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Structure and Mechanical Properties of TiAlN Coatings under High-Temperature Ar^+ Ion Irradiation

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Using the method of reactive magnetron sputtering, nanostructured TiAlN coatings were formed on the substrates of AISI 304 stainless steel. The formed TiAlN coatings were irradiated with argon ions Ar^+ with an energy of 200 keV in the fluence range from 2.5×10^{16} ions/cm^2 to 2×10^{17} ions/cm^2 at a temperature of 480°C. The elemental composition and structural-phase state of virgin and irradiated coatings were investigated by methods of energy-dispersive X-ray spectroscopy, scanning electron microscopy as well as X-ray phase analysis. The mechanical properties of the obtained structures were studied by nanoindentation using the Oliver and Pharr method; hardness and Young's modulus were measured. The indicators of the impact strength, as the H/E^* ratio, as well as the resistance to plastic deformation, as the H^3/E^{*2} ratio, of the coatings under study were calculated. It was found that the nanostructured TiAlN coatings retain their structure up to the irradiation fluence of 2×10^{17} ions/cm^2, at which the beginning of phase segregation of solid solution (Ti, Al)N as the main phase of the coating as well as blistering is observed. The nonlinear nature of changes in the hardness H, Young's modulus E, impact strength H/E^*, and resistance to plastic deformation H^3/E^{*2} on the irradiation fluence was found.

topics: nanostructured TiAlN coatings, high-temperature ion irradiation, nanoindentation, hardness

1. Introduction

The intensive development of nuclear power and cosmonautics has become a driver for the intensive development of radiation-resistant materials capable of ensuring the immutability of their operational characteristics at high temperatures and radiation fluences [1]. In nuclear materials science, radiation resistance issues are primarily relevant to the structural materials of nuclear power plants and nuclear reactors. The issue of ensuring the stability of the structure of fuel elements of nuclear reactors throughout the entire period of their operation is particularly relevant. The shells of fuel elements are subjected to a number of extreme impacts in a nuclear reactor, including high-temperature effects from nuclear fuel (400–500°C) and from the coolant (300–350°C), as well as corrosive effects from the decay products of nuclear fuel and from the coolant (usually water or Na–K eutectic). However, the most destructive effect on the material is irradiation with neutrons, fragments of uranium nuclear fission, and gamma radiation. Irradiation of materials with particle beams, in particular ions and neutrons, leads to the formation of defects in the crystal structure. Their accumulation leads to a number of negative consequences, such as embrittlement of the material, loss of plasticity, increased creep, and radiation-stimulated corrosion. In space materials science, new radiation-resistant materials are relevant as protection against the effects of high-energy ions and other particles in space. The characteristic feature of nuclear materials science is the development of materials resistant to high ion fluences (10^{16}–10^{18} ions/cm^2) with an energy of 1 MeV, while space materials science requires materials resistant to low fluences (10^{11}–10^{14} ions/cm^2) of heavy ions with high energy, over 100 MeV. The most attractive in this regard are nanostructured ceramic coatings, which have high radiation resistance due to the presence of a large integral length of interfaces that work as effective sinks for radiation-induced structural defects [2].

In the theoretical papers, the influence of crystallite boundaries was considered from the point of view of classical thermodynamics [1]. It was found that the presence of a nanostructure increases the resistance to phase transitions under the influence of irradiation. The smaller grain size reduces the Gibbs free energy of the system by suppressing the accumulation of point defects (mainly vacancies) at the grain boundary. However, a decrease in the grain size also leads to an increase in the Gibbs free energy due to an increase in the integral area of grain boundaries. The mixing heat for a two-phase system is usually high, and therefore mixing with an ion beam is impossible. In addition, it was found that reducing the grain size increases the Gibbs free energy, and thus it negatively affects the resistance to the phase transition under the influence of irradiation (amorphization). Therefore, radiation resistance depends on the grain size. The grain size should be optimal. If the grain size is too large, the material behaves like a microcrystalline one due to the absence of a large integral extent of grain boundaries.

Another important feature of coatings of this kind is the large strength they can provide. Due to the use of coatings, it is possible to improve the strength properties of the material without a significant increase in its mass. As was shown in the other work of the authors [3], the formation of protective ceramic coatings makes it possible to provide high resistance to abrasive wear. The surface erosion of ZrN/SiN_x multilayer films irradiated with He^+ ions (30 keV) and annealed in vacuum at $t = 600°C$ was studied in [4]. It was concluded that ZrN/SiN_x multilayer films remain resistant to blistering and peeling when irradiated with He ions (30 keV) up to a fluence of 8×10^{16} ions/cm^2. The authors of the paper [5] studied the nanostructured TiAlN coatings irradiated with N^+ ions with an energy of 1.4 MeV at various fluences and temperatures. It was shown that phase segregation and amorphization of the structure were not detected in all irradiated samples, however, at a fluence of 2×10^{16} ions/cm^2, the formation of a large number of nitrogen bubbles was observed. According to the results of nanoindentation, the authors recorded the effect of some radiation-induced decrease in the hardness of TiAlN coatings.

In this regard, it is urgent to study the properties of nanostructured nitride coatings based on metals and their combinations for radiation resistance with the preservation of mechanical characteristics, including those at elevated temperatures.

2. Experimental details

The deposition of nanostructured TiAlN coatings with a thickness of 2–2.5 μm was performed using the method of reactive magnetron sputtering (RMS) on the modernized UVN-2M installation. The components made of AISI 304 stainless steel were used as substrates for coatings. Before the deposition of TiAlN coatings, the surfaces of the substrates were ground and polished, and thus their surface roughness was $R_a \approx 0.1$ μm. The deposition of coatings was made in the optimal mode with the formation of nitride with the stoichiometric concentration regarding the nitrogen content [6].

The formed TiAlN coatings were irradiated with 200 keV Ar^+ ions using the UNIMAS ion implanter of the Institute of Physics, Lublin. The irradiations were performed at a target's temperature of 480°C with the fluences of 2.5×10^{16} ions/cm^2, 5×10^{16} ions/cm^2, 1×10^{17} ions/cm^2, and 2×10^{17} ions/cm^2. The current density of ions was $J = 1.2$ μA/cm^2.

The structure and morphology of coatings were studied by scanning electron microscopy (SEM) using a Hitachi SU3400 microscope. The accelerating voltage of the electron beam was 15 kV. The electron microscope was equipped with an X-ray radiation sensor (energy-dispersion spectrometer) which allows us to determine the elemental composition of the coatings under study by energy-dispersive X-ray spectroscopy (EDRS). The error in measuring the atomic concentration of the main elements was less than 1 at.%. The analysis of the structural-phase state of the TiAlN coatings was carried out using an ADANI PowDiX 600/300 X-ray powder diffractometer, and the radiation CoKa wavelength was $\lambda = 1.7889$ Å.

Hardness measurements of the obtained samples were made based on the Oliver and Pharr method [7, 8] using a Nano Hardness Tester (NHT2) device from CSM Instruments (Switzerland) equipped with a Berkovich diamond indenter. In the measurements, Poisson's ratio ν was taken to be equal to 0.3 [9].

3. Results and discussion

Table I shows the concentrations of elements in the TiAlN coatings before and after Ar^+ ions irradiation with various fluences. According to the results of EDRS spectroscopy, the concentration of oxygen and carbon in the coatings was detected at the level of measurement error, indicating their high quality and purity of the reactive magnetron sputtering process. The concentration of argon atoms recorded in the experiment was not detected completely, due to its high diffusion mobility [10].

Calculated using the SRIM software package [11], the average projected range of 200 keV Ar^+ions in the TiAlN coatings was $R_p = 285$ nm, and the straggling ΔR_p was 51 nm.

TABLE I

Elemental composition of TiAlN coatings before and after irradiation with argon ions of different fluences.

Irradiation fluence ($\times10^{16}$) [ions/cm^2]	Element concentration [at.%] Ti	Al	N
as-deposited	29.90	23.60	46.50
2.5	30.70	24.20	45.10
5	31.40	25.80	42.80
10	31.63	26.32	42.05
20	33.70	25.80	40.50

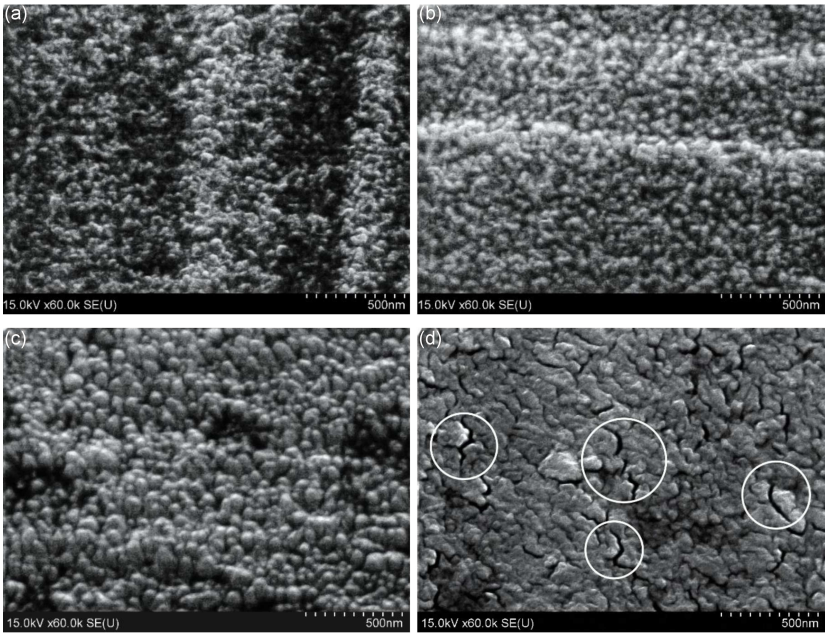

Fig. 1. SEM micrographs of surface of TiAlN coatings irradiated by 200 keV Ar^+ ions at 480°C with fluences: (a) 2.5×10^{16} ions/cm^2; (b) 5×10^{16} ions/cm^2; (c) 1×10^{17} ions/cm^2; (d) 2×10^{17} ions/cm^2.

Before the irradiation, the concentration of the elements in the TiAlN coating corresponds approximately to the stoichiometric state (Table I). With an increase in the irradiation fluence, the coating becomes depleted in the lightest component, nitrogen, and enriched in the heavier components — titanium and aluminum. Such a change in the concentration of elements indicates the effect of selective sputtering of nitrogen from the TiAlN coatings. Under the influence of irradiation with argon ions, the nitrogen atoms leave the surface of the coating more efficiently compared to other elements. As a result, the concentration of titanium and aluminum increases relatively.

Figure 1 shows the SEM micrographs of the studied TiAlN coatings after the irradiation. It was found that at the minimum irradiation fluence equal to 2.5×10^{16} ions/cm^2 as well as 5×10^{16} ions/cm^2, there are no changes in the morphology of the coatings. When the samples are irradiated with a fluence of 1×10^{17} ions/cm^2, dark areas are observed on the coatings surface, the presence of which can indicate the beginning of blister formation in the structure. The effect of radiation blistering consists of the accumulation of inert gas in the structure of the material, followed by its agglomeration into bubbles, which leads to the destruction of the material. At the irradiation fluence of 2×10^{17} ions/cm^2, the pronounced blisters with cracks are observed on the surface of TiAlN coatings (Fig. 1d — blisters are marked). Thus according to the SEM results, the fluence of 200 keV Ar^+ irradiation at 480°C equal to 2×10^{17} ions/cm^2 can be considered as the threshold of radiation resistance of TiAlN coatings to the blistering effect.

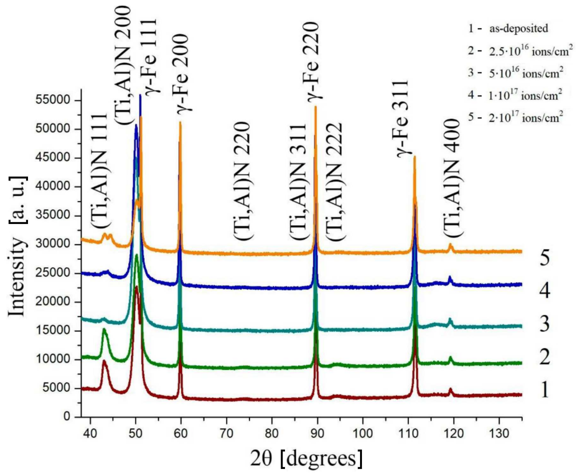

Fig. 2. X-ray diffractograms from TiAlN coatings in the initial state and irradiated by 200 keV Ar^+ ions at a temperature of 480 °C with various fluences.

As shown in the obtained diffraction patterns from the TiAlN coatings (Fig. 2), the diffraction peaks of the austenite phase γ-Fe 111, γ-Fe 200, γ-Fe 220, γ-Fe 311 from the stainless steel substrate were detected. The diffraction peaks from the (Ti, Al)N phase were also found. This phase is a disordered substitutional solid solution based on a face-centered cubic (fcc) lattice of the NaCl type of titanium nitride TiN. It was found that the diffraction peaks are shifted to the region of large 2θ angles relative to pure nitride. This fact indicates the replacement of titanium atoms

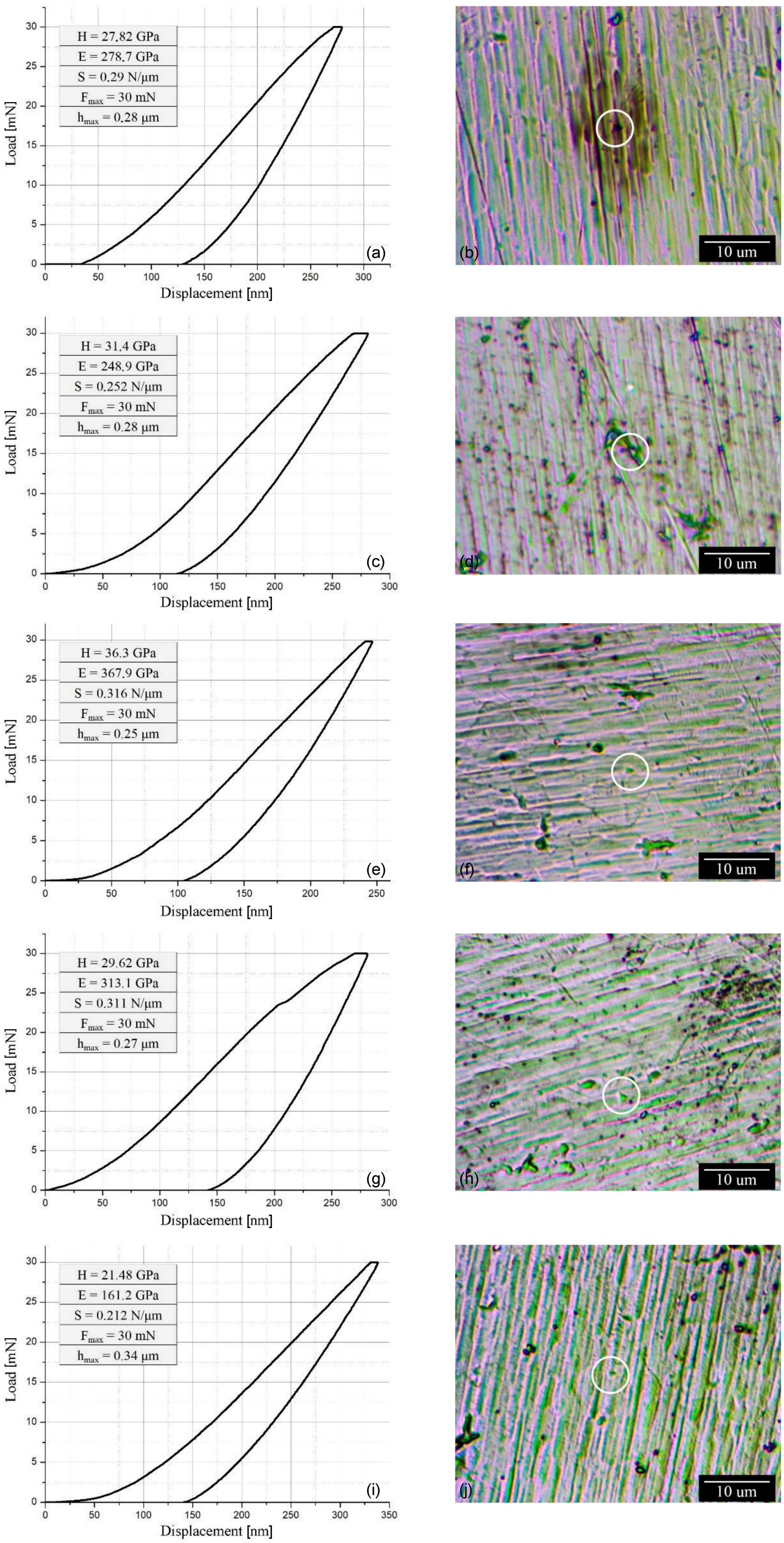

Fig. 3. Load-unload curves (a, c, e, g, i) and micrographs of indenter prints (b, d, f, h, j) from a TiAlN coating irradiated with Ar^+ ions with various fluences: (a, b) — as-deposited; (c, d) — 2.5×10^{16} ions/cm^2; (e, f) — 5×10^{16} ions/cm^2; (g, h) — 1×10^{17} ions/cm^2; (i, j) — 2×10^{17} ions/cm^2.

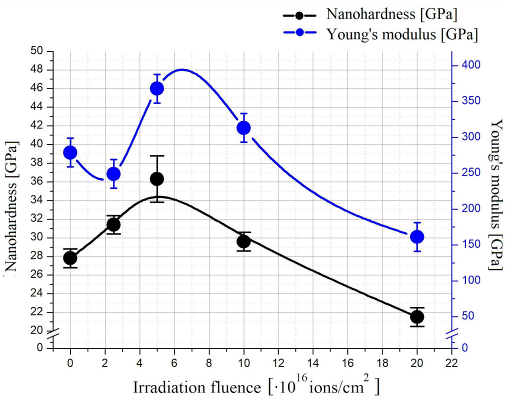

Fig. 4. Dependence of nanohardness and Young's modulus of TiAlN coatings on the fluence of irradiation with 200 keV Ar^+ ions at a temperature of 480°C.

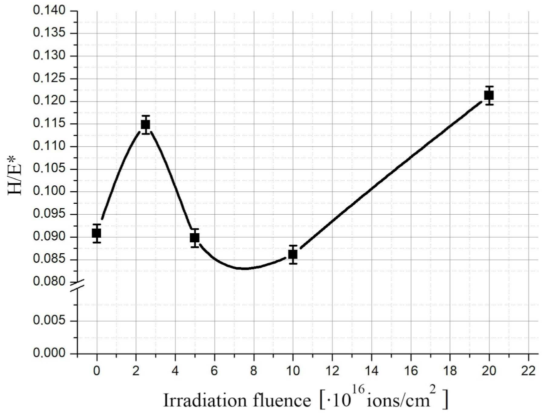

Fig. 5. Dependence of the index of impact strength (H/E^*) of the TiAlN coating on the fluence of irradiation with 200 keV Ar^+ ions at a temperature of 480 °C.

by aluminum atoms, which have a smaller atomic radius ($R_{\mathrm{Ti}} = 1.47$ Å, $R_{\mathrm{Al}} = 1.43$ Å) [12]. Calculated by Scherrer's formula, the average size of the crystallites of the TiAlN coating varies in the range of 10–50 nm. It follows from the diffraction patterns that at a given irradiation temperature, the fluence of 2×10^{17} ions/cm^2 is the threshold one, after which a change in the coating structure begins to appear. Namely, the beginning of spinodal phase segregation of the solid solution is observed. Below this irradiation fluence, there are no significant changes in the phase composition and structure, as well as any signs of amorphization of the TiAlN coating.

Figure 3 shows the results of nanoindentation using the Oliver and Pharr technique [7, 8] and micrography of indenter prints on the TiAlN coatings in the initial state and after irradiation with various fluences. In the measurements, in accordance with the literature data, Poisson's ratio ν was taken as equal to 0.3 [9]. Based on the results of the nanohardness measurements, it was found that TiAlN coatings have a high hardness (more than 26 GPa) and are suitable for applications under high-temperature radiation irradiation with a fluence of up to 2×10^{17} ions/cm^2. The smooth nature of the load-unload curves indicates the uniformity of the coatings in depth and shows their high crack resistance. In addition, the effect of radiation hardening of the coatings is observed due to the influence of formed radiation defects and their accumulation on the movement of dislocations.

In the micrographs (Fig. 3), we observe the absence of crack formation and delamination of the TiAlN coatings near the nanoindenter imprint, which makes it possible to assess the good impact strength and a high degree of adhesion of the coating to the substrate. The absence of delaminations, cracks, and droplet fractions allows us to conclude that the formed coating is homogeneous over the surface and depth, i.e., the TiAlN coatings are of high quality.

Figure 4 shows the dependence curves of the nanohardness and Young's modulus of the studied TiAlN coatings on the irradiation fluence. The largest values of hardness $H = 36.3$ GPa and Young's modulus $E = 367.9$ GPa were found for the TiAlN coating irradiated with a fluence of 5×10^{16} ions/cm^2. The smallest hardness $H = 21.48$ GPa and Young's modulus $E = 161.2$ GPa were demonstrated for the TiAlN coating irradiated with a fluence of 2×10^{17} ions/cm^2. The average hardness $H = 29.62$ GPa and Young's modulus $E = 313.1$ GPa were shown for the coating with an irradiation fluence of 1×10^{17} ions/cm^2. From these results, it can be concluded that the TiAlN coating retains high hardness and elasticity under the conditions of high-temperature irradiation with argon ions up to a fluence of 2×10^{17} ions/cm^2.

The ratios H/E^* were calculated for the formed TiAlN coatings in the initial state and after the irradiation with different fluences. According to the literature data, if the H/E^* ratio is higher than 0.1, the coatings can be considered hard and, at the same time, sufficiently plastic, that is, having a high fracture toughness [13, 14]. For the virgin, i.e., non-irradiated TiAlN coating, the calculated ratio was $H/E^* = 0.092$. As shown in Fig. 5, with an increase in the irradiation fluence to a value of 2.5×10^{16} ions/cm^2, an increase in impact strength is observed, followed by a non-critical decrease in this indicator by a sufficiently small amount (about 5%) at the fluences of 5×10^{16} ions/cm^2–1×10^{17} ions/cm^2. This fact indicates the ability of the coating to retain its strength properties under the conditions of high-fluence irradiation. The observed significant increase in the value of impact strength $H/E^* = 0.121$ at an ultra-high irradiation fluence of 2×10^{17} ions/cm^2 cannot be considered reliable due to the influence of the detected blistering effect.

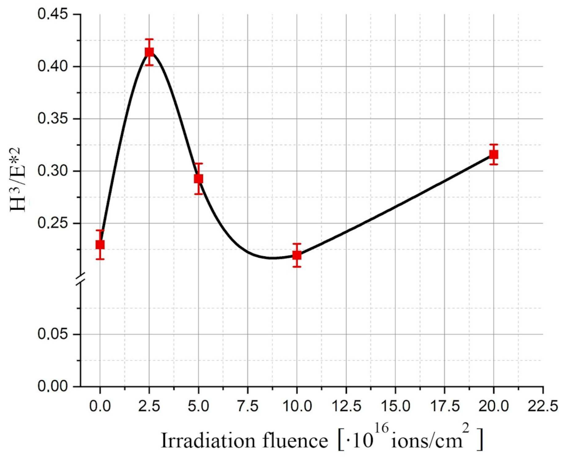

Fig. 6. Dependence of the plastic deformation index (H^3/E^{*2}) of the TiAlN coating on the fluence of irradiation with 200 keV Ar^+ ions at a temperature of 480°C.

The indices of plastic deformation, as the expression H^3/E^{*2} [15], were calculated for the TiAlN coatings in the initial state and after irradiation with various fluences. Figure 6 shows a graph of the dependence of the plastic deformation resistance index on the irradiation fluence. The non-irradiated TiAlN coating has a plastic deformation index $H^3/E^{*2} = 0.230$. With an increase in the irradiation fluence to a value of 2.5×10^{16} ions/cm^2, an increase in the plastic deformation index is observed, followed by a decrease in this indicator by a rather small value relative to the original sample, at fluences of 5×10^{16}–1×10^{17} ions/cm^2. This fact indicates the ability of the coating to maintain resistance to plastic deformation under conditions of accumulation of a high fluence of radiation. The observed significant increase in the value of the impact strength H^3/E^{*2} at an ultra-high irradiation fluence of 2×10^{17} ions/cm^2 cannot be considered reliable due to the influence of the detected blistering effect, as well as the beginning of segregation of the solid solution (Ti, Al)N, according to the results of X-ray phase analysis (Fig. 2). Thus, the behavior of the plastic deformation resistance index with an increase in the irradiation fluence is similar to that of the impact strength index.

4. Conclusion

Using the method of reactive magnetron sputtering, TiAlN coatings were formed on substrates made of AISI 304 stainless steel. High-temperature (480°C) irradiation of TiAlN coatings by argon ions with an energy of 200 keV was carried out in the fluence range of from 2.5×10^{16} ions/cm^2 to 2×10^{17} ions/cm^2.

Based on the results of the elemental composition of coatings, a change in the percentage ratio of the coating components was found, which is due to the effect of selective sputtering of the lightest component, nitrogen. The formation of a single-phase structure of the solid solution (Ti, Al)N coatings was revealed. The Ar^+ irradiation at a temperature of 480°C with a fluence up to 1×10^{17} ions/cm^2 does not induce significant changes in the structural-phase state of the formed coatings. No amorphization of coatings was detected at all irradiation fluences. According to the results of X-ray phase analysis, it was found that at the irradiation fluence of 2×10^{17} ions/cm^2, the beginning of spinodal phase segregation of the solid solution into titanium nitride TiN and aluminum nitride AlN was observed. Also, with the specified irradiation fluence, the effect of blistering of TiAlN coatings was detected.

Nanoindentation of the virgin and irradiated coatings was carried out according to the method of Oliver and Pharr. The hardness H, as well as Young's modulus E, were determined. The impact strength index as the H/E^* ratio, as well as the plastic deformation resistance index H^3/E^{*2}, were calculated. The improvement of strength properties set of TiAlN coatings under the irradiation with a fluence of 2.5×10^{16} ions/cm^2 was found. With a further increase in the irradiation fluence, an increase in the hardness of the coatings was revealed, but a decrease in the impact strength index, as the H/E^* ratio, and the plastic deformation resistance index, as the H^3/E^{*2} ratio, were found.

The TiAlN nanostructured coatings are radiation-resistant and are able to retain their mechanical properties up to the Ar^+ ion irradiation fluence of 2×10^{17} ions/cm^2 at a temperature of 480°C. They are promising for increasing the service life of cutting tools, as protective tools under the conditions of high-temperature corpuscular irradiation, and as wear-resistant tools in mechanical engineering and space technology.

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