



Article Study of the Application Efficiency of Irradiation with Heavy Ions to Increase the Helium Swelling Resistance of BeO Ceramics

Maxim V. Zdorovets ^{1,2,3}, Dmitriy I. Shlimas ^{1,2}, Artem L. Kozlovskiy ^{1,4,*} and Daryn B. Borgekov ^{1,2}

- ¹ Laboratory of Solid State Physics, The Institute of Nuclear Physics, Almaty 050032, Kazakhstan; mzdorovets@inp.kz (M.V.Z.); shlimas@mail.ru (D.I.S.); borgekov@mail.ru (D.B.B.)
- ² Engineering Profile Laboratory, L.N. Gumilyov Eurasian National University, Nur-Sultan 010008, Kazakhstan
- ³ Department of Intelligent Information Technologies, Ural Federal University, 620075 Yekaterinburg, Russia
- ⁴ Institute of Geology and Oil and Gas Business, Satbayev University, Almaty 050032, Kazakhstan
 - Correspondence: kozlovskiy.a@inp.kz; Tel.: +77024413368; Fax: +77024413368

Abstract: This paper considers the possibilities of increasing radiation resistance to helium swelling of beryllium oxide ceramics due to preliminary irradiation with heavy ions. Interest in this topic is due to the possibility of using these ceramics as materials for inert matrices of nuclear fuel and structural materials reflectors of high-temperature reactors. The samples studied were irradiated in two stages, namely irradiation with heavy Ar^{8+} , Kr^{15+} , and Xe^{22+} ions with a fluence of 10^{12} ion/cm² and subsequent irradiation with He^{2+} ions with a fluence of $5x10^{17}$ ion/cm². The main parameters used to compare and determine radiation modification efficiency were the crystal-structure swelling degree, a decrease in the hardness, and wear resistance of ceramics after irradiation with He^{2+} ions. During the studies carried out, it was found that preliminary irradiation with heavy Ar^{8+} , Kr^{15+} , and Xe^{22+} ions leads to a significant increase in radiation swelling resistance, as well as to an increase in crack resistance and wear resistance.

Keywords: helium swelling; ceramics; beryllium oxide; heavy ions; dislocations; radiation damage

1. Introduction

As is known, one of the key problems in the use of structural materials in nuclear power, including high-temperature reactors, is the problem of the transmutation helium accumulation and the subsequent gas swelling of the near-surface layer of protective materials or materials of inert matrices [1-3]. These processes are based on the high mobility of the implanted helium in the structure and its poor solubility, which leads to the fact that gas-filled regions in the structure of the material can be formed at high accumulated-helium concentrations. The formation of such areas can lead to the formation of stressed and deformed areas filled with helium, and if critical pressure is reached inside a cavity, this will lead to its rupture, thereby destroying the integrity of the near-surface layer structure [4,5]. The so-called processes of radiation embrittlement and swelling of materials play an important role in determining the service life and application areas of certain materials in the nuclear industry, as they are both directly exposed to ionizing radiation and interact with the coolant [6–10]. These processes can lead to the accelerated destruction of materials as a result of changes in their properties and the accumulation of deformation stresses, and the high content in the structure leads to the formation of microcracks. Moreover, swelling can lead to a change in geometric dimensions, as was often observed in the first nuclear reactors during the long-term operation of fuel elements. In turn, structure deformation and change in structural properties can have a negative impact on the thermal conductivity of materials and reduce the heat-removal efficiency. In this regard, one of the promising areas of research in the field of radiation materials



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). science and structural materials is the search for solutions to the problem of radiation resistance of materials, as well as various ways to increase the resistance of materials to radiation-induced damage and swelling processes [11–13].

The purpose of this work was to test the hypothesis about the effect of dislocation defects caused by exposure to heavy ions on the concentration of radiation-induced damage and helium swelling of the near-surface layer of BeO ceramics. This hypothesis is based on the assumption that dislocation defects isolated from each other due to small fluences of irradiation with heavy ions will create additional obstacles to migrating helium ions, thereby preventing them from agglomeration into large gas-filled bubbles. The basis for this hypothesis was a number of experimental works [14-20] aimed at studying the applicability of ionizing radiation to increase the radiation resistance of materials, as well as studying the mechanisms of radiation hardening of the near-surface layer of ceramics, steels, and multilayer coatings. Therefore, for example, in a number of works, the effect of radiation hardening at irradiation with high-precision pulse beams of near-surface layers of refractory materials and ceramics is considered [14–22]. The authors of these works call the main hardening mechanism changes in dislocation density and amorphization processes, followed by the formation of amorphous inclusions in the structure of the near-surface radiation-modified layer. The influence of amorphous inclusions or amorphous layers on the change in resistance to helium swelling is also reflected in References [23,24]. In them, the authors associate an increase in the swelling resistance of multilayer coatings with the formation of additional interfaces between amorphous and crystalline layers, as such a formation leads to a sharp decrease in the migration and agglomerating ability of helium ions in the coating structure.

Thus, by analyzing the literature data of previously carried out experimental works [14–25], one can make an assumption about the possible positive effect of radiation hardening of the near-surface layers of irradiated materials that consists in changing the dislocation density and defect structure of the layer. These changes can play both a positive effect, initiating changes that contribute to an increase in degradation resistance of materials, and a negative effect, consisting in the creation of active defect regions, near which subsequent radiation-induced defects will agglomerate. In this regard, it is of interest to test this hypothesis, as well as to study changes in the properties of ceramics as a result of irradiation with various types of heavy ions, such as Ar⁸⁺, Kr¹⁵⁺, and Xe²²⁺ with energies of 70, 150, and 230 MeV, respectively, at an irradiation fluence of 10¹² ion/cm², and their effect on the change in the stability of ceramics to subsequent helium irradiation. The choice of these types of ions makes it possible to vary the concentration of vacancy defects during the passage of ions through the material. At the same time, irradiation with heavy ions makes it possible to vary the degree of structural changes caused by the difference in the energy losses of ions. Interest in this study is due to verification of the hypothesis about the possibility of increasing the helium swelling resistance of oxide ceramics by creating additional obstacles to helium agglomeration as a result of irradiation with heavy ions.

2. Experimental Part

The object of study was polycrystalline beryllium oxide ceramics with a density of 3.02 g/cm^3 that were obtained by hot-pressing [26]. The porosity of the ceramics was 2%, and the grain size was no more than 100 nm. The choice of BeO ceramics as objects of study is due to their physicochemical properties, high thermal conductivity, and absorbing characteristics, which make them one of the most promising materials in the field of structural materials for nuclear reactors and a basis for inert nuclear fuel matrices.

The samples were irradiated at a DC-60 heavy ion accelerator located at the Astana branch of the Institute of Nuclear Physics (Nur-Sultan, Kazakhstan). Irradiation of the test samples was carried out in two stages. The first step was to irradiate the samples with heavy Ar^{8+} , Kr^{15+} , and Xe^{22+} ions with energies of 70, 150, and 230 MeV, respectively. The irradiation fluence for the selected ions was 10^{12} ion/cm²; irradiation was carried out at room temperature, which was maintained during irradiation by using a special

target holder with water cooling. The choice of this fluence for irradiation was based on a theoretical analysis of the diameters of damaged areas arising along the trajectory of ion movement in the material [27]. According to estimates, the diameters of these regions are 7–15 nm, which, taking into account the irradiation density (fluence), indicates the isolation of these regions from each other and the absence of irradiation-caused defect overlapping effect.

The second stage of irradiation was carried out with He²⁺ ions with an energy of 40 keV and an irradiation fluence of 5×10^{17} ion/cm². The choice of the irradiation fluence is based on previous studies on helium embrittlement and swelling in oxide and nitride ceramics, according to which it was found that, when this fluence is reached in the structure of ceramics, there is an accumulation of implanted helium, the concentration of which is sufficient for the formation of gas-filled bubbles. At the same time, as was shown in Reference [26], in the case of irradiation of BeO ceramics with helium ions, at a dose above 10^{17} ion/cm², the formation of an impurity cubic BeO phase was observed, the presence of which was associated with disordering processes and polymorphic transformations of the BeO-hexagonal \rightarrow BeO-cubic type.

Table 1 shows the results of simulation of the energy losses of selected ion types in the near-surface layer of BeO ceramics, as performed in the SRIM Pro 2013 program code [28], as well as the values of atomic displacements at a depth of 300-400 nm. The choice of depth for determining the value of dpa is due to the maximum penetration depth of He²⁺ ions in ceramics. It should be mentioned that the calculations of the dpa value for heavy ions were carried out by taking into account the irradiation fluence of 10^{12} ion/cm²; for He²⁺ ions, the dpa value was calculated for the irradiation fluence of 5×10^{17} ion/cm². According to the calculations performed, it was found that a change in the type of ions and their energy leads to an increase in the concentration of formed vacancies by a factor of 3.5-4 in the case of Ar^{8+} and Kr^{15+} ions, and by a factor of 1.5–1.7 in the case of Kr^{15+} and Xe^{22+} ions. A similar situation occurs with the energy losses of ions that are calculated by taking into account the density of ceramics and the binding energy of atoms. At the same time, the change in the penetration depth with an increase in the energy of incident particles is not significant, and it is no more than 10-15%. In this case, it should be noted that, for heavy ions, the main contribution to structural changes is made by the electron losses of ions during interaction with the crystal structure, the value of which is 2.5–3 orders of magnitude higher than nuclear losses. According to estimates of atomic displacement value calculated at a depth of 300–400 nm for heavy ions, this parameter varies from 0.0001 to 0.0009 dpa, depending on the type and energy of incident ions. Thus, a change in the ion type and their energy at the same irradiation fluences makes it possible to simulate different degrees of structural isolated changes caused by irradiation and to compare their effect on changes in the radiation resistance to helium swelling. Figure 1 shows a schematic representation of the ion damage trajectories in ceramics caused by various irradiation types.

Table 1. Energy-loss results calculated in SRIM Pro 2013.

Ion/Energy, MeV	Fluence, Ion/cm ²	Vacancies/Ion	dE/dx _{electron} , eV/nm	dE/dx _{nuclear} , eV/nm	Displacements per Atom at a Range of 300–400 nm, dpa	Penetration Depth of Ions, µm
Ar ⁸⁺ , 70 MeV		4500	6473	7.43	0.0001	11.9
Kr ¹⁵⁺ , 150 MeV	10 ¹²	16,000	14,170	26.61	0.0006	14.3
Xe ²²⁺ , 230 MeV		29,700	22,470	57.34	0.0009	15.5
He ²⁺ , 40 keV	$5 imes 10^{17}$	500	10	180	8.8	0.3–0.4





The study of structural changes caused by various types of radiation, as well as swelling and structural degradation processes, was carried out by using the X-ray structural analysis method. The analysis was carried out by evaluating changes in the parameters and volume of the crystal lattice, as well as crystallite sizes of the samples under study before and after ion irradiation. Calculation of these parameters was carried out on the basis of the data obtained from analysis of X-ray diffraction patterns of the samples. Diffraction patterns were recorded in the Bragg–Brentano geometry, in the angular range of $2\theta = 35-75^{\circ}$, with a step of 0.03° . The desired diffraction patterns were obtained on a D8 ADVANCE ECO (Bruker, Karlsruhe, Germany) powder diffractometer.

Mechanical properties were determined by changing the hardness of the near-surface layer at indenter pressure (Vickers pyramid) with a force of 500 N. The studies were carried out on a LECO LM700 (Leco Corporation, St. Joseph, MI, USA) microhardness tester. From the indenter prints obtained, as well as their depth, hardness and softening degrees were determined to characterize the resistance of ceramics to external effects.

The wear resistance of the near-surface layer to mechanical effects was carried out by using the standard tribological method of determining the dry-friction coefficient during 20,000 cycles of tests of rolled metal ball at a load of 200 N. The tests were carried out on a Ducom POD-4.0 (Ducom, New York, NY, USA) instrument. The samples were determined depending on the type of external effects.

3. Results and Discussion

As is known, one of the most informative study methods for structural changes without destroying or externally affecting samples is the X-ray diffraction analysis method, which allows us to assess the structural parameter change kinetics, determining the formation of disordering or amorphization regions of the structure as a result of external influences, etc. At the same time, not only can the basic parameters of the crystal structure be determined from the shape and position of the diffraction lines, but also the effects associated with deformation and distortion of the crystal lattice caused by external influences can be qualitatively described. Figure 2 shows a series of X-ray diffraction patterns of the samples under study both before and after irradiation, with various types of ions, the main purpose of which is to clearly reflect the structural changes in the samples depending on exposure type.



Figure 2. Results of X-ray diffraction analysis of the samples under study, depending on different irradiation types: (**a**) X-ray diffraction patterns of initial samples before and after irradiation with He^{2+} ions, (**b**) X-ray diffraction patterns of samples modified with heavy Ar^{8+} ions before and after irradiation with He^{2+} ions, (**c**) X-ray diffraction patterns of samples modified with heavy Kr^{15+} ions before and after irradiation with He^{2+} ions, and (**d**) X-ray diffraction patterns of samples modified with heavy Kr^{15+} ions before and after irradiation with He^{2+} ions and (**d**) X-ray diffraction patterns of samples modified with heavy Ke^{22+} ions before and after irradiation with He^{2+} ions.

A full-profile analysis of the initial sample showed that the obtained diffraction pattern with a high probability degree (more than 97%) corresponds to the structure of BeO with a hexagonal crystal lattice and the spatial system P63mc(186) (PDF-00-035-0818). At the same time, the shape of diffraction lines and the ratio of diffraction reflections and background radiation areas, as obtained by approximation with pseudo-Voigt functions of the obtained diffraction patterns, indicate a high structural ordering degree (more than 98%). The crystal lattice parameters of the samples in the initial state were a = 2.6699 Å and c = 4.3369 Å, and the crystal lattice volume was 26.77 Å³.

In the case of irradiation of the initial samples with He²⁺ ions with a fluence of 5×10^{17} ion/cm², the main changes in the diffraction pattern consist of a sharp decrease in the intensity of diffraction reflections, their distortion, and also a shift toward small angles, indicating a strong deformation and swelling of the crystal structure. At the same time, our analysis of the shape of the (002) reflection at $2\theta = 44-45^{\circ}$ showed that the reflection shape is characteristic of the presence of two highly distorted maxima characteristics of the hexagonal BeO and the cubic BeO phases. The presence of this maximum of the BeO-cubic phase indicates the processes of polymorphic transformation of the BeO-hexagonal \rightarrow BeO-cubic type caused by the cumulative effect of irradiation, as was reported earlier in Reference [27]. A decrease in the intensity of reflections, as well as a distortion of their shape, indicates not only the crystal lattice deformation, but also the appearance of disordering regions in the structure, leading to its amorphization.

In the case of samples pre-irradiated with heavy Ar⁸⁺, Kr¹⁵⁺, and Xe²²⁺ ions, the main structural changes, according to the data obtained, are associated with a change in the intensity of diffraction reflections that indicates the texture reorientation processes, as well as a size factor caused by a change in the shape and size of crystallites. At the same time,

a change in the type of ions leads to large changes in the intensities of reflections. This behavior of changes in diffraction reflections is associated with the local nature of structural changes caused by irradiation.

According to the presented X-ray diffraction patterns of modified samples after irradiation with He²⁺ ions, the structural changes are of a different nature than in the case of irradiation with He²⁺ ions of the original unmodified samples. First, for the samples modified with heavy ions, the formation of reflections characteristic of cubic-phase impurity inclusions is not observed, thus indicating the absence of polymorphic transformation processes in the amount necessary for possible registration by using the X-ray diffraction method. Second, the change in the position and shape of diffraction reflections is less pronounced than for unmodified samples, thus also indicating that preliminary modification with heavy ions leads to an increase in the stability of the crystal structure to deformation and swelling.

Figure 3 shows the results of changes in the swelling of the crystal lattice after irradiation with He²⁺ ions with an irradiation fluence of 5×10^{17} ion/cm². The determination of the swelling value was carried out by using Formula (1):

$$Swelling = \left(\frac{V - V_0}{V_0}\right) \times 100\% \tag{1}$$

where V and V_0 are the crystal lattice volume of the studied samples in the irradiated and initial state. The calculations were carried out on the basis of changes in the structural parameters of the crystal lattice of the studied samples before and after irradiation.



Figure 3. Results of the crystal-lattice helium swelling.

This change characterizes crystal-lattice swelling and deformation as a result of the helium ion accumulation in the surface-layer structure and their subsequent agglomeration into gas-filled bubbles. It should be mentioned that, according to theoretical calculations performed according to the methodology proposed in the work of Egeland et al. [29], the concentration of implanted helium at a given irradiation fluence is no more than 0.6–0.7 at. %.

According to the data obtained, in the case of unmodified ceramics, the swelling value is 0.7% of the initial volume, and this indicates crystal structure deformation as a result of helium agglomeration in the near-surface layer. For modified ceramics, this swelling value is significantly less, and in the case of modification with heavy Kr^{15+} and Xe^{22+} ions, the swelling value decreases by 70 and 95%, respectively, in comparison with

unmodified ceramics. This change indicates an increase in the resistance of the modified ceramics to helium swelling and subsequent degradation of the crystal structure. This is based on the mechanism of change in the dislocation density in the structure of the surface layer of ceramics exposed to heavy ion irradiation. According to X-ray diffraction data, the dominant contribution to the change in the crystal structure upon irradiation with heavy ions is the size effect associated with a change in the size of crystallites as a result of crushing or their reorientation. This behavior of crystallites is caused by the fact that, when irradiated with heavy ions, the main contribution is made by the electron losses of ions, which, upon interaction, are transformed from kinetic energy into thermal energy, thus leading to the formation of local regions with an increased temperature along the trajectory of ions in the material. The formation of such local regions leads to the appearance of a temperature gradient, which initiates recrystallization processes and crystallite mobility. In this case, the time intervals for which these changes occur are 10⁻¹¹⁻¹³ s, after which the system stabilizes. As a result, modified local regions appear in the structure of ceramics, and in the case of low fluences, these regions remain isolated, leading to the absence of the effect of overlapping these regions. At the same time, as is known, the sizes of crystallites are related by an inverse quadratic dependence with the dislocation density, and in the case of their decrease, thus leads to an increase in dislocations in the structure of ceramics. The dislocation density was determined by using Formula (2):

$$\delta = \frac{1}{L^2} \tag{2}$$

where *L* is the crystallite size, which was determined from X-ray diffraction data.

Thus, upon irradiation with heavy Ar^{8+} , Kr^{15+} , and Xe^{22+} ions, the dislocation density was 0.071×10^{10} , 0.076×10^{10} , and 0.091×10^{10} dislocations/cm², while, for the initial samples, this value was 0.068×10^{10} dislocations/cm². As can be seen from the calculations obtained, a change in the type of ions under irradiation leads to an increase in the dislocation density, which is associated with both the energy losses of ions and the amount of energy transferred to the crystal structure, as well as the concentration of vacancy defects formed during the interaction of incident ions with the crystal lattice.

It is also worth noting that, in view of the dielectric nature of ceramics, in contrast to metals and alloys, the change in the electron density as a result of irradiation with heavy ions is associated with its redistribution along the ion trajectory, which also contributes to structural changes.

By analyzing the obtained data on reduction of helium-swelling value and comparing them with the literature data [15–17,19,20] on other methods of modification and protection against helium embrittlement, the following conclusions can be drawn. As is known from References [15–17], one method of increasing swelling resistance and subsequent structure degradation is the method of high-precision pulsed irradiation with electrons and ions. This process is based on the effect of remelting the near-surface layer due to the powerful influence of a pulsed beam of electrons or ions with a high current density (in some cases, the current is μA or mA) in a very short period of time. The result of this action is a rapid heating of the near-surface layer, followed by recrystallization and the creation of a high density of dislocation effects. Previously, in Reference [15], we showed that the use of such pulsed beams makes it possible to increase the resistance of nitride ceramics to helium swelling by changing the dislocation density and crystallite size in the modified near-surface layer. Another way to reduce the rate of helium accumulation and subsequent swelling is to create multilayer coatings consisting of amorphous and crystalline layers of oxides or nitrides [21–23]. This method is based on the effect of the appearance of interfaces between crystalline and amorphous layers, which lead to the retention of implanted helium near the boundaries and a decrease in the rate of its agglomeration. Thus, in all the proposed methods for increasing stability, there is an effect of changing the dislocation density, as well as the structural characteristics of the near-surface layer of ceramics, and this results in the creation of additional obstacles to the agglomeration of implanted helium in the

structure. A decrease in the agglomeration rate due to additional defects leads to a decrease in the effect of swelling, and, consequently, to a decrease in the degradation of the strength properties of ceramics.

The study of strength properties, in particular, hardness, resistance to softening, and wear resistance, is presented in Figures 4 and 5.



Figure 4. (a) Results of changes in ceramic hardness after irradiation with He²⁺ ions. (b) Results of near-surface layer softening degree and softening resistance change.

The softening degree (*SD*) was determined by the change in hardness in the initial (H_0) and irradiated (H) states and was calculated by using Formula (3):

$$SD = \left(\frac{H_0 - H}{H}\right) \times 100\% \tag{3}$$

This value characterizes the preservation of the stability of the near-surface layer to external influences, as well as crack resistance.



Figure 5. Cont.



Figure 5. (a) Graph of the dry-friction coefficient change over 20,000 test cycles. (b) Dry friction coefficient reduction diagram after 20,000 test cycles. (c) Results of changes in volume loss during wear, depending on the type of external influences.

As can be seen from the data presented, in the case of the initial samples, the decrease in the surface layer hardness and the softening degree is more than 30% after irradiation with helium ions and helium accumulation in the structure. This behavior is due to the degradation processes caused by helium implantation, with the subsequent formation of helium bubbles and swelling. In the case of pre-modified ceramics with heavy ions, a decrease in the ceramic strength-degradation degree is observed, and this indicates an increase in the resistance to mechanical damage during irradiation. It should be mentioned that, in the case of irradiation with heavy Xe²²⁺ ions, the softening degree is no more than 5%, thus indicating a high degree of resistance to degradation of the surface layer. An increase in resistance to mechanical damage and external influences for modified samples is due to the fact that, in the case of preliminary irradiation with heavy ions, additional dislocations and grain boundaries are formed in the structure of the surface layer that prevent helium agglomeration and the subsequent formation of helium inclusions and gas-filled regions. Moreover, as shown from the results of X-ray phase analysis, in the case of initial samples, irradiation with He^{2+} ions at a given dose leads to the initiation of polymorphic transformations of the BeO-hexagonal \rightarrow BeO-cubic type, resulting in the formation of cubic phase impurity inclusions in the structure. In this case, the analysis of the shape of the diffraction lines for the irradiated samples indicates that, upon irradiation with He^{2+} ions, the formation of a strong crystal-lattice distortion is observed in the structure, which, in turn, negatively affects the resistance to external influences. For modified samples, the preliminary formation of dislocations, leading to an increase in dislocation density, leads to a significant increase in crack resistance and resistance to softening of the surface layer as a result of external influences.

Figure 5 shows the results of changes in the dry-friction coefficient of the studied ceramics after irradiation with He²⁺ ions. This value characterizes the stability of the near-surface layer to external mechanical long-term influences, as well as the degree of surface defectiveness as a result of irradiation. As can be seen from the data presented, in the case of the modification of ceramics with heavy Ar^{8+} , Kr^{15+} , and Xe^{22+} ions, the initial change in the dry-friction coefficient after irradiation with He²⁺ ions is insignificant, which indicates the resistance to deformation of the near-surface layer, and this is associated with a decrease in the ceramic swelling value. At the same time, in the case of initial ceramics irradiated with He²⁺ ions, the initial change in the dry-friction coefficient is more than 20%, which indicates a strong deformation of the ceramic surface as a result of the radiation-induced damage accumulation and subsequent crystal-structure swelling.

The dynamic indexes of changes in the dry-friction coefficient, indicating a surface deterioration and an increase in friction, show that the main changes associated with an increase in the value of the coefficient are observed after 10,000–12,000 cyclic tests. These changes indicate a fairly high degree of stability and wear resistance of irradiated ceramics to mechanical stress. In the case of unmodified ceramics, the decrease in wear resistance after 20,000 test cycles is more than four times, thus indicating a strong surface degradation and deterioration of the tribological characteristics of the ceramics. At the same time, a sharp decrease in wear resistance for the initial ceramics irradiated with He²⁺ ions is observed after 10,000 cyclic tests. For modified specimens after cyclic tests, the dry-friction coefficient changes much less than for unmodified specimens, thus indicating an increase in the friction-resulted wear resistance of ceramics. Figure 5c shows the results of the change in volume loss as a function of the number of cycles, which also show the efficiency of heavy ion modification and loss reduction in the case of helium swelling of the modified ceramics.

4. Conclusions

The obtained results of the studies carried out have shown that the application of the preliminary ionic modification of the near-surface layer of ceramics is promising for the helium-swelling processes at a high radiation dose. During research, it was found that irradiation with heavy Ar^{8+} , Kr^{15+} , and Xe^{22+} ions with energies of 70, 150, and 230 MeV, respectively, and a fluence of 10^{12} ion/cm² leads to a decrease in the crystal structure swelling by 36, 70, and 95%, respectively. The main mechanism affecting the reduction of the swelling degree is the formation of additional dislocations, thus leading to a decrease in the agglomeration rate and filling of voids in the ceramic with helium. It was also found that additional modification with heavy ions leads to a decrease in the degradation of the near-surface layer as a result of helium irradiation, which positively affects the mechanical and strength properties of ceramics. Thus, it is possible to conclude from the obtained dependencies the positive effect of radiation-induced hardening of the near-surface layer to helium swelling and subsequent degradation.

During the determination of strength characteristics, it was found that modification with heavy ions leads to a decrease in the degree of softening and degradation of the near-surface layer subject to additional irradiation with helium ions. It has been found that the main strengthening mechanism for reducing the effect of helium swelling is the effect of changing dislocation density.

In conclusion, it should be noted that, despite the high cost and energy consumption of the proposed method for modifying ceramics by means of additional preliminary irradiation with heavy ions in order to create additional defects that prevent helium agglomeration and swelling processes, the results obtained for increasing the degradation-resistance efficiency have great prospects in practical application. In the case of using BeO ceramics as the basis for inert matrix materials, preliminary ionic modification can significantly increase their resistance to the transmutation helium accumulation in the near-surface layer, thus increasing their service life, which is one of the key requirements for inert nuclear fuel matrices. In the case of using BeO ceramics as structural materials of reflectors or absorbers, one should take into account the factors of irradiation with heavy ions in the processes of swelling and accumulation of defects in the structure when exposed to various types of ionizing radiation.

It is also worth noting that the results of the studies carried out are in good agreement to confirm the theory of radiation hardening of materials under irradiation with low fluences, as this theory is quite actively used to describe the effects of phase transformations in steels and alloys that occur under the action of irradiation. In this case, the effect of changing the dislocation density, which makes it possible to slow down the processes of helium swelling, is one of the main ones in this theory.

Further studies will be aimed at studying the efficiency of reducing helium swelling and the radiation-damage accumulation rate in modified ceramics, under irradiation conditions that are as close as possible to real conditions in the reactor. Author Contributions: Conceptualization, M.V.Z., D.I.S., D.B.B. and A.L.K.; methodology, D.B.B., D.I.S. and A.L.K.; formal analysis, M.V.Z.; investigation, D.I.S., A.L.K. and M.V.Z.; resources, M.V.Z.; writing—original draft preparation, D.I.S., M.V.Z., D.B.B. and A.L.K.; writing—review and editing, D.I.S., M.V.Z., D.B.B. and A.L.K.; visualization, M.V.Z.; supervision, M.V.Z. All authors have read and agreed to the published version of the manuscript.

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References

- Leclerc, S.; Declémy, A.; Beaufort, M.F.; Tromas, C.; Barbot, J.F. Swelling of SiC under helium implantation. J. Appl. Phys. 2005, 98, 113506. [CrossRef]
- Hofmann, F.; Nguyen-Manh, D.; Gilbert, M.R.; Beck, C.E.; Eliason, J.K.; Maznev, A.A.; Dudarev, S.L. Lattice swelling and modulus change in a helium-implanted tungsten alloy: X-ray micro-diffraction, surface acoustic wave measurements, and multiscale modelling. Acta Mater. 2015, 89, 352–363. [CrossRef]
- 3. Zhang, Y.; Wang, X.; Osetsky, Y.N.; Tong, Y.; Harrison, R.; Donnelly, S.E.; Weber, W.J. Effects of 3d electron configurations on helium bubble formation and void swelling in concentrated solid-solution alloys. *Acta Mater.* **2019**, *181*, 519–529. [CrossRef]
- 4. Zdorovets, M.; Dukenbayev, K.; Kozlovskiy, A. Study of helium swelling in nitride ceramics at different irradiation temperatures. *Materials* **2019**, *12*, 2415. [CrossRef] [PubMed]
- 5. Zdorovets, M.V.; Kozlovskiy, A.L. Study of the stability of the structural properties of CeO₂ microparticles to helium irradiation. *Surf. Coat. Technol.* **2020**, *383*, 125286. [CrossRef]
- Ryazanov, A.I.; Klaptsov, A.V.; Kohyama, A.; Katoh, Y.; Kishimoto, H. Effect of helium on dislocation loop formation and radiation swelling in SiC. J. Nucl. Mater. 2004, 329, 486–491. [CrossRef]
- Barbot, J.F.; Beaufort, M.F.; Texier, M.; Tromas, C. Swelling and stacking fault formation in helium implanted SiC. J. Nucl. Mater. 2011, 413, 162–165. [CrossRef]
- 8. Van Veen, A.; Konings, R.J.M.; Fedorov, A.V. Helium in inert matrix dispersion fuels. J. Nucl. Mater. 2003, 320, 77–84. [CrossRef]
- 9. Lamontagne, J.; Béjaoui, S.; Hanifi, K.; Valot, C.; Loubet, L. Swelling under irradiation of MgO pellets containing americium oxide: The ECRIX-H irradiation experiment. *J. Nucl. Mater.* **2011**, *413*, 137–144. [CrossRef]
- 10. Wiss, T.A.G.; Damen, P.M.G.; Hiernaut, J.P.; Ronchi, C. Helium and xenon behaviour in irradiated Am-containing MgAl2O4 (reactor experiment EFTTRA-T4). *J. Nucl. Mater.* **2004**, *334*, 47–57. [CrossRef]
- 11. Tiwari, P.G.; Singh, J. Effect of temperature on the growth of inert gas bubbles in metals. *J. Nucl. Mater.* **1990**, 172, 114–122. [CrossRef]
- 12. Agarwal, S.; Bhattacharya, A.; Trocellier, P.; Zinkle, S.J. Helium induced microstructure damage, nano-scale grain formation and helium retention behaviour of ZrC. *Acta Mater.* **2019**, *163*, 14–27. [CrossRef]
- Zou, J.X.; Zhang, K.M.; Hao, S.Z.; Dong, C.; Grosdidier, T. Mechanisms of hardening, wear and corrosion improvement of 316 L stainless steel by low energy high current pulsed electron beam surface treatment. *Thin Solid Film.* 2010, 519, 1404–1415. [CrossRef]
- Ghyngazov, S.A.; Vasil'ev, I.P.; Surzhikov, A.P.; Frangulyan, T.S.; Chernyavskii, A.V. Ion processing of zirconium ceramics by high-power pulsed beams. *Tech. Phys.* 2015, 60, 128–132. [CrossRef]
- 15. Kaikanov, M.; Kozlovskiy, A.L.; Abduvalov, A.; Dukenbayev, K.; Zdorovets, M.V.; Tikhonov, A. Study of using pulsed beams to increase the radiation resistance of nitride ceramics to helium swelling. *Appl. Phys. A* **2019**, *125*, 555. [CrossRef]
- Tarbokov, V.; Pavlov, S.; Smolyanskiy, E.; Uglov, V.; Slobodyan, M.; Remnev, G. Effect of Preliminary Irradiation of 321 Steel Substrates with High-Intense Pulsed Ion Beams on Scratch Test Results of Subsequently Deposited AlN Coatings. *Coatings* 2021, 11, 1169. [CrossRef]
- Yang, S.; Guo, Z.; Zhao, L.; Zhao, L.; Guan, Q.; Liu, Y. Surface microstructures and high-temperature high-pressure corrosion behavior of N18 zirconium alloy induced by high current pulsed electron beam irradiation. *Appl. Surf. Sci.* 2019, 484, 453–460. [CrossRef]
- 18. Guo, G.; Tang, G.; Ma, X.; Sun, M.; Ozur, G.E. Effect of high current pulsed electron beam irradiation on wear and corrosion resistance of Ti6Al4V. *Surf. Coat. Technol.* **2013**, 229, 140–145. [CrossRef]
- 19. Wei, J.; Wang, L.; Wang, X. Studies on surface topography and mechanical properties of TiN coating irradiated by high current pulsed electron beam. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* **2018**, 436, 63–67.
- 20. Guo, F.; Jiang, W.; Tang, G.; Xie, Z.; Dai, H.; Wang, E.; Liu, L. Enhancing anti-wear and anti-corrosion performance of cold spraying aluminum coating by high current pulsed electron beam irradiation. *Vacuum* **2020**, *182*, 109772. [CrossRef]
- 21. Laptev, R.; Svyatkin, L.; Krotkevich, D.; Stepanova, E.; Pushilina, N.; Lomygin, A.; Uglov, V. First-Principles Calculations and Experimental Study of H+-Irradiated Zr/Nb Nanoscale Multilayer System. *Metals* **2021**, *11*, 627. [CrossRef]

- 22. Uglov, V.V.; Abadias, G.; Zlotski, S.V.; Saladukhin, I.A.; Kozlovskiy, A.L.; Zdorovets, M.V.; O'Connell, J. Tolerance of MeN/Si3N4 (Me = Zr, Al, Cr) multilayered systems to radiation erosion. *Surf. Coat. Technol.* **2020**, *399*, 126146. [CrossRef]
- 23. Uglov, V.V.; Abadias, G.; Zlotski, S.V.; Saladukhin, I.A.; Cherenda, N.N. Surface blistering in ZrSiN nanocomposite films irradiated with He ions. *Surf. Coat. Technol.* 2020, 394, 125654. [CrossRef]
- Uglov, V.V.; Abadias, G.; Zlotski, S.V.; Saladukhin, I.A.; Malashevich, A.A.; Kozlovskiy, A.L.; Zdorovets, M.V. Blistering in helium-ion-irradiated zirconium, aluminum, and chromium nitride films. *J. Surf. Investig. X-ray Synchrotron Neutron Tech.* 2020, 14, 359–365. [CrossRef]
- 25. Reutov, V.F.; Sokhatsky, A.S. Ordered helium bubbles and nanocrystallites in amorphous Si induced by low-energy He ions implantation. In *Microscopy of Semiconducting Materials* 2003; CRC Press: Boca Raton, FL, USA, 2018; pp. 383–388.
- 26. Kislitsin, S.B.; Ryskulov, A.E.; Kozlovskiy, A.L.; Ivanov, I.A.; Uglov, V.V.; Zdorovets, M.V. Degradation processes and helium swelling in beryllium oxide. *Surf. Coat. Technol.* **2020**, *386*, 125498. [CrossRef]
- Rymzhanov, R.A.; Gorbunov, S.A.; Medvedev, N.; Volkov, A.E. Damage along swift heavy ion trajectory. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At. 2019, 440, 25–35. [CrossRef]
- Ziegler, J.F.; Ziegler, M.D.; Biersack, J.P. SRIM–The stopping and range of ions in matter. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At. 2010, 268, 1818–1823. [CrossRef]
- Egeland, G.W.; Valdez, J.A.; Maloy, S.A.; McClellan, K.J.; Sickafus, K.E.; Bond, G.M. Heavy-ion irradiation defect accumulation in ZrN characterized by TEM, GIXRD, nanoindentation, and helium desorption. J. Nucl. Mater. 2013, 435, 77–87. [CrossRef]