Study of the effect of irradiation on nitride ceramic materials

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The paper presents the results of a study of the effect of proton and ion radiation on structural changes in nitride ceramics, which have a high potential for using as a structural material for GenIV nuclear reactors. Proton beams with an energy of 1.5 MeV and low-energy helium (He^{2+}) and carbon (C^{2+}) ions with an energy of 40 keV were used, to simulate defect formation and to estimate ceramics radiation resistance. According to the data obtained, it has been established that AlN nitride ceramics have high radiation resistance to the effects of proton radiation. While under irradiation with C^{2+} ions, the observed degradation of the surface layer is due to the accumulation of carbon in the structure with the subsequent formation of impurity carbide inclusions. It is established that the accumulation of slightly soluble ions of helium and carbon in the structure of the surface layer leads to an increase in the strain and distortion of crystal lattice due to introducing ions into the interstitial lattice and breaking chemical and crystalline bonds.

Keywords: nitride materials, radiation defects, ionizing radiation, structural materials, radiation swelling.

Introduction

In recent years, great attention has been paid to the development and use of new structural materials for nuclear and hydrogen energy, as the first wall materials of GenIV reactors. The basic concept of creating a new generation of nuclear reactors is to increase the level of safety, durability of work, as well as increase the burning of nuclear fuel and the power of nuclear facilities [1]. The main problem with increasing power and duration of use is with radiation swelling

and degradation of structural materials with prolonged exposure to ionizing radiation. In this connection, great hopes are pinned on the development of new structural materials such as ferritic/martensitic steels, carbide and nitride ceramics. They are due to their unique properties and high radiation resistance to external influences [2, 3]. The main requirement for new structural materials is increased radiation resistance to swelling and degradation, the possibility of using at high temperatures (above $700\,^\circ$C) and corrosive environments [4, 5]. Today, the main candidates for structural materials for gas-cooled fast reactor are nitride (AlN, TiN, Si_3N_4) and carbide (SiC, WC, ZrC) ceramics with high electrical resistivity, thermal conductivity, high melting point, and excellent insulating properties [6-10]. In this case, the most studied of all these materials is SiC ceramics, which was considered as a material for fusion reactors [11]. One of the promising materials is AlN-based ceramics. The potential of their use is due to the low vacancy swelling and creep, a small amount of induced activity, a high rate of radiation resistance to various types of external influences [12-15]. Also, this class of materials is able to withstand temperatures above $1200\text{-}1400\,^\circ$C, which makes them promising materials for GenIV reactors [16]. The problem of hydrogen permeability of the first wall is related to the fact that the concentration of hydrogen created in the first wall material during the penetration of hydrogen isotopes may be close to the value that is critical for ceramics in terms of its resistance to hydrogen embrittlement. In turn, due to the low solubility of helium and carbon ions in the structure of the surface layer, gas inclusions and areas with a high concentration of defects can occur, which can have a significant effect on the change in the performance characteristics of ceramics. In connection with the foregoing, it is of particular interest to study the effect of irradiation with protons and low-energy ions on the structural and heat-conducting properties of ceramic materials, since the problem of the radiation resistance of nitride ceramics has not yet been fully resolved.

Experimental

The initial samples are polycrystalline ceramics based on aluminum nitride, 20 μm thick (CRYSTAL GmbH, Germany). According to the technology for producing nitride ceramics by thermal sintering under pressure, the structure of ceramics contains impurity inclusions characteristic of the phase of aluminum oxide (Al_2O_3) in a percentage not exceeding 4%. Also, according to the energy dispersive analysis (EDA), the impurity distribution is uniform over the entire thickness of the ceramics.

Ceramics were irradiated with 1.5 MeV protons at the UKP-2-1 accelerator (Almaty, Kazakhstan), irradiation with low-energy helium ions (He^{2+}) and carbon (C^{2+}) with an energy of 40 keV was carried out at the DC-60 heavy ion accelerator (Astana, Kazakhstan). Ceramics were irradiated in vacuum, on water-cooled targets, with the aim of reducing the effect of heating arising from the interaction of incident beams with a crystal structure, on defects formation. The study of the structural characteristics of ceramics before and after irradiation was carried out using a Hitachi TM3030 scanning electron microscope with a Bruker XFlash MIN

SVE microanalysis system at an accelerating voltage of 15 kV.

X-ray diffraction analysis (XRD) was performed on a D8 ADVANCE ECO diffractometer (Bruker, Germany) using $CuK\alpha$ radiation. To identify the phases and study the crystal structure, the software BrukerAXSDIFFRAC.EVAv.4.2 and the international database ICDD PDF-2 were used. The conditions for shooting X-ray diffraction patterns: voltage 40 kV, current 20 mA, 2θ=30-75$°$, step 0.03$°$, time of standing at the point of 1 sec.

Results and Discussion

Figure 1 shows a schematic representation of the trajectory of the passage of incident particles in nitride ceramics with a thickness of 20 µm. The trajectory and penetration data were obtained by the simulation method in the SRIM Pro 2013 program using the Kinchin-Pease model.
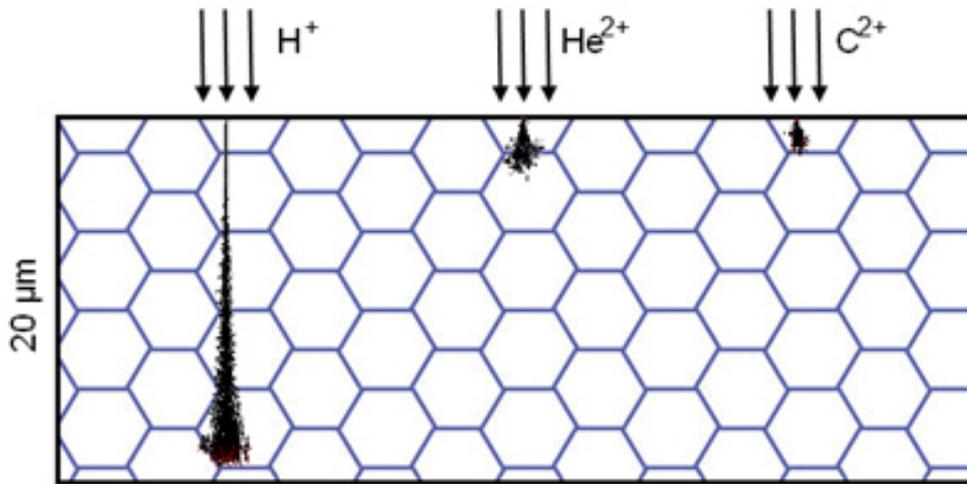

Figure 1. Schematic representation of the trajectory of the passage of ions in ceramics.

According to the data obtained, protons (19.8 µm) possess the greatest penetration depth, which are capable of initiating defect formation processes throughout the depth of samples. Unlike protons, the main ionization losses of He^{2+} and C^{2+} ions occur at a depth not exceeding 0.3-0.5 µm. In this case, the low solubility and high mobility of incident ions, as well as a large number of vacancy defects resulting from the interaction of ions with the crystal structure, can lead to the appearance of displacement atoms and defect cascades. The accumulation of poorly soluble ions in the structure of the surface layer can lead to the formation of new impurity phases with a subsequent increase in the strain and distortion of the crystal lattice. Small depth of penetration at large fluences of irradiation can lead to processes of partial sputtering of the surface layer or the formation of gas inclusions and hillocks on the surface. To study the effect of irradiation on the change in surface morphology relief and the degradation of the surface layer, we used the methods of scanning electron and atomic force microscopy. Figure 2 shows SEM images of the surface of the studied ceramics before and after irradiation.
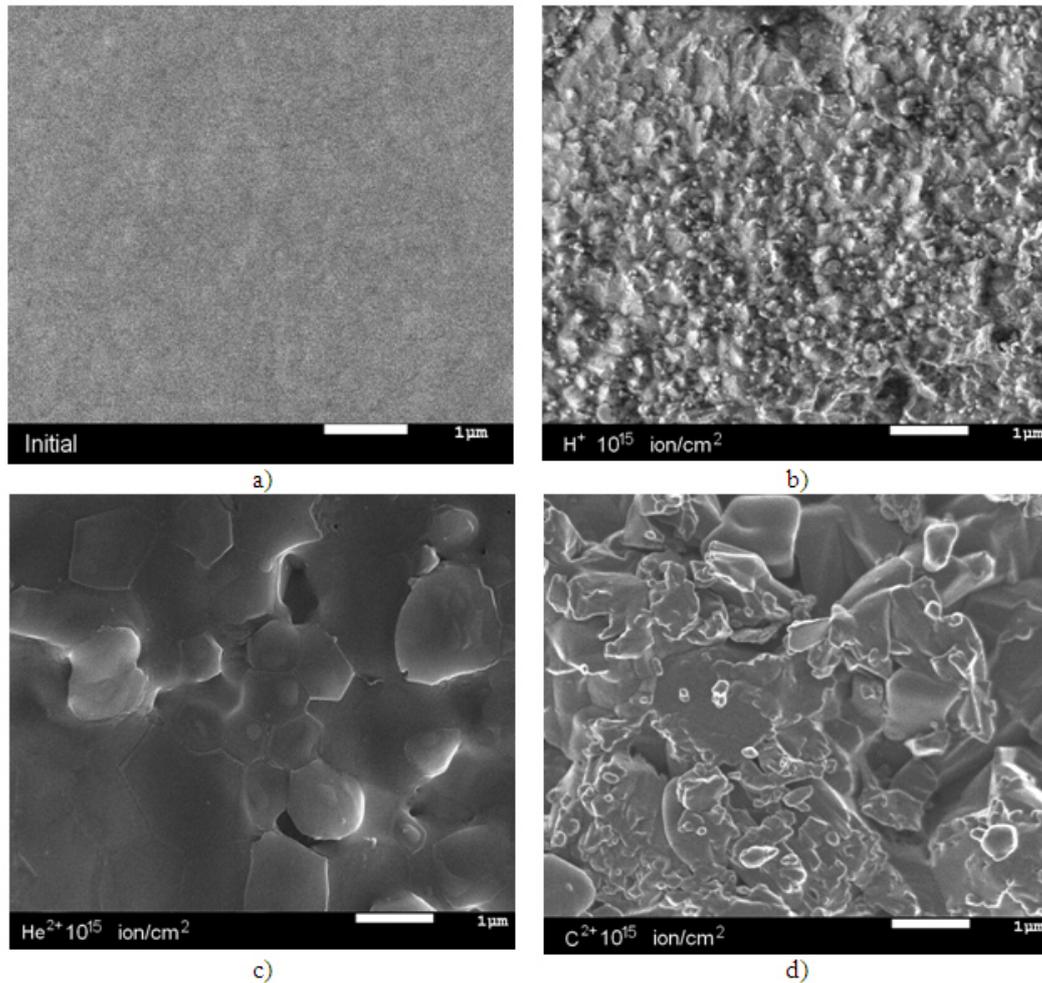
Figure 2. SEM images of the studied ceramics before and after irradiation: a) Initial; b) H $^+$ 10^{15} ion/cm^2 ; c) He $^{2+}$ 10^{15} ion/cm^2 ; d) C $^{2+}$ 10^{15} ion/cm^2 .

For the initial samples, a relatively smooth surface is observed, with no visible defects and grain boundaries. When irradiated by protons on the surface of ceramics, the formation of small grains is observed, the formation of which is due to the interaction of incident ions with the crystal structure. When irradiated with He^{2+} and C^{2+} ions, large hexagonal grains are observed on the surface. In this case, the greatest degradation of the surface layer is observed at irradiation with C^{2+} ions. In this case, the formation of cracks and cavities, as well as small inclusions, is observed in the surface layer, which indicates a strong degradation of the layer, which may be due to sputtering or the formation of metastable impurity phases, leading to a partial destruction of the crystal structure. The average grain size when irradiated with H+ was (100-150) nm; when irradiated with He^{2+} ions was (700-800) nm; when irradiated with C^{2+} ions was (500-600) nm.

One of the most important characteristics of structural materials is the stability of the crystal structure to the effects of ionizing radiation. The most reliable and non-destructive method for assessing the effect of ionizing radiation on the structural properties of materials and studying the dynamics of changes in the main crystallographic characteristics is the X-ray analysis method. This method allows to estimate the changes in the crystal structure, as well as the occurrence

and further evolution of distortions and deformations of the crystal lattice as a result of exposure to ionizing radiation. Figure 3 shows the X-ray diffraction patterns of the studied samples before and after irradiation with various types of ionizing radiation.
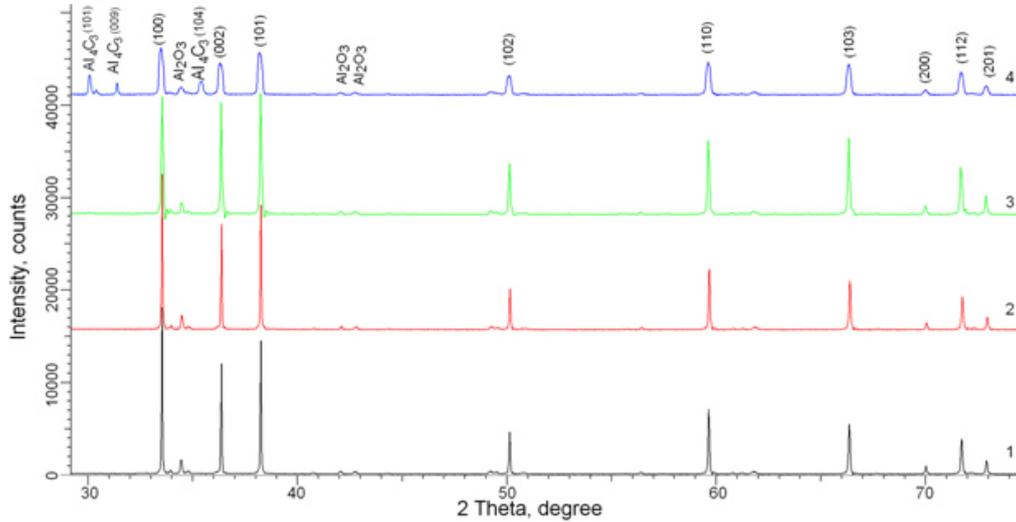

Figure 3. X-ray diffraction patterns of the studied ceramics before and after irradiation: 1) initial; 2) proton irradiation; 3) irradiation with He $^{2+}$ ions; 4) irradiation with C $^{2+}$ ions.

As can be seen from the presented data, the initial samples are polycrystalline structures of aluminum nitride with a high degree of crystallinity and a selected texture orientation along the (100), (002), (101) directions characteristic of hexagonal type structures similar to wurtzite. The presence of low-intensity peaks characteristic of impurity inclusions of the Al_2O_3 phase (no more than 4%) is due to the technological processes of sintering nitride ceramics from Al_2O_3 powders. In this case, according to previous studies, the distribution of impurity inclusions in the structure is equally probable by volume [17, 18]. Figure 4 shows the dynamics of changes in the main diffraction maxima of the samples under study.
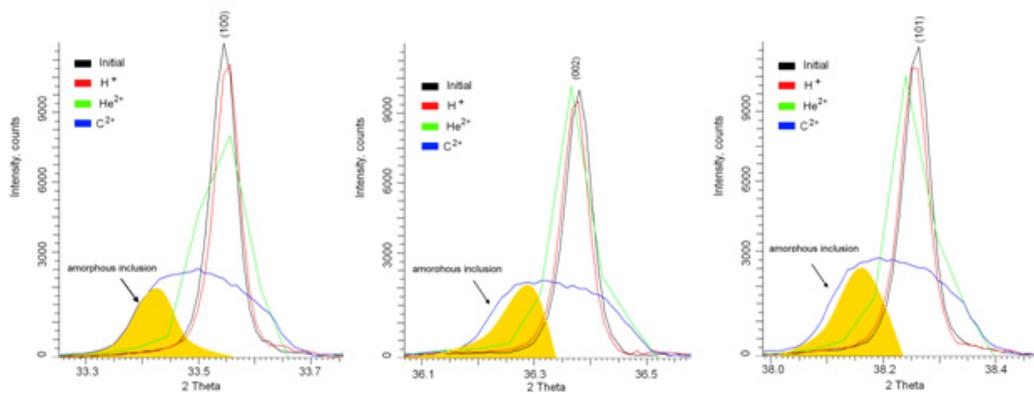

Figure 4. Detailed change of the main diffraction maxima depending on the type of exposure.

As can be seen from the presented data (Figure 3-4) for the samples irradiated with protons, the change in diffraction peaks, which reflects the change in stress concentration and deformations in the structure, is insignificant. Moreover, there is no significant shift in the diffraction maxima. This indicates a low concentration

of the resulting defects as a result of the interaction of protons with the crystal structure and high radiation resistance to proton irradiation. For samples irradiated with He^{2+} ions, a decrease in intensities and a slight asymmetry of the diffraction lines along the (100) texture direction are observed. When irradiated with low-energy ions, the main energy losses occur due to nuclear collisions. They lead to the formation of primary knocked-out atoms from the lattice sites and their subsequent migration with the formation of cascades of secondary defects. In this case, the polycrystalline structure and the presence of several texture orientations leads to a non-equilibrium distribution of distortions along different directions. This causes the radiation resistance of the material to external influences at the macroscopic level. Also, the shift of the position of diffraction maxima in the region of small angles may be due to introduction of helium ions into the interstices of the crystal lattice or the substitution of atoms in the lattice sites. It leads to an increase in interplanar distances. In this case, the largest change in diffraction maxima is observed for samples irradiated with C^{2+} ions, which indicates a low radiation resistance to carbon accumulation in the structure and accelerated degradation. According to the data obtained, the diffraction pattern of samples of carbon irradiated shows the appearance of new low-intensity diffraction peaks characteristic of the rhombohedral phase Al$_2$C$_3$, the formation of which is due to the introduction of carbon ions into the nodes and interstitial of the new phase. Also, for samples irradiated with carbon ions, a sharp decrease in the diffraction peaks with the formation of amorphous inclusions in the structure is observed. The appearance of amorphous inclusions is due to the destruction of crystalline and chemical bonds in the structure as a result of the migration of carbon ions and the resulting defects. To estimate the distortions and deformations of the crystal structure as a result of external influences, a method was used to measure changes in the RMS displacements of atoms from lattice sites. The estimation of the magnitude of displacements is carried out by measuring the ratios of the two most intense lines of the same sample before and after irradiation and is calculated using the formula (1):

$$U^2 = 3a^2 \ln\left[(I_1/I_2)_{irradiated} \,/\, (I_1/I_2)_{initial}\right] \,/$$
$$/\, 4\pi^2 \left[\left(h_2^2 + k_2^2 + l_2^2\right) - \left(h_1^2 + k_1^2 + l_1^2\right)\right], \tag{1}$$

where a is the lattice parameter, $(I_1/I_2)_{initial}$, $(I_1/I_2)_{irradiated}$ is the ratio of intensities of the diffraction lines before and after irradiation, respectively. The change in ceramics density during irradiation was calculated using formula (2):

$$p = \frac{1.662 \sum AZ}{V_0}, \tag{2}$$

where V_0 is the volume of the unit cell, Z is the number of atoms in the crystal cell, A is the atomic weight of atoms. The assessment was carried out by determining the change in the volume of the unit cell under irradiation. The concentration of amorphous-like inclusions in the crystal structure of the studied ceramics was found according to formula (3):

$$p_{dil} = (1 - p/p_0) * 100\%, \tag{3}$$

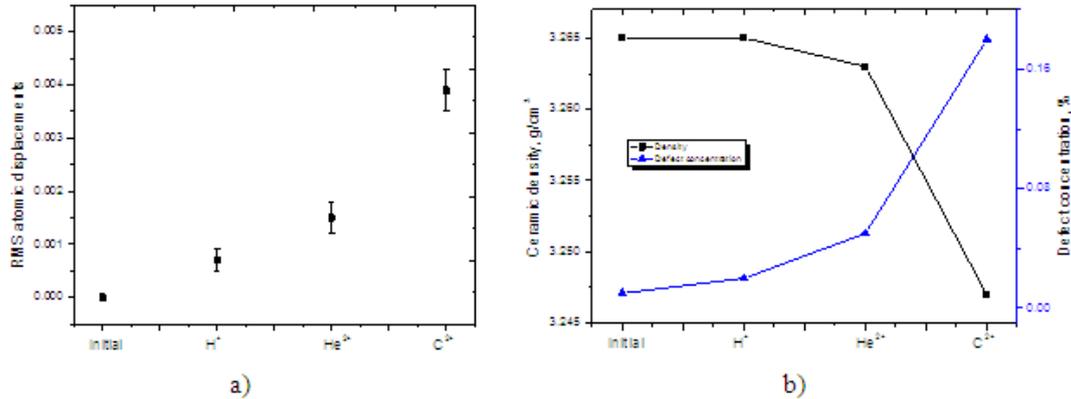where p_0 is the density of the reference sample.

Figure 5. a) Dynamics of changes in the magnitude of the RMS displacements of atoms in the crystal lattice under external influence; b) Graph of the change in ceramics density and the concentration of amorphous-like inclusions on the type of irradiation.

Figure 5a and Figure 5b presents the results of changes in the magnitude of atoms displacement from lattice sites, as well as changes in ceramics density and the concentration of amorphous-like inclusions in the structure as a result of irradiation with various types of ions. A sharp increase in atoms displacement from lattice sites at irradiation with He^{2+} and C^{2+} ions is due to the occurrence of a large concentration of point defects in the structure. These migrate through the structure and destroy chemical and crystalline bonds and can lead to knocking atoms out of lattice sites. As can be seen from the presented data, during the formation of a large number of vacancy defects as a result of ballistic collisions of incident ions and weak solubility of helium and carbon ions in the structure of ceramics, the formation of amorphous-like inclusions and regions of disorder is observed, which leads to a decrease in ceramics density. In this case, as is well known, the occurrence of defect overlap areas at high irradiation fluences leads to a decrease in the recombination of the resulting defects and the formation of local defect areas in the structure [16-18]. It is also worth noting that the formation of these areas occurs at a depth not exceeding (0.5-0.7) microns, resulting in a large concentration of defects and distortions in the subsurface layer, leading to changes in the structural, optical and strength characteristics that have a significant impact on radiation resistance and operation time of ceramics under conditions of increased exposure to ionizing radiation.

Conclusion

The paper presents the results of a study of the effects of proton and ion radiation on the structural changes of nitride ceramics. To simulate the processes of defect formation and to estimate the radiation resistance of ceramics, proton beams with an energy of 1.5 MeV and low-energy helium (He^{2+}) and carbon (C^{2+}) ions with an energy of 40 keV were used. According to the data obtained, it has been established that AlN nitride ceramics have high radiation resistance to the effects of proton radiation. The study found that when irradiated with He^{2+} and C^{2+} ions, the formation of large hexagonal grains on the surface is observed.

In this case, the greatest degradation of the surface layer is observed at irradiation with C^{2+} ions. In this case, the formation of cracks and depressions, as well as small inclusions, is observed in the near-surface layer, which is caused by both sputtering processes and the formation of metastable impurity phases, leading to a partial destruction of the crystal structure.

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