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Radiation effects in coatings ZrTiN induced by impact of high energy krypton ions

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Abstract. This paper presents research results of the impact of high-energy krypton ions on structure and mechanical properties of ZrTiN coatings. The ZrTiN coatings were synthesized by the magnetron sputtering method on the substrates from Cr18Ni10Ti steel. Samples irradiated by $^{84}Kr^{14}$ with energy 125 MeV to fluence 10^{16} cm^{-2} at room and 600˚C temperatures. It established that irradiation resulted in significant changes in the surface structure, i.e. appearance of the coral-like structure. Formation of coral-like structure leads to degradation of mechanical properties such as hardness and corrosion resistance. Most significant changes surface structure and properties of coating observed after irradiation at room temperature.

1. Introduction

One of the promising directions for the development of radiation-resistant materials for nuclear and thermonuclear installations is the use of multicomponent coatings on traditional materials used with properties unattainable for pure materials or alloys. For applying such coatings, advanced technologies, such as magnetron sputtering, vacuum condensation, etc., are usually used [1]. It can be ceramic coatings, as well as coatings based on transition metal nitrides. In particular, coatings based on transition metal nitrides have demonstrated good properties [2-3]. The series of works [4-6] are devoted to the synthesis of ZrTiN coatings by magnetron and vacuum-arc methods with different contents of zirconium and titanium on different substrates (silicon, steel) and the study of their structure and properties. It was shown that these coatings have a good set of properties — high strength characteristics, corrosion resistance, electrical conductivity, etc. Studies of the radiation resistance of ZrTiN coatings showed high stability of the structure and properties when irradiated with heavy low-energy ions and alpha particles [7–8]. This work is a continuation of studies of the stability of the structure and properties of ZrTiN coatings [7] as applied to irradiation with high-energy heavy ions (Kr).

2. Materials and experimental methods

To study the effect of ion irradiation on the structure and properties of the ZrTiN coatings, were prepared the samples with the ZrTiN coatings on substrates of Cr18Ni10Ti structural steel . Since the coatings with the content of Zr and Ti of 50/50 at.% [7] showed the highest stability of properties under irradiation with low-energy heavy ions, we synthesized the coatings with such ratio of Zr and Ti in the coating.

The procedure of sample preparation can be divided on two stages. The first stage was to prepare the substrate for coating application. The substrates of 20 mm × 20 mm × 1 mm dimensions were cut from a massive plate of stainless steel Cr18Ni10Ti by the method of electro-erosion cutting, followed by the standard preparation procedure for coating application: mechanical grinding with a gradual reduction in the particle size of abrasive paper and polishing on cloth using GOI paste. Before coating, the substrates were cleaned from contamination by ion etching with low-energy argon ions.

At the second stage ZrTiN coatings were synthesized by the method of magnetron sputtering of targets from two magnetrons. The sputtered targets were the discs of Zr (99.96 wt.% purity) and Ti (99.99 wt.% purity). The gas mixture with nitrogen content of ~ 25% was used as a plasma-forming gas. The thickness of the applied coatings was controlled by the coating time. As a result, the samples with the ZrTiN coatings ~600 - 700 nm thick were produced.

Thickness of the coatings was checked by the Rutherford backscattering (RBS) method on protons at the accelerator UKP of the Institute of Nuclear Physics [9]. According to the results of processing the spectra of backscattered protons, it was established that the thickness of the ZrTiN coating is 780 nm, and the elemental composition as follow: Zr is 30 at.%, Ti is 31 at.% and N is 39 at.%.

The studies of the structure and elemental composition of the coatings were performed by X-ray structural analysis (XSA), scanning electron microscopy (SEM), energy dispersive analysis (EDS) and atomic force microscopy (AFM).

According to XSA, the initial, before irradiation, structure of the ZrTiN coating consists of two-phase: main phase is a solid solution of ZrN in TiN. Lattice parameter of the solid solution is 4.377 Å. Also, a phase of pure titanium with the lattice parameter of 4.0357Å is observed in minor amounts in the coatings. The diffraction patterns of the steel substrate also show the reflections.

The surface structure of the ZrTiN coating revealed by SEM and AFM methods is shown in figure 1 a,b. We can see from images on the figure 1 that the surface structure follows the structure of the steel substrate - there are bands characteristic of the surface after grinding before coating application.

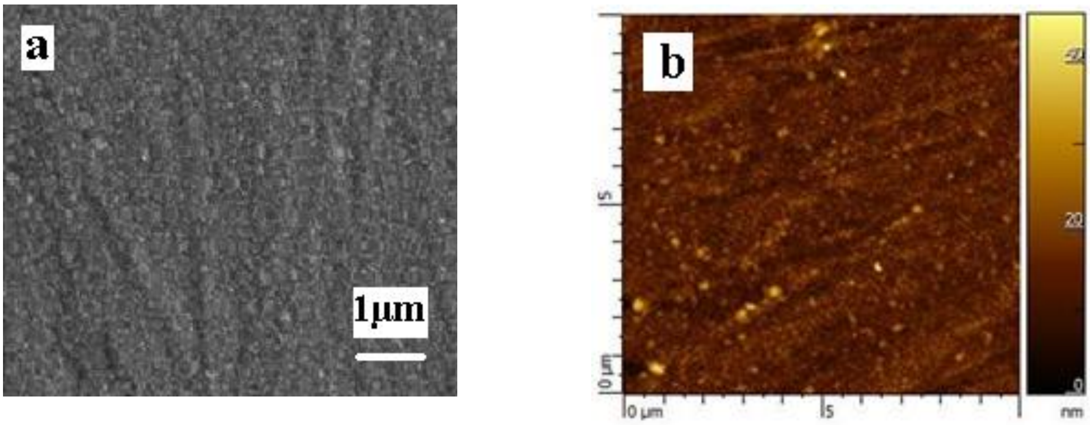

Figure 1. SEM (a) and AFM (b) images of the ZrTiN coating surface before irradiation.

The coating surface has a characteristic relief, which is a finely dispersed globular-shaped particle with an average diameter of ~ 0.4 μm (~ 75% of the surface). The minimum particle diameter is ~ 0.15 μm (~ 20%), the maximum is 0.8 μm (~ 5%).

The results of determining the elemental composition of the ZrTiN coating by EDS method are shown in figure 2.

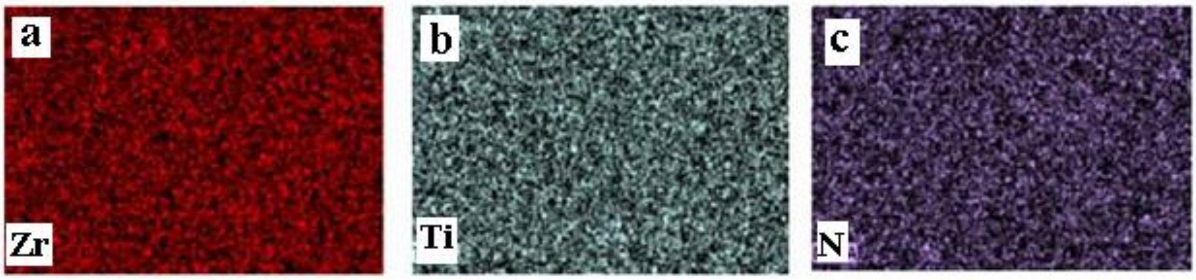

Figure 2. Distribution of Zr, Ti, and N elements in the coating according to EDS analysis.

The figure 2 shows that zirconium, titanium and nitrogen are evenly distributed over the surface of the coating.

The physical-mechanical properties were determined by hardness (Hn) of the coatings measured on the nanohardness meter "Nanoscan Compact" and the corrosion resistance (CR) in a 3% NaCl solution using the “Gamry Instruments” corrosion cell.

The measured hardness of the ZrTiN coating (on surface) before ion irradiation was Hn = 10.8 GPa. We shall note, that hardness of the ZrTiN coating is more than 2 times higher than hardness of steel (4.4 GPa). The corrosion rate of the ZrTiN coating was - 12.3×10^{-3} mm/year. The results of hardness and corrosion resistance measurements are also shown below in Table 2.

3. Irradiation procedure

The ZrTiN samples were irradiated with high-energy krypton ions on the high-energy channel of the heavy ion accelerator DC-60 at the Institute of Nuclear Physics branch in Nursultan city. Irradiation at room temperature means that was no special heating of specimen during irradiation. Real temperature at the surface of specimen under action of ion beam does not exceed 100˚C. The target holder with electric heating was used to irradiate the sample at 600 °C temperature. The parameters of ion beam and conditions of irradiation with high-energy krypton ions are shown in Table 1.

Table 1. Irradiation conditions for the samples with ZrTiN coatings by high-energy krypton ions

	Ion	Energy, MeV	Irradiation temperature	Fluence, cm^{-2}	Beam current, μA	Irradiation area, cm^2
ZrTiN	$^{84}Kr^{14+}$	125	Room	10^{16}	0.35	4
ZrTiN	$^{84}Kr^{14+}$	125	600˚C	10^{16}	0.21	3.01

4. Experimental results and discussion

Surface sputtering of the ZrTiN coating under high-energy krypton ions bombardment is minimal. Thickness measurement of the coating, irradiated with 125 MeV krypton ions by the POP method showed that, within the accuracy of the method, the coating thickness did not change for both the sample irradiated at room temperature and the sample irradiated at 600 °C.

The phase structure of the ZrTiN coating did not change both after irradiation at room temperature and at a temperature of 600 °C. On diffractograms observed reflections the phase of solid solution ZrN in TiN, and phase of pure titanium. Shift of X-ray peaks allowed revealing increase in the lattice parameters of both phases. An increase in the lattice parameter is caused by the formation of radiation defects upon irradiation with krypton ions. It should be noted that irradiation at a temperature of 600 °C leds to a larger increase in the lattice parameter of phases both solid solution and pure titanium compare with irradiation at room temperature.

No changes in the ratio of Zr and Ti concentrations in the samples irradiated at room temperature and 600 °C were detected by EDS. Zirconium, titanium and nitrogen are evenly distributed over the surface of the coating as before irradiation, see figure 2.

The surface morphology (SEM and AFM images) of the ZrTiN coating irradiated with 125 MeV Kr ions to the fluence of 10^{16} cm^{-2} at room temperature is shown in figure 3 a, b. From these images can see that the surface structure has changed drastically: on the irradiated surface of the ZrTiN coating is observed formation of the coral-like structure. At high magnifications, it can be seen that the surface is covered with rounded and oblong hillocks. Rounded-shaped hillocks are traces from single incident heavy ions, and oblong is overlapping traces from two or more incident heavy ions. Hillocks appearance is caused by the energy release at braking of Kr ions in the surface layers of the coating. As already mentioned above, the appearance of hillocks does not accompanied in changes of coating elemental composition.

Figure 3c, d shows the structure of the ZrTiN coating surface irradiated with the same energy Kr ions and up to the same fluence, but at the temperature of 600 °C.

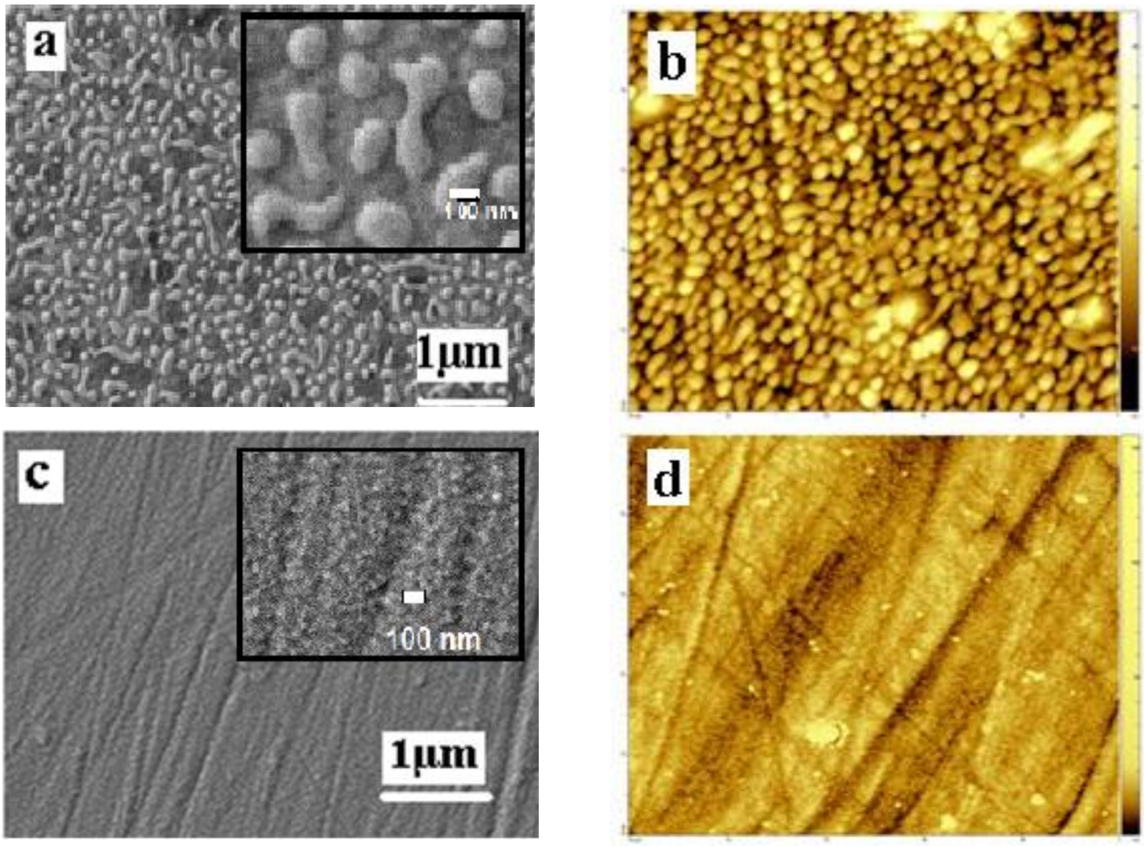

Figure 3. SEM (a,c) and AFM (b,d) images of the ZrTiN coating surface after irradiation with 125 MeV Kr ions to the fluence of 10^{16} cm^{-2} at room temperature (a,b) and 600 C (c,d).

Irradiation at 600 °C to a much lesser extent affects the change in surface structure. Small hillocks ~5-8 nm in size are observed on the irradiated surface, which, apparently, also represents the traces of incident Kr ions. Apparently, due to the relatively high irradiation temperature, the damage region from the incident Kr ion partially anneal, and, as a result, the hillocks on the surface are much smaller in size compared to irradiation at room temperature.

Changes in physical and mechanical properties (hardness and corrosion resistance) correlate with the changes in surface structure. The measurement results are shown in Table 2. It follows from the Table 2 that the decrease in hardness of the surface, irradiated at room temperature is more significant compared with hardness of the surface, irradiated at 600 °C. A similar dependence is observed for corrosion resistance – corrosion resistance degrades to a greater extent after irradiation at room temperature.

Table 2. Hardness and corrosion resistance of the ZrTiN coatings before and after irradiation with high-energy krypton ions.

Non-irradiated		Irradiated with 125 MeV Kr ions			
Hardness GPa	Vcorr, mm/year	Fluence, cm^{-2}	Irradiation temperature	Hardness, GPa	Vcorr, mm /year
10.8	12.3×10^{-3}	10^{16}	room	5.8	75×10^{-3}
			600 ˚C	9.3	24×10^{-3}

5. Conclusion

The article presents the results of experimental studies of the effect of irradiation with 125 MeV Kr ions on the structure and properties of thin (~ 800 nm) ZrTiN coatings. It is established:

- Irradiation of the ZrTiN coating with high-energy Kr ions at room and 600 °C temperatures does not lead to changes in the structural-phase composition of the coating and redistribution of the coating components;

- Irradiation of the ZrTiN coating with 125 MeV by Kr ions led to significant changes in the surface structure – the appearance of a coral like structure. Rounded and oblong hilloks formed on the surface at the sites of interaction of incident ions with the coating surface. Irradiation at room temperature causes more significant changes in the surface structure compared with irradiation at elevated (600 °C) temperatures.

- Irradiation of the ZrTiN coating with high-energy krypton ions leads to a decrease in the hardness and corrosion resistance of the coating. Irradiation at low temperature leads to greater degradation of physical and mechanical properties.

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