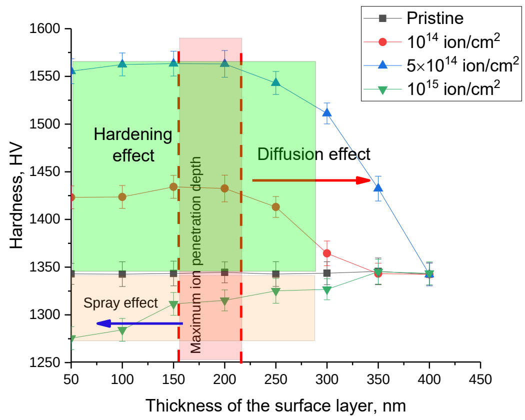
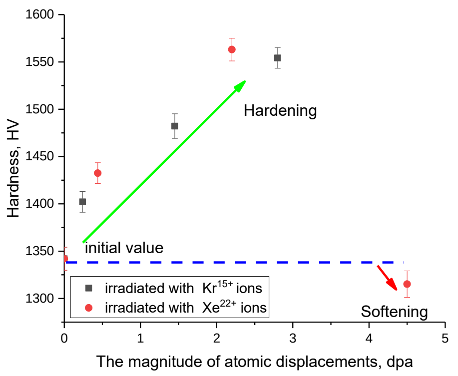


b)

Figure 3 - Results of evaluation of change in hardness value of $ZrO_2 – Al_2O_3$ ceramics by depth in case of heavy ion irradiation: a) when irradiated with Kr^{15+} ions; b) when irradiated with Xe^{22+} ions (the dotted lines indicate the region of maximum ion penetration depth in ceramics)

In the case of irradiation with Kr^{15+} ions, two effects can be distinguished in changes in hardness values, associated with the strengthening of the damaged layer, as well as diffusion effects, which lead to an increase in the thickness of the modified layer. Analysis of changes in hardness by depth demonstrated that an elevation in irradiation fluence leads to an expansion of the depth of the modified layer, which has higher hardness values than the base material. Such effects are caused by diffusion processes of ion penetration and consequences associated with their interactions in the form of cascade effects that can penetrate to a greater depth than the maximum ion penetration depth. In this case, an increase in the irradiation fluence, and, as a consequence, the magnitude of atomic displacements, leads to the fact that the number of structural changes occurring in the surface layer can have an impact at a deeper level as a result of cascade effects, which is in good agreement with the results of [36]. A general analysis of the observed changes in hardness values by depth showed that irradiation fluence growth from 10^{14} ion/cm^2 to 10^{15} ion/cm^2 in the case of irradiation with Kr^{15+} ions leads to an increase in the thickness of the modified layer by approximately 70 – 100 nm, while the hardening value decreases as the depth increases, which also confirms the diffusion nature of the propagation of structural damage deep into the material with increasing irradiation fluence [[37], [38]].



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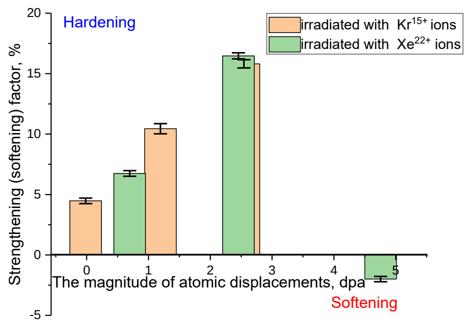


b)

Figure 4 - a) Results of a comparative analysis of changes in hardness values at the maximum (at a depth of 150 - 200 nm) upon irradiation with heavy ions Kr^{15+} and Xe^{22+}; b) Results of assessment of the factors of hardening (softening) of the surface layer of ZrO_2 – Al_2O_3 ceramics depending on the value of atomic displacements caused by irradiation

In the case of irradiation with Xe^{22+} ions, depending on the irradiation fluence, not only hardening effects are observed (at a fluence of 10^{14} – 5×10^{14} ion/cm^2), but also reverse effects associated with a decline in hardness in the damaged surface layer. Such a reduction can be explained by the effects of overstresses as a result of the accumulation of a large number of structural distortions in the near-surface layer, which can lead to deformation embrittlement and peeling of the surface under external mechanical influences, as well as partial sputtering of the near-surface damaged layer, an effect that is characteristic of high-dose irradiation [[39], [40]]. Moreover, in the case of irradiation with Xe^{22+} ions, the magnitude of the change in hardness at the same irradiation fluence in comparison with samples irradiated with Kr^{15+} ions is slightly larger, which indicates a more intense modification of the surface layer when irradiated with Xe^{22+} ions. This effect can be explained by differences in the values of ionization losses, which are significantly higher in the case of irradiation with Xe^{22+} ions. At the same time, the observed softening at an irradiation fluence of 10^{15} ion/cm^2 can be explained by the contribution to the structural changes from the effects of more intense accumulation of atomic displacements due to higher values of ionization losses of Xe^{22+} ions during interaction with nuclei.

Results of a comparative analysis of changes in the maximum hardness values of the samples depending on the value of atomic displacements are presented in Figure 4a.

According to the presented comparative analysis data, it is clear that the change in the hardness of the near-surface damaged layer of ZrO_2 – Al_2O_3 ceramic samples has a clear dependence on the value of atomic displacements, which is different for the two types of ions. In this case, we can conclude that the most effective way to modify the surface layer is irradiation with heavy Kr^{15+} and Xe^{22+} ions with fluences at which the value of atomic displacements is no more than 3 dpa. At the same time, for Kr^{15+} ions, this value is achieved at a fluence of the order of 10^{15} ion/cm^2, while in the case of irradiation with Xe^{22+} ions, the achievement of atomic displacements of the order of 3 dpa can be achieved at fluences of the order of 5 – 6×10^{14} ion/cm^2. It should also be noted that the use of Xe^{22+} ions with fluences below 10^{15} ion/cm^2 allows modification of the damaged layer at a greater depth (the depth of the modified layer in ZrO_2 – Al_2O_3 ceramics when irradiated with Xe^{22+} is about

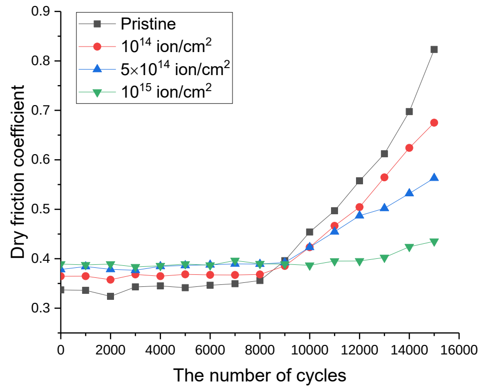
300 – 350 nm, taking into account diffusion effects).

Figure 4b reveals the results of the hardening (softening) value determined by comparative analysis of the hardness values in the initial (non-irradiated) state and the values obtained during irradiation with different irradiation fluences. The data is presented as a dependence of the change in the hardening factor as a percentage on the magnitude of atomic displacements, determined from the data presented in Figure 2b-c. The results presented in Figure 4b confirm the above assumption about the influence of the magnitude of atomic displacements on the strengthening of the near-surface layer of ceramics, according to which the most effective is irradiation with Xe^{22+} ions with fluences of 5 – 6×10^{14} ion/cm^2.

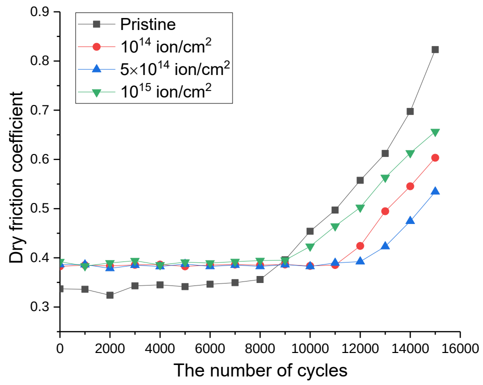
Figure 5 demonstrates the results of tribological tests of ZrO_2 – Al_2O_3 ceramics depending on the type of modification of the surface layer (in the case of varying the type of ion irradiation and irradiation fluence). The observed changes in the dry friction coefficient in the initial state when comparing the values for non-irradiated and irradiated ceramics indicate that ionic modification leads to a slight increase in the dry friction coefficient (no more than 3 – 5 %), which can be explained by the effects of changes in the morphological features of the surface of ceramics as a result of ion modification. As a rule, during low-energy irradiation, a change in morphology is caused by deformation extrusion of the damaged volume in the near-surface layer onto the surface in the form of hillock-like inclusions, which in turn can lead to an increase in friction and resistance during tribological tests.

The results of tribological tests revealed that the main changes for ZrO_2 – Al_2O_3 ceramics in the initial (non-irradiated) state are observed after 8000 – 10000 cycles, and consist in a sharp increase in the dry friction coefficient, which indicates surface degradation and a decline in wear resistance. At the same time, for samples modified with Kr^{15+} ions, irradiation fluence growth from 10^{14} ion/cm^2 to 5×10^{14} ion/cm^2 results in a decrease in the trend in the dry friction coefficient value, which indicates an increase in resistance to surface degradation under mechanical influences, and in the case of modification of fluences of 10^{15} ion/cm^2, in addition to reducing the trend of deterioration of the dry friction coefficient, there is also an increase in the number of test cycles in which changes in the dry friction coefficient are within the measurement error.

For ZrO_2 – Al_2O_3 ceramics modified with Xe^{22+} ions at fluences of 10^{14} – 5×10^{14} ion/cm^2, a similar decrease in the trend of changes in the dry friction coefficient is observed depending on the number of test cycles. Moreover, it should be noted that with an irradiation fluence of 5×10^{14} ion/cm^2, and in the case of irradiation with Kr^{15+} ions with an irradiation fluence of 10^{15} ion/cm^2, an increase in surface resistance to wear is observed over a greater number of cycles than under other irradiation conditions. At the same time, samples of ZrO_2 – Al_2O_3 ceramics irradiated with Xe^{22+} ions with a fluence of 10^{15} ion/cm^2, as in the case of hardness determination, during tribological tests show a negative trend due to the lower stability of the ceramic surface associated with a destructive change in structural properties at a high concentration of atomic displacements.



a)



b)

Figure 5 - Results of tribological tests of ZrO_2 – Al_2O_3 ceramics: a) when irradiated with Kr^{15+} ions; b) when irradiated with Xe^{22+} ions

Figure 6 shows the results of the specific volumetric wear of the surface of ZrO_2 – Al_2O_3 ceramics as a result of tribological tests, determined based on changes in the dry friction coefficient before and after cyclic tests.

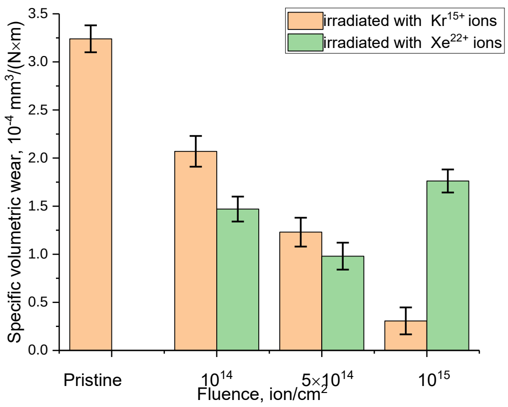
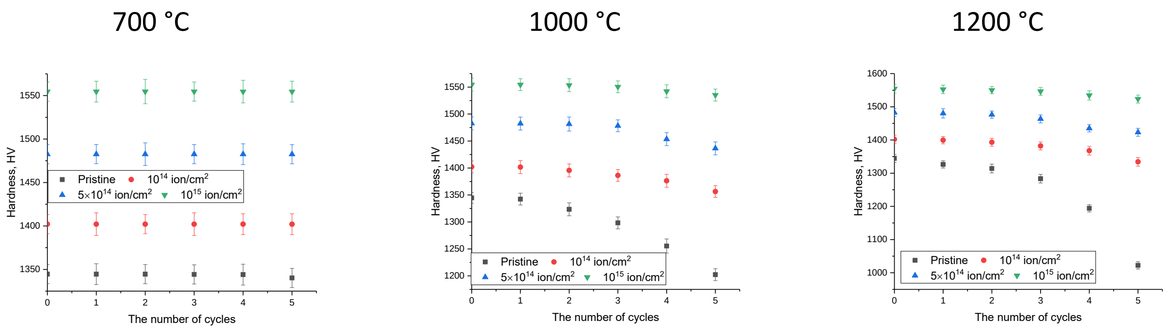
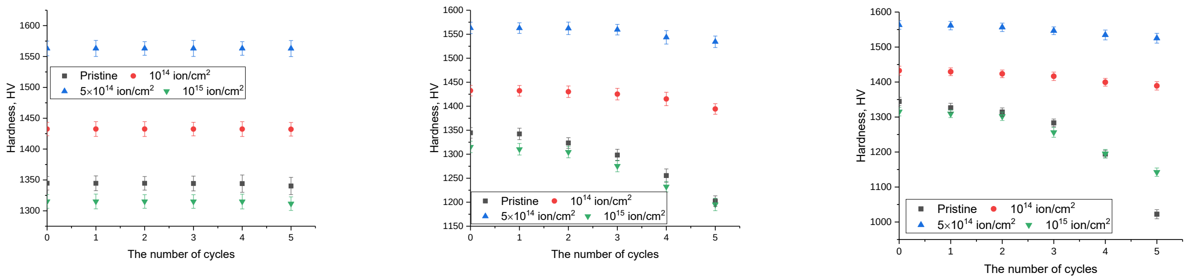


Figure 6 - Results of a comparative analysis of the specific volumetric wear of the surface of $ZrO_2 – Al_2O_3$ ceramics as a result of tribological tests



a)



b)

Figure 7 - Results of experiments on thermal cycling of ceramics depending on irradiation conditions: a) when irradiated with Kr^{15+} ions; b) when irradiated with Xe^{22+} ions

Analysis of the specific wear of the surface as a result of tribological tests showed that ionic modification with fluences of $10^{14} – 5×10^{14}$ ion/cm^2 leads to an increase in wear resistance, which is due to dislocation strengthening of the near-surface layer. Moreover, in the case of samples of $ZrO_2 – Al_2O_3$ ceramics irradiated with Kr^{15+} ions, the reduction in the specific wear volume is more than 2 – 2.5 times compared to the original (non-irradiated) ceramics, which indicates the high prospects of using ion irradiation to increase the strength and wear resistance of the ceramic surface.

Figure 7 demonstrates the assessment results of changes in the hardness of $ZrO_2 – Al_2O_3$ ceramics as a result of thermal cycling at different test temperatures (700, 1000 and 1200 °C) depending on the number of test cycles.

As can be seen from the data presented, there are practically no changes in hardness depending on the number of thermal cycling cycles, there are practically no significant changes at a temperature of 700 °C for all studied samples, regardless of the type of ion exposure, which indicates a fairly high resistance of ceramics to thermal shocks at this temperature. It is worth to note that a slight decrease after 4-5 test cycles at a given temperature can be explained by a low degradation degree of the surface layer, but this decrease is less than 0.5 %, which is within the permissible error. Growth in the temperature of thermal cycling tests to 1000 – 1200 °C in the case of original (non-irradiated) ceramics results in a decline in hardness values after 2-3 test cycles and a sharp deterioration in strength characteristics after 5 test cycles. So, after 5 cycles of tests at a temperature of 1200 °C for the initial samples, the decrease in hardness is more than 20 %, which indicates degradation of the resistance of ceramics to mechanical stress. Moreover, in the case of ion modification, a less pronounced trend of decrease in hardness is observed during thermal cycling tests, which indicates the positive effect of the presence of a radiation-deformed layer, which prevents oxidation processes of the surface layer as a result of temperature changes, as well as during interaction with the atmosphere in the case of rapid removal of samples from the furnace chamber into the air.

Figure 8 shows the results of a comparative analysis of changes in the softening degree of ceramics in the original (non-irradiated) and irradiated ceramics, reflecting a decrease in the stability of the strength properties of ceramics with changes in thermal cycling conditions (with an increase in the number of cycles and temperature). The softening degree was assessed by comparing the hardness values of the ceramics in the initial state (before thermal cycling) with the hardness value after each test cycle.

As can be seen from the results of the degree of softening to thermal cycling processes and the accompanying oxidation processes of the surface layer when interacting with air, ceramics are least resistant to high-temperature thermal shocks at 1200 °C, at which successive thermal cycling leads to accelerated degradation of the hardness of the surface layer. In the case of modified ceramics, the decrease in hardness after 5 consecutive cycles of thermal cycling at temperatures of 1000 °C and 1200 °C is about 2-5 % (with the exception of ceramic samples irradiated with Xe^{22+} ions), which indicates fairly high resistance of ceramics to external influences and thermal shocks that may occur during operation.

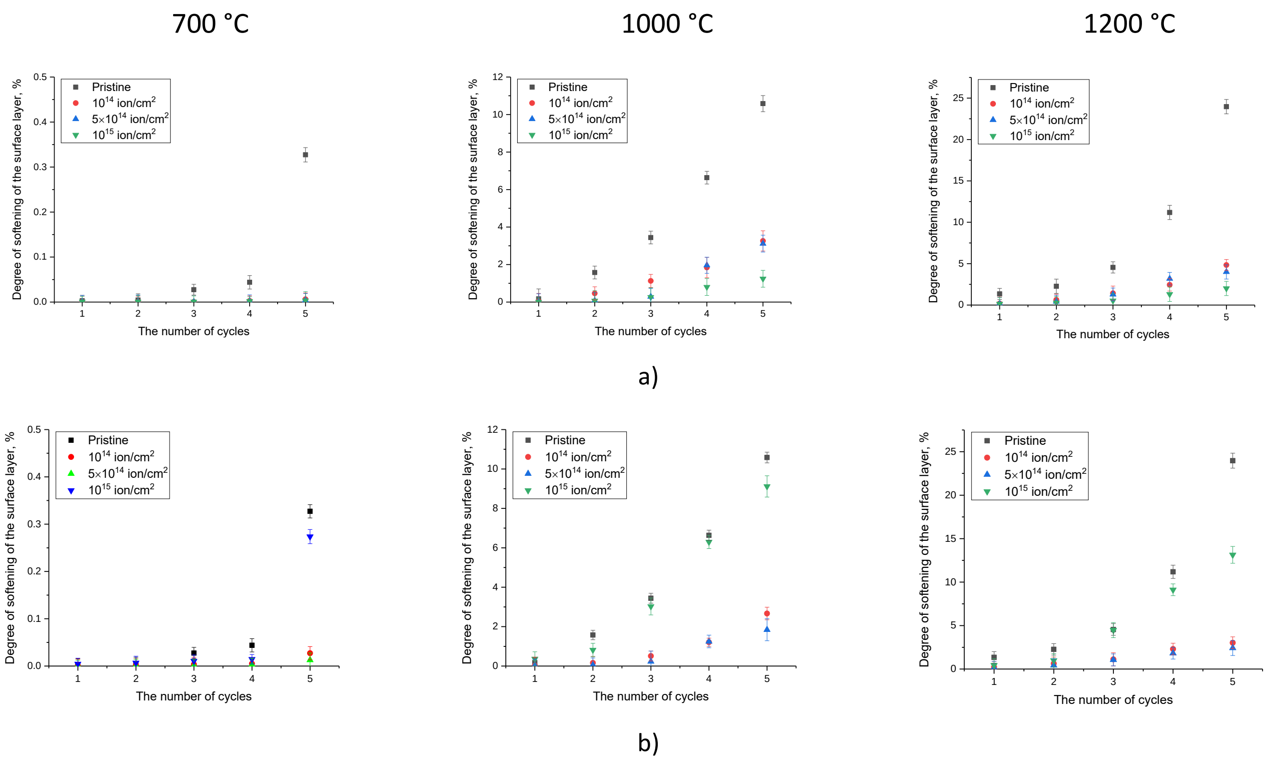


Figure 8 - Assessment results of the surface layer softening degree (changes in surface hardness) depending on the amount of thermal cycling of ceramic samples: a) when irradiated with Kr^{15+} ions; b) when irradiated with Xe^{22+} ions

Conclusions

The paper presents the assessment results of the influence of low-energy ion irradiation (with Kr^{15+} and Xe^{22+} ions) on changes in the near-surface layer of composite $ZrO_2 - Al_2O_3$ ceramics, which have great prospects for use as structural materials capable of withstanding high temperatures and large mechanical loads during operation. The method of low-energy ion irradiation with Kr^{15+} and Xe^{22+} ions with energies of 300 and 440 keV and irradiation fluences from 10^{14} to 10^{15} ion/cm^2 was chosen as a method for modification of the near-surface layer. The choice of ions for irradiation is determined by the possibility of carrying out targeted modification of a near-surface layer with a thickness of about 200 – 250 nm.

During the studies, it was found that the use of Xe^{22+} ions with fluences below 10^{15} ion/cm^2 makes it possible to modify the surface layer at greater depths. The depth of the modified layer in $ZrO_2 - Al_2O_3$ ceramics when irradiated with Xe^{22+} is about 300 – 350 nm, taking into account diffusion effects, while when irradiated with Kr^{15+} ions, the thickness of the modified layer is no more than 300 nm.

The results of tribological tests showed that for unmodified $ZrO_2 - Al_2O_3$ ceramics, a decrease in wear resistance appears after 8000 – 10000 cycles, while for ceramics modified with Kr^{15+} ions, an elevation in irradiation fluence from 10^{14} ion/cm^2 to 5×10^{14} ion/cm^2 results in a decrease in the trend in the value of the dry friction coefficient, which indicates an increase in resistance to surface degradation under mechanical influences. It should also be noted that in the case of modification of fluences of 10^{15} ion/cm^2, in addition to reducing the trend of deterioration of the dry friction coefficient, there is also an increase in the number of test cycles in which changes in the dry friction coefficient are within the measurement error.

The results of thermal cycling (determining resistance to thermal shock) revealed that modification by ion irradiation results in a rise in degradation resistance and a reduction in hardness. Moreover, in the case of an exposure temperature of 700 °C, no changes in hardness are observed during cyclic tests, which indicates the high resistance of ceramics to external influences at this temperature regime.

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

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

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Композиттік керамиканың беткі қабаттарының беріктік қасиеттерін мақсатты өзгерту үшін ионды модификациялау әдістерін қолдану

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Қабылданды: *10 ақпан 2025*

ТҮЙІНДЕМЕ
Магнетронды шашырату және механикалық индукцияланған деформациялық әсер сияқты әдістермен қатар материалдардың беткі қабаттарының беріктік қасиеттерін мақсатты өзгертудің перспективалы әдістерінің бірі ионды модификациялау әдістері болып табылады Зерттеудің осы бағытына қызығушылық, ең алдымен, материалдардың сыртқы механикалық және темтературалық әсерлерге төзімділігін арттыру, сонымен қатар өнеркәсіпте пайдалану, металлургия саласы мен реактор жасауда үлкен перспективалары бар баяу балқитын керамикалардың тозуға төзімділігін арттыру мүмкіндігімен байланысты. Бұл жұмыста беттік қабатта сыртқы әсерге төзімділігі жоғары радиациялық модификацияланған қабат құру мақсатында $ZrO_2 – Al_2O_3$ керамикасының беткі қабатын энергиясы 300 және 440 кеВ төмен энергиялы Kr15+ және Xe22+ иондарымен сәулелендіру арқылы ионды модификациялау әдісін қолдану мүмкіндігін бағалау нәтижелері ұсынылған. Жүргізілген зерттеулер барысында Xe^{22+} иондары үшін 10^{14} - $5×10^{14}$ ион/см^2 және Kr^{15+} иондары үшін 10^{15} ион/см^2 флюенсімен сәулелендіру беткі қабатты модификациялаудың оңтайлы шарттары болып табылатыны анықталды, нәтижесінде сәулелендірілмеген керамикалармен салыстырғанда, тозуға төзімділік 2.0 - 2.5 есе артты және беріктік 15 - 20%-ға дейін күшейді.

Түйінді сөздер: беріктену, иондық модификация, қаттылық пен тозуға төзімділікті арттыру, $ZrO_2 – Al_2O_3$ керамикалары, төмен энергиялы иондар.

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Использование методов ионной модификации для направленного изменения прочностных свойств приповерхностных слоев композитных керамик

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АННОТАЦИЯ
Использование методов ионной модификации является одним из перспективным методов направленного изменения прочностных свойств приповерхностных слоев материалов наравне с такими методами как магнетронное напыление и механически индуцированное деформационное воздействие. Интерес к данному направлению исследований обусловлен в первую очередь возможностью повышения устойчивости материалов к внешним механическим и термическим воздействиям, а также увеличению износостойкости тугоплавких керамик, обладающих большими перспективами в промышленном использовании и металлургии и реакторостроении. В данной работе представлены результаты оценки возможности применения метода ионной модификации путем облучения приповерхностного слоя $ZrO_2 – Al_2O_3$ керамик низкоэнергетическими ионами Kr^{15+} и Xe^{22+} с энергиями 300 и 440 кэВ с целью создания в приповерхностном слое радиационно-модифицированного слоя, обладающего высокой устойчивостью к внешним воздействиям. В ходе проведенных исследований было установлено, что облучение с флюенсами 10^{14} - $5×10^{14}$ ион/см^2 для ионов Xe^{22+} и 10^{15} ион/см^2 для ионов Kr^{15+} являются оптимальными условиями модификации приповерхностного слоя, в результате которых наблюдается увеличение износостойкости в 2.0 – 2.5 раза и упрочнение более чем на 15 – 20 % по сравнению с необлученными керамиками.

Ключевые слова: упрочнение, ионная модификация, повышение твердости и износостойкости, $ZrO_2 – Al_2O_3$ керамики, низкоэнергетические ионы.

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