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The Effect of High-voltage Pulse Potential Applied to the Substrate on the Phase Composition and Structure of the Vacuum-arc TiN Coatings

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The effect of the high-voltage supply capacity in the form of different pulse duration on the formation of preferentially oriented crystallites and the stress-strain state of the vacuum-arc TiN coatings was analyzed. It is shown that deposition of the coatings in a high-voltage cascade forming exposure leads to the growth of the crystallites with axis texture [110] and the change in the stress-strain state: strengthening of a strain in a group of crystallites with the axis [110] and reduction of the strain in a group of crystallites with axis [111]. The results are explained by the increase in mobility of atoms and ordering processes in the field of displacement cascades, formed under the influence of high-energy bombarding ions accelerated in the field of high-voltage pulse potential. A generalized graph of the texture type on the pulse potential and influence of the pulse duration, applied to the substrate, on the total deposition time are plotted.

Keywords: TiN, Coatings, Pulse influence, Bias potential, Duration, Radiation factor, Texture, Deformation.

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1. INTRODUCTION

One of the most actual directions of development of nanotechnologies is associated with the formation of superhard nanocomposite coatings, identifying the regularities of their synthesis, studies of the phase-structural states of the material and its physical and mechanical properties. Such investigations based on the structural engineering open new possibilities for the predictable formation of the structure and properties of the coatings during deposition [1].

Nitrides of the transition metals (titanium, zirconium, chromium) are known by their high mechanical characteristics, namely, hardness and strength. Therefore, coatings synthesized on their basis are applied to improve the operating characteristics of the cutting tools, friction units and machine parts [2-7]. It is possible to influence the structure of the synthesized coatings using different technological conditions of the vacuum arc deposition. Plasma-based ion implantation method (PBII-method), which is being actively developed now, allows to substantially expand opportunities on structural engineering of the coatings leading to the increase in their physical and mechanical properties [8].

Titanium nitride is the most used material with high mechanical characteristics due to high manufacturability. Progress in improving operating characteristics of this type of materials concerned, mainly, the development of new, more efficient deposition methods of TiN coatings, which provide high hardness and operability of the products [9-11].

The aim of this work was to study the effect of the duration of pulse high-voltage action on the formation of TiN coatings with account of the radiation factor during vacuum arc deposition, which substantially influences the possibilities of the structural engineering of the coatings, in particular, considerably changes the formation conditions of preferred orientation of crystallites.

2. METHOD OF OBTAINING AND STUDYING THE SAMPLES

The samples were obtained using the modernized vacuum arc plant "Bulat-6" which was additionally equipped by a high voltage pulse generator (Fig. 1) [8].

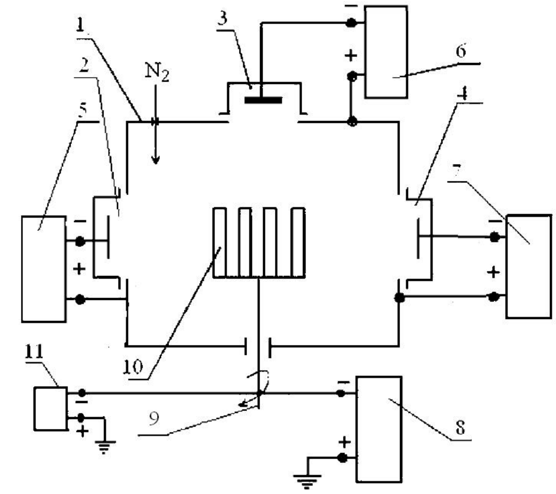

Fig. 1 – The scheme of the modernized vacuum arc plant: 1 – vacuum chamber body; 2, 3, 4 – vacuum arc evaporators; 5, 6, 7 – evaporator power supplies; 8 – generator of the constant negative bias potential on the substrate; 9 – rotating device; 10 – work samples; 11 – high-voltage pulse generator

Polished substrates made of 12X18H9T stainless steel with the sizes of 20 × 20 × 3 mm and copper foil of the thickness of 0.2 mm were pre-washed by the alkaline solution in an ultrasonic bath and then in an oil solvent C2-80/120. After evacuating the vacuum chamber to the pressure of $1 \cdot 10^{-3}$ Pa, a constant negative potential of 1000 V was applied to the substrate. Cleaning and activation of surface atoms by titanium ion bombardment during 3-4 minutes were performed at the arc current of

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100 A. Then, the chamber was filled with nitrogen and a constant negative bias potential of $U_b = -200$ V was applied to the substrate. To study the influence of the high-voltage pulse action, pulses of a negative potential (U_{pp}) of the amplitude of – 850 V, – 1200 V, and – 2000 V by the duration of $\tau = 4$, 10 or 16 μm and frequency of 7 kHz were applied to the substrate during deposition along with the constant bias potential. The arc current in evaporator (I_d) was equal to 100...110 A and nitrogen pressure – $P_N = 0.03...0.66$ Pa.

Phase composition and structural state were studied by the X-ray diffraction method on the difractometer DRON-3M in Cu-K$_\alpha$-radiation using the graphite monochromator in the secondary beam. The survey was carried out in a pointwise mode with the scanning step of $\Delta(2\theta) = 0.05 \div 0.2^o$ and duration of pulse accumulation in each point of 20÷40 s. Analysis of the phase composition was performed using the ASTM file.

Calculation of the pole density P_{hkl} in the direction of the normal to the sample surface by the Harris method was carried out in the work in the texture analysis. The following relations were used for the calculation of P_{hkl}:

$$P_{hkl} = \frac{w_{hkl}}{\sum w_{hkl}},$$

$$w_{hkl} = \frac{I_{hkl}^{sam} / I_{hkl}^{st}}{\sum I_{hkl}^{sam} / I_{hkl}^{st}},$$

where I_{hkl}^{sam}, I_{hkl}^{st} are the experimentally obtained integral intensities of reflections (hkl) for the sample under consideration and non-textured standard (JCPDS 35-0753); $\sum I_{hkl}^{sam}$, $\sum I_{hkl}^{st}$ are the total relative intensities of all reflections of the sample and standard.

The stress-strain state was studied by the method of multiple inclined surveys ("a-sin$^2\psi$"-method) [12].

3. RESULTS AND DISCUSSION

Three pulse durations of 4 μs, 10 μs and 16 μs were used in the work that at the pulse frequency of 7 kHz is respectively equal to $\Delta t = 3$ %, 8 % and 12 % of the total exposure time (t).

Relative integral intensity of diffraction peaks from crystallite planes, which are the constituents of the material, is the basis for determination of the degree of texture of the coatings, when using the X-ray structural analysis for this method.

Diffraction spectra for the lowest ($\tau = 4$ μs) exposure time of high-voltage pulse stimulation of the mobility of film-forming atoms at different values of U_{pp} are given in Fig. 2. As seen, in this case spectra without pulse action and at the lowest $U_{pp} = -850$ V have similar behavior. A significant difference in the spectra is observed at larger $U_{pp} = -1200$ V and – 2000 V (Fig. 2, spectra 3 and 4). The main difference consists in the change of the ratio of the peak intensities from the planes (111) and (220) that implies the change of preferred orientation of crystallites from the texture with the axis [111] perpendicular to the growth plane to the texture with the axis [110] when applying large U_{pp}.

It is seen from the shown in Fig. 3 dependences of the ratio of the integral intensity ($I_{(hkl)}$) to the total integral intensity (I_Σ) on the value of the pulse potential that I(111) (Fig. 4a, dependence 1) for the whole range of U_{pp} exceeds the tabulated values that indicates the maintenance of preferred orientation for this range. At that, degree of texturing (111) decreases with increasing U_{pp}, and at U_{pp} exceeding – 1200 V in absolute value one can observe the formation of the secondary type of preferred orientation of crystallites with the axis [110] perpendicular to the growth plane (Fig. 4c, dependence 1).

Besides preferred orientation of crystallites, which largely determines the elastic characteristics of the coating, the macro stress-strain state of the coating is the second very important factor of its operability. The macro-strain measured by the method of multiple inclined surveys ("a-sin$^2\psi$"-method) is illustrated in Fig. 4. It is equal to $\varepsilon = -2.5$ % for the case of the pulse potential of – 850 V ($\varepsilon = -1.96$ % without U_{pp}). The obtained value, apparently, is critically withstand for the film-substrate system, even if take into account that effect of implantation is "smoothed" by larger $U_b = -200$ V.

With increasing U_{pp} to – 1200 V one can observe the decrease in the stress-strain state in crystallites of the texture group with the texture axis [111] (Fig. 4a, dependence 1) at a simultaneous increase in the stress-strain state in the texture group with the axis [110] (Fig. 4b, dependence 1) formed under the action of the cascade factor [8].

With increasing U_{pp} to – 2000 V, the above described changes are amplified. As seen from the X-ray diffraction spectra shown in Fig. 5, increase in the pulse duration to 10 μs ($\Delta t = 8$ %) leads to the appearance of a strong texture with the axis [110] parallel to the incident beam of high-energy film-forming particles.

Macro stress-strain state is changed rather monotonously at $\tau = 10$ μs increasing for the fraction of crystallites with the texture axis [110] with increasing U_{pp} to 2 kV (Fig. 4b). At the same time, relaxation processes leading to the decrease in the macro stress-strain state (see Fig. 4a) occur in the crystal fraction with preferred orientation of crystallites with the axis [111].

Shift of the diffraction reflections towards smaller angles (see Fig. 5) is associated with the action of high compressive stresses, which deform the crystal lattice of grains-crystallites.

Relaxation processes are more intense in the case of the maximum pulse duration ($\tau = 16$ μs) of high-voltage high-energy impact.

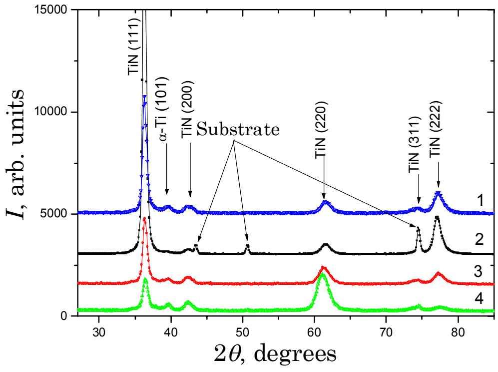

Fig. 2 – X-ray diffraction spectral regions of titanium nitride coatings obtained at $U_b = -200$ V ($\tau = 4$ μs), U_{pp}: 1 – without high-frequency pulses; 2 – – 850 V, 3 – – 1200 V, 4 – – 2000 V

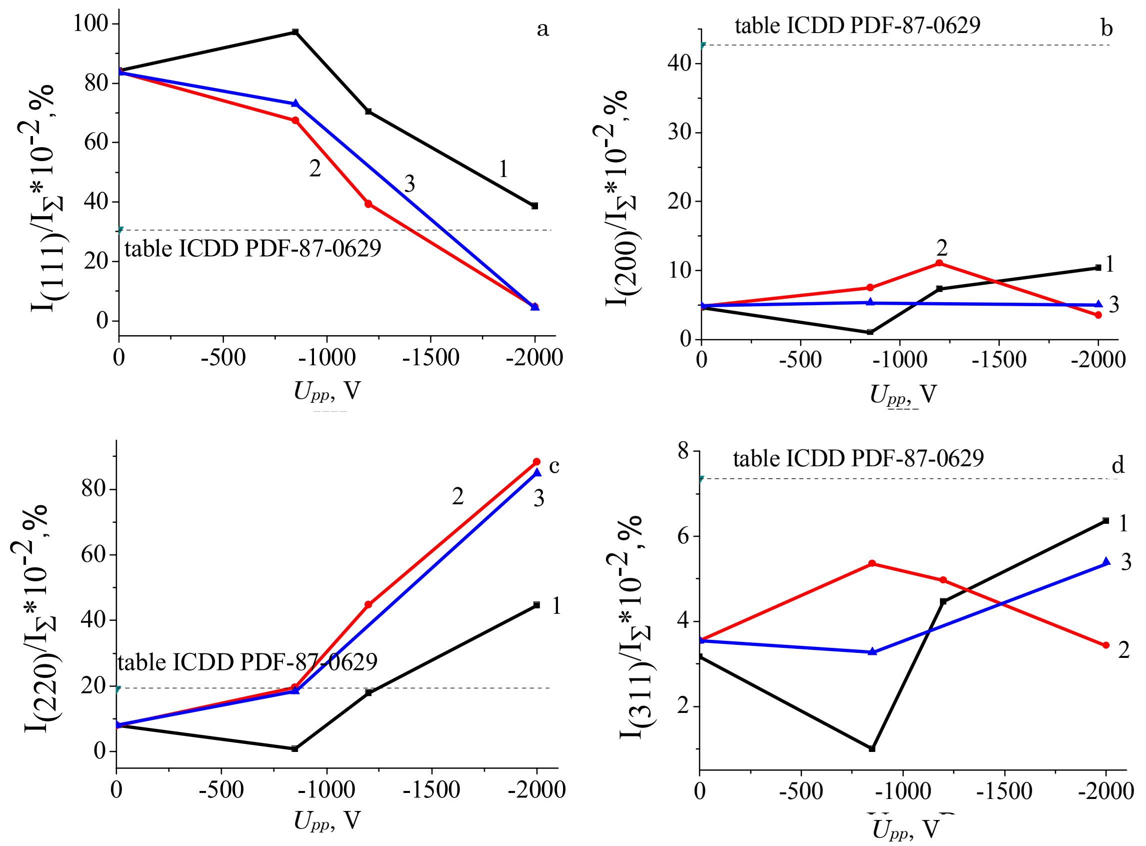

Fig. 3 – Ratios of the integral intensities from different planes $I_{(hkl)}$ for TiN coatings obtained at different pulse duration: 1 – 4 μs, 2 – 10 μs, 3 – 16 μs: a – $I_{(111)}/I_{\Sigma}$, b – $I_{(200)}/I_{\Sigma}$, c – $I_{(220)}/I_{\Sigma}$, d – $I_{(111)}/I_{\Sigma}$

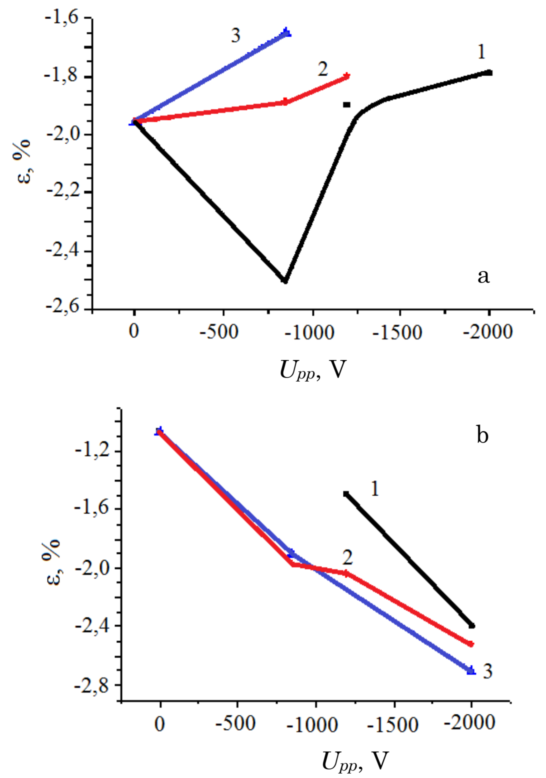

Fig. 4 – Dependences of the macrostrain on the pulse high-voltage potential U_{pp} applied to the substrate (a – texture group with the axis [111], b – texture group with the axis [110]): 1 – $\tau = 4$ μs, 2 – $\tau = 10$ μs, 3 – $\tau = 16$ μs

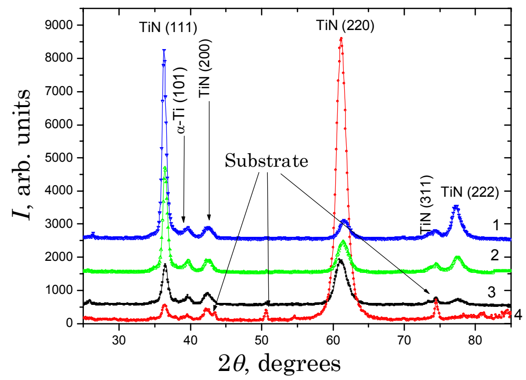

Fig. 5 – X-ray diffraction spectral regions of titanium nitride coatings obtained at $U_b = -200$ V ($\tau = 10$ μs), U_{pp}: 1 – without high-frequency pulses; 2 – – 850 V, 3 – – 1200 V, 4 – – 2000 V

With increasing duration of the pulse exposure to the value of $\tau = 16$ μs ($\Delta t = 12$ %), the effect of radiation-induced texture-formation is enhanced, and almost mono-textured state with the axis [110] at $U_{pp} = -2000$ V is manifested on the diffraction spectra for the given type of coatings (see Fig. 6).

Based on the obtained results and the literature data [13-16], a generalized texture diagram, which reflects the dependence of the texture axis type on the potential amplitude under high-voltage pulse exposure and time fraction of this exposure during deposition, is plotted (Fig. 7).

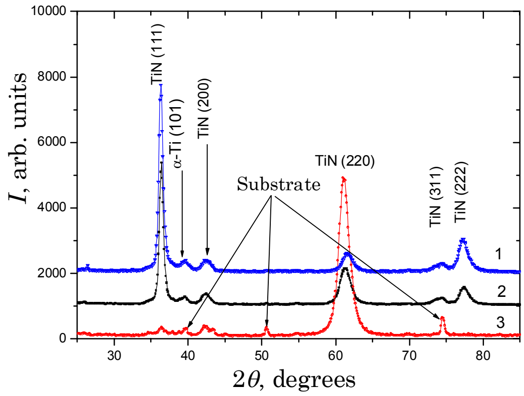

Fig. 6 – X-ray diffraction spectral regions of titanium nitride coatings obtained at $U_b = -200$ V ($\tau = 16$ μs), U_{pp}: 1 – without high-frequency pulses; 2 – – 850 V, 3 – – 2000 V

The construction of this texture diagram is based on the radiation action, mainly, as the determining factor during the formation of the texture state. Supply of U_{pp} of the value to – 1000 V leads to the formation of preferred growth orientation of grains-crystallites with the strain texture axis [111], which is determined by the minimization of the strain energy (which the decrease in the crystallite size is also associated with). Formation of the radiation-induced texture [110] occurs in the range of $U_{pp} \approx -1000...-2500$ V. Such an action is a kind of modeling one, which allows to predict the behavior of the coatings under the action of high-energy ion implantation by the particles accelerated to keV energies. Further increase in the amplitude of the pulse potential ($U_{pp} \approx -2500...-4000$ V) promotes the formation of texture with the axis [100] determined by high mobility of deposited atoms.

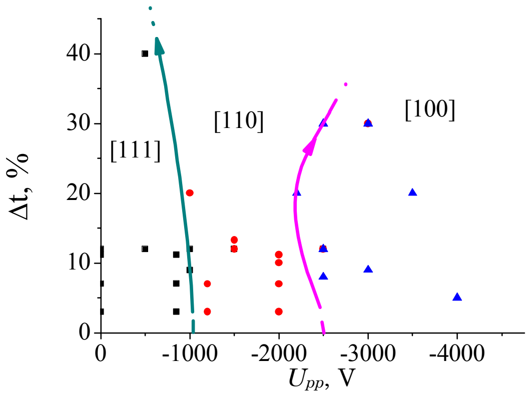

Fig. 7 – Texture type depending on the amplitude of the pulse potential (U_{pp}) and time fraction of pulse exposure (Δt)

4. CONCLUSIONS

Using the regularities of structural engineering of coatings, depending on the pulse potential there are the possibilities to influence in a wide range the texture during deposition, thus providing the production of coatings with a necessary complex of functional properties.

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