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Effect of Ion Irradiation on the Structural State of the Vacuum-Arc Nitride Coatings

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The effect of irradiation with ions Ar^+ (energy of 1 MeV and 1.8 MeV) and He^+ (energy of 0.6 MeV) on the structure and mechanical properties of the vacuum-arc nitride coatings. It is shown that the level of exposure to radiation materials can be divided into 3 classes: a) "the most persistent" - significant changes occur only on the substructure level (as an example - multi-element system Ti-Zr-V-Hf-Nb-Ta-N), b) "the medium resistance "- significant changes occur in the macro stress-strained state (as an example - the system Ti-N), c) "structural variable" – significant changes in the macro-level and phase composition (as an example, the system Mo-N).

Keywords: Ion irradiation, Ions Ar +, Vacuum-arc, Nitride coatings, Multi-element system, Phase composition, Substructure level.

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1. INTRODUCTION

Certain elements of NPP structure are subjected to ion irradiation of different energies, resulting in their rapid degradation due to a decrease in the physical and mechanical properties of the materials from which they are made. Therefore, one of the priorities of modern materials science is the development of materials resistant to radiation damage and the potential use of radiation processing technology as improving functional properties.

From a position of high functionality (and especially mechanical properties) recently carried out extensive studies on the use to create radiation-resistant surface coatings, refractory transition metal nitrides. This primarily refers to the finder of great practical use – vacuum arc coating of titanium nitride, which is inherent high hardness, adhesion, corrosion resistance.

This explains the interest in the study of physical and mechanical properties of TiN coatings subjected to ion irradiation. Besides titanium nitride with high energy of the covalent bond as materials for the study were chosen from MoN average binding energy and the new class of materials nitride high entropy multicomponent alloy Ti-Zr-V-Hf-Nb-Ta.

The paper analyzes the effect of irradiation with Ar+ (and, for comparison He+ with the energy of 0.6 MeV) to a dose of 10^{16} ion/cm^2 (to simulate exposure in the work area NPP) with energies of 1 MeV and 1.8 MeV, which provides an average depth of projective path about 1 micron and 1.8 microns, respectively.

2. EXPERIMENTAL DETAILS

Samples were prepared using vacuum arc equipment "BULAT-6" provided with an additional high-voltage pulse generator.

Table 1. Modes of coatings

Series number, №	Type of system	U_b, V	U_{pulse}, V	P, Torr
1	Ti-N	-200	-	$4 \cdot 10^{-3}$
2	Ti-N	-200	-1200	$4 \cdot 10^{-3}$
3	Mo-N	-100	–	$1,5 \cdot 10^{-3}$
4	Mo-N	-100	-1200	$1,5 \cdot 10^{-3}$
5	Mo-N	-200	–	$3 \cdot 10^{-3}$
6	Mo-N	-200	-1200	$3 \cdot 10^{-3}$
7	Mo-N	-200	-2000	$3 \cdot 10^{-3}$
8	Ti-Zr-V-Hf-Nb-Ta-N	-70	–	$4 \cdot 10^{-3}$
9	Ti-Zr-V-Hf-Nb-Ta-N	-200	–	$4 \cdot 10^{-3}$

Labeling of irradiated samples: Ar^+ (1 MeV) – № – 1, Ar^+ (1,8 MeV) – № – 2, He^+ (0,6 MeV) – № – 3

To increase the adhesive bond strength of the material and its characteristics on the stainless steel substrate 12X18H9T fed a constant negative bias potential value U_b = (-70 ... -200) V, and along with the constant potential supplied pulses amplitude negative potential 2 kV and 1.2 kV, duration of 10 μs and a repetition frequency of 7 kHz. Arc current in the evaporator was

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(100 ... 110) A, nitrogen pressure 0.66 Pa. Receiving modes are shown in Table 1.

Phase composition and structural state was studied by X-ray diffraction on a DRON-3M Cu-Kα radiation using a secondary beam graphite monochromator. Determination of residual macroscopic stresses in the coatings was carried out by X-ray strain measurement ("α-$\sin^2\psi$" method) and its modification in the event of a strong texture of the axial type.

The coatings were irradiated with ions of argon and helium an accelerator "Sokol". The hardness measurement was carried out using mikroindentora "Micron-Gamma" with a pyramid Berkovich load within 50 grams.

3. RESULTS AND DISCUSSION

The study of structural and phase state of coatings showed that titanium nitride with strong covalent bonds in the entire range of constant potentials fed offset U_b = (-70 ... -200) V is formed in a single-phase structural state of titanium nitride with the preferred orientation of crystallites (111) [1]. The increase in U_b leads only to an increase in the degree of perfection of texture, which affects in reducing the spread of angular disorientation of crystallites of 19° (half-width of the rocking curve) at U_b = -70 V to 10.5° at U_b = -200 V.

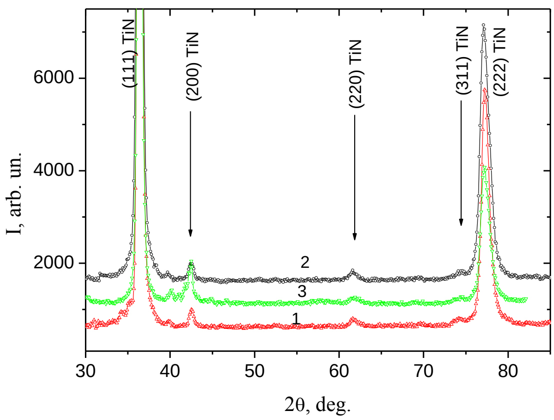


Fig. 1 – X-Ray diffraction spectra coating system Ti-N series 1: Unexposed – 1, 2: irradiated – 1-1 (1 MeV) and 3: 1-2 (1.8 MeV)

Analysis of the diffraction spectra of the Series 1 (before and after irradiation, Ar) showed that not fundamentally changing the phase composition of the coating (Fig. 1a), the irradiation causes a change in stress condition (the shift of the peaks) and the characteristics of the substructure (the broadening of the peaks).

Study of the substructure of the characteristics defined by the approximation of the profile shape Cauchy function shown that irradiation leads to a decrease in the average grain size of crystallites of 100 nm in its initial state to 45 nm and 38 nm, respectively, at different irradiation energies Ar. Microstrain equilibrated grain volume is also changed by irradiation. With increasing irradiation energy it varies from 0.52% at baseline to 0.58% after the exposure to the maximum energy.

Analysis of the diffraction spectra of the two series of samples (before and after irradiation with Ar) showed that after the pulse action (1200 V) does not change the phase composition of the coating (Fig. 2a). The change in the position of distant reflections (Fig. 2b). They shift to larger angles due to changes in the stress - strain state, which indicates a decrease in the value of condensation of compressive stresses in the coating.

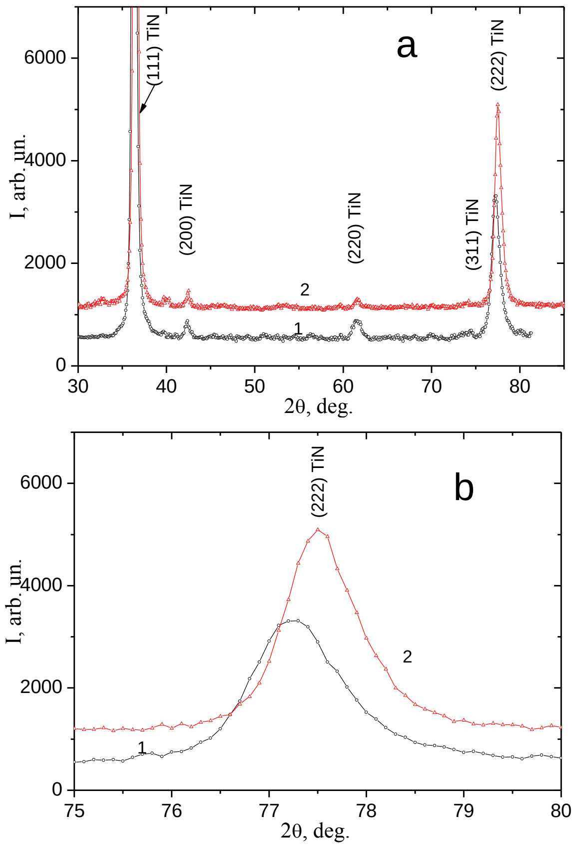


Fig. 2 – X-Ray of diffraction spectra coatings of series 2. Unexposed (1) irradiated – 2-1 (2). a – general view of the spectra, b – a site distant reflex (222)

The study of the characteristics substructure, which is similar to the Series 1 marked by irradiation decreases the average grain size of the crystallites from 110 nm to 38 nm. In this case, unlike the Series 1 to Series 2 microstrain decreases from 0.58% to 0.38%.

Investigation of the stress-strain state of «α-$\sin^2\psi$» - method showed that the Ar^+ irradiation with the highest energy of samples of series 2 leads to a strong relaxation of the stress-strain state of compression deformation of -2.11% in the initial state (after deposition) able to -1.38% - after irradiation ..

In molybdenum nitride metal component (Mo) has a larger atomic weight than titanium and considerably weaker covalent bond with the metal atoms by nitrogen atoms. This is manifested in the difference in not only structural, but also the phase state of coatings. Fig. 3 shows plots of the diffraction spectra of coatings Mo-N, received at different potentials bias -100 V and-200 V, as well as applying a pulsed bias potential.

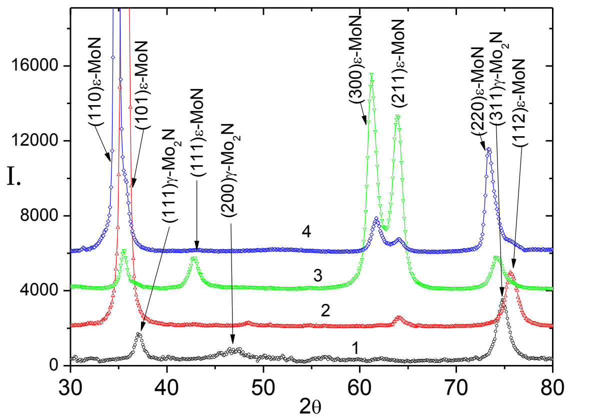


Fig. 3 – X-Ray diffraction spectra of samples of Mo-N, series 3 (spectrum 1), 5 (spectrum 2), 6 (spectrum 3) and 7 (spectrum 4)

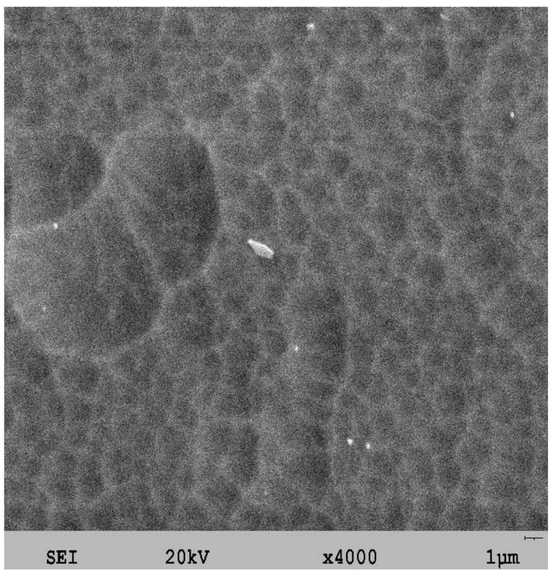
As can be seen from the diffraction spectra with less potential bias -100 V shaped γ-Mo_2N phase with fcc metal sublattice, the NaCl-type structure with a characteristic [2] for this phase of the preferred orientation (311).

If U_b = -200 V occurs in the formation of a new phase MoN with a hexagonal lattice of the space group P6/mmm, referred to as ε-MoN phase. No pulse impact of texture (101), which is at the highest pulse action U_{pulse} = 2000 V is changed to (110).

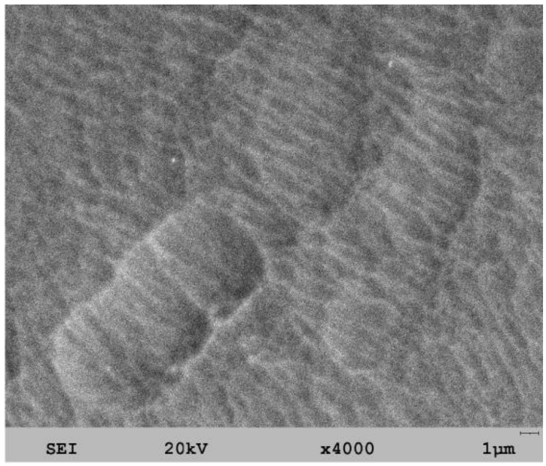
Under the irradiation of the coatings obtained with U_b = -100 V with γ-Mo_2N phase and texture (311) (phase composition and texture effects when switching is not changed) are the relaxation stress state and a decrease in crystallite size of up to 5 ... 7 nm.

Irradiation coatings obtained with high U_b = -200 V leads to stronger changes accompanied by a reorientation of crystallites in series samples 6 and 7 obtained by the impact impulse further. Thus, in the sample 6 series irradiation leads to the formation of preferred orientation (112), and a series of 7 - (101).

Note that unlike titanium nitride for which irradiation from erosion not noticeable to evident erosion molybdenum nitride surface after irradiation (Fig. 4).



a



b

Fig. 4 – View of the surface of the sample 7: a, before irradiation, b-after irradiation (1 MeV, Ar^+)

The least impact on the initial state of the material had exposure **high entropy nitride alloy**. In the initial state in the coatings formed of the cubic phase with a lattice-type structural NaCl, characteristic of the titanium nitride, which also increases with U_b amplified texture (111) – (Fig. 5).

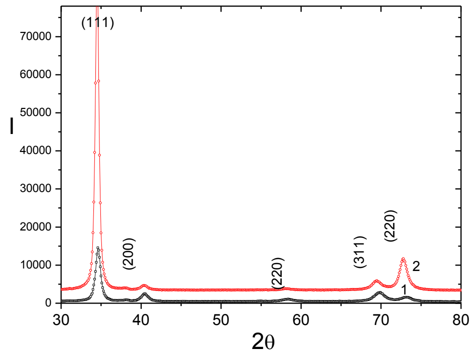


Fig. 5 – Land diffraction spectra of samples of Ti-Zr-V-Hf-Nb-Ta-N, series 8 (spectrum 1), 9 (spectrum 2)

At high bias potential is increased in the lattice relaxed section of 0.443 nm U_b = -70 V to 0,445 nm U_b = -200 V, and also noted a higher macrostrain -2.8% compared to -2.25% at smaller U_b.

Even the most intense radiation Ar^+ -1,8 MeV leads to a small relaxation of the stress state (about 5%), which appears to be associated with a fairly heavy masses of metal components high entropy alloys. At the substructure level the impact of irradiation effect on reducing the microstrain and a particulate formation structure, which in the case of multi-alloys can be considered a transition to a system equilibrium state. It should be noted that in case a strong texture in U_b = -70 V main radiation exposure has been reduced to a substantial reduction in the average crystallite size of 96 nm to 53 nm.

Test results by indentation presented in Table 2 showed that irradiation binary coating systems Ti-N and Mo-N causes degradation of mechanical properties. Moreover, to the greatest extent it affects the coating obtained in the dual circuit supplying negative bias potentials: a permanent and high-voltage pulse.

Table 2. The results of the test indentation method nitride coatings before and after exposure.

Series number, №	H, GPa	E, GPa
1	36	433
1-1	33	433
1-2	28	420
1-3	30	400
2	44	480
2-1	33	415
2-2	22	422
2-3	27	402
3	40	400
3-1	36	340
3-2	38	380
3-3	33	320
4	44	410
4-1	39	350
4-2	34	350
4-3	30	340
5	41	398
5-1	36	358
5-2	39	374
6	39	390
6-1	30	268
6-2	38	358
7	42	398
7-1	41	399
7-2	38	382
8	39.5	355
8-1	40	475
8-2	45	487

Unlike binary, high entropy multielement alloy showed not only its mechanical resistance characteristics to the radiation, but their growth. The reason for the latter can not only be ordered components in the metal sublattice irradiation, but reduction in the average grain size.

Thus, the greatest structural instability under irradiation showed a coating of Mo-N in which there have been significant changes, both on the substructure level and at the level of the macro stress-strained state, and the phase-structural level as a change in the phase composition at higher U_b and preferred orientation with additional exposure to U_{pulse} and irradiation.

The coating of titanium nitride, obtained at a constant negative potential bias of -200 V, and in the absence of the action of high-voltage (-1200 V) pulsed bias potential exposure without changing the phase composition and preferred orientation in varying degrees change their mode of deformation and substructural characteristics depending on with or without high-voltage pulse causes deposition coatings.

In the case of multi-element high entropy nitride alloys effect of irradiation has a significant effect only on the substructure level. Moreover, such effects, indicating the atomic ordering of the metal atoms and the reduction in the average size of the crystallites increases the mechanical properties of the coating, in particular by increasing the hardness of more than 10%.

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