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The Influence of the Bias Potential on the Phase Composition, Structure, Substructure and Mechanical Properties of Multilayer TiN / ZrN System Obtained by Vacuum Arc Evaporation

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Influence of constant and pulsed negative bias potentials applied to the substrate during the deposition on the phase composition, structure, substructure and mechanical properties of multilayer ZrN / TiN coatings with a bilayer thickness of 50-200 nm was studied. Two-phase coating obtained from ZrN and TiN phases of the fcc structure of NaCl type without a significant loss of planarity and mixing layers is established. The use of high-voltage pulses would greatly change the structure and properties at $U_b < 100$ V. At larger value of U_b, constant potential becomes crucial for the structural engineering of the coating. It is shown that the greatest hardness is inherent to the coatings obtained by $U_b = -140...-150$ V, and H/E reaches a large value of 0.14, which is difficult to obtain in the single-layer coatings.

Keywords: Vacuum-arc method, Pressure, Bias potential, ZrN, TiN, Texture, Substructure, Micro-deformation, Crystallite size, Hardness, Modulus of elasticity.

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1. INTRODUCTION

Wear and corrosion are critical factors of the working capacity in such devices as, for example, pump assemblies and turbine blades [1, 2]. In these cases, in order to reduce the devastating impact of the wear and corrosion factors, hard coatings are used, which have found widespread adoption in such fields of industrial application as metal working, aircraft building, mineral resource industry, and oil processing [3]. Physical vapor deposition (PVD) and, in particular, vacuum arc evaporation in the reactive (nitrogen mainly) medium belongs to coating deposition methods, which have the greatest demand in these areas of use. Ceramic coatings, obtained in such a way, with high melting temperature based on the transition metals (TiN, ZrN, Mo_2N, CrN) [4-15] have found now wide application as an outer layer on the edge tool, high-speed steel parts, hard alloy; and in recent years – a superhard tool based on boron nitride [16-20]. Such a wide use is conditioned by a number of high functional properties inherent to these coatings, namely:

a) high hardness and wear resistance at low friction coefficient that promotes better slip under load during cutting;

b) high corrosion resistance and good chemical and thermal stability at high temperatures;

c) high thermal conductivity and good adhesion to the substrate.

Nevertheless, further improvement of the physical and mechanical properties of these nitride coatings is limited. This caused the development and use of multi-component and multilayer coatings [16, 17, 21]. Due to the significant increase in universality, multilayer coatings, which are also called the heterostructures or superlattices, have a number of unique functional (and, primarily, mechanical) properties because of the fact that interlayer boundaries do not allow to develop cracks dissipating energy and increasing viscosity. Moreover, change in the modulation period (in the majority of cases – bilayer) is the possibility of hardening substantially increasing it due to synergetic effects compared with hardness of the initial components of a multilayer coating.

This work is devoted to the study of TiN / ZrN multilayer coating, which, as the investigations show, is one of the most promising for protection against abrasive wear and extreme effects of radiation and temperature [22-25]. A negative bias potential applied to the substrate during deposition was used in the work as the main physical and technological parameter for engineering of the structural state of the coatings.

2. METHOD OF OBTAINING AND STUDYING THE SAMPLES

Multilayer two-phase nanostructural TiN/ZrN coatings were deposited in the vacuum arc plant "Bulat-6" [17]. Titanium VT 1-0, chemically pure zirconium, active gas – nitrogen of special purity (99,999 %) were used as the cathode materials. Coatings were deposited on the surface of the 18H10T steel samples of 20 × 20 × 2 mm prepared by standard grinding and polishing methods. The deposition procedure of multilayer coatings included the following operations. Vacuum chamber was evacuated to the pressure of 10^{-5} torr. Then, negative potential of 1 kV was applied to the rotating device with the substrate-holder, evaporator was switched on, and cleaning of the surface of the first of two substrates was performed by bombardment of zirconium ions during 3-5 min. Thereafter, substrate-holder was rotated by 180° and the same cleaning of the second substrate was carried out. Then, both evaporators were simultaneously switched on, nitrogen was supplied to the chamber, and the first ZrN

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layer was deposited on one side and TiN layer – on another side.

Deposition process was performed under the following technological conditions. After deposition of the first layer, both evaporators were switched off, substrate-holder was rotated by 180°, and both evaporators were simultaneously switched on again. Arc current during deposition was 100 A, nitrogen pressure (P_N) in the chamber was about $3\cdot10^{-3}$ torr, distance between evaporator and substrate was equal to 250 mm, substrate temperature (T_s) varied in the range of 250…350 °C. Deposition rate of the ZrN layers was approximately equal to 3 nm/s and of TiN – 2 nm/s. Coatings of the thickness of 12-17 μm were obtained. Negative bias potential of the value of $U_b = -30…-200$ V was applied to the substrate during deposition of the coatings.

Multilayer nanostructural TiN/ZrN coatings with simultaneous ion implantation were deposited when applying to the substrate-holder, along with a negative bias potential, a pulsed potential with the pulse duration of 10 μm, pulse repetition frequency of 7 kHz and amplitude up to 2000 V [6]. The main advantage of the given plasma based ion implantation and deposition method (PBII&D-method) in the synthesis of two-phase TiN/ZrN nanostructures consists in the significant decrease in the substrate temperature (below 200 °C) that should block an appreciable diffusion mixing of the system components.

Phase composition, structure and substructural characteristics were investigated by the X-ray diffractometry method (DRON-4) using Cu-K_α-radiation. Graphite monochromator which was placed in the secondary beam (in front of the detector) was applied for monochromatization of the detected radiation. Study of the phase composition, structure (texture, substructure) was carried out by traditional techniques of the X-ray diffractometry by the analysis of the position, intensity and shape of the diffraction reflexes profiles. Tables of The International Center for Diffraction Data (ICDD) the Powder Diffraction File were used to interpret the diffraction patterns. Substructural characteristics were determined by the approximation method [26].

Microindentation was performed on the plant "Microngamma" under load to $F = 0.5$ N by diamond Berkovich pyramid with the sharpening angle of 65°, with automated loading and unloading during 30 s.

3. RESULTS AND DISCUSSION

As the investigations of the fracture microstructure have shown, multilayer coatings even when applying a large bias potential of – 200 V (Fig. 1), leading to high energy of charged film-forming particles, maintains good planarity of the deposited layers without explicit large drop inner (between layers and inside layers) defects.

According to the data of the X-ray diffractometry, formation of a two-phase state from TiN and ZrN phases with crystal lattices of the NaCl structural type is typical for all modes used in the work [6, 8]. Supply of high-voltage pulses during deposition, even at the smallest $U_b = -30$ V, does not change neither structural type of the coatings nor two-phase state typical for alternating TiN and ZrN layers (Fig. 2). However, supply of high-voltage pulses influences the development of orientation level of the crystal lattice. Thus, formation of texture with the axis [111] of low perfection occurs without supply of high-voltage pulses (Fig. 2, spectrum 1). Supply of high-voltage pulses leads to a fundamental change in the texture and formation of the bi-textured state with the axes [100] and [110] perpendicular to the growth plane. This is seen in Fig. 2 (spectrum 2) by a relative increase in the peak intensity from the planes (200) and (220) in both TiN and ZrN phases. At that, lattice spacing decreases in both phases under the action of pulse stimulation. In ZrN lattice spacing decreases from 0.4609 to 0.4583 nm, and in TiN – from 0.4259 to 0.4248 nm. Supply of a pulsed potential at the substructural level leads to a slight increase in the microdeformation and decrease in the average crystallite size. Such structural changes somewhat increase the coating hardness from 33 GPa without a pulse action to 34 GPa with supply of high-voltage pulses during deposition.

Change in the constant bias potential without a pulse action for a multilayer system with the smallest bilayer thickness of about 50 nm and number of bilayers of 262 also leads to the formation of preferred orientation of crystallites with the axis [111] and strengthening of this texture in both TiN and ZrN layers with increasing U_b (see Fig. 3).

On the substructural level, increase in the constant bias potential without a pulse action leads to the decrease in the microdeformation and crystallite size in the TiN component and increase in the sizes in the ZrN component (Fig. 4).

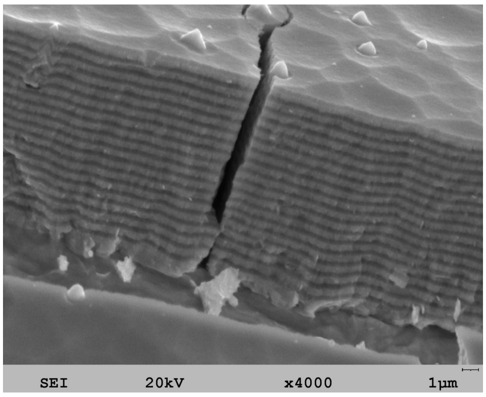

Fig. 1 – Fracture microstructure of TiN/ZrN multilayer coating obtained at $P_N = 3\cdot10^{-3}$ torr and under $U_b = -200$ V

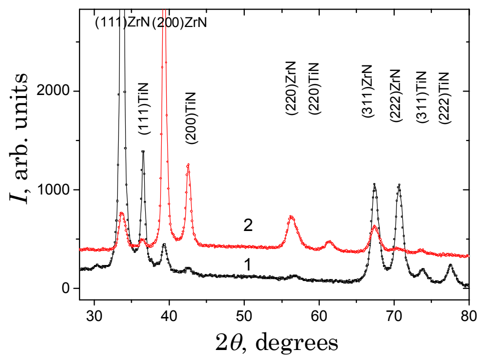

Fig. 2 – Diffraction spectral regions of TiN/ZrN coatings obtained at constant bias potential of $U_b = -30$ V and number of bilayers of 134 without a pulse high-voltage action (1) and when applying high-voltage pulses ($U_{ip} = -1200$ V) during the formation of the coating (2)

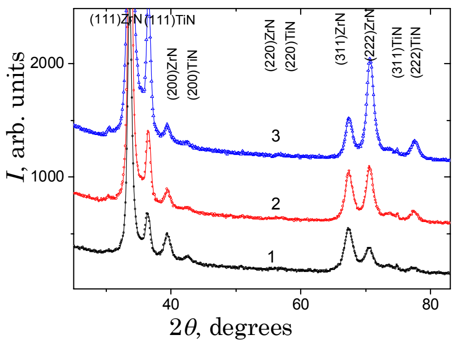

Fig. 3 – Diffraction spectral regions of TiN/ZrN coatings obtained at number of bilayers of 162 without a pulse high-voltage action at constant potential U_b: 1) – 70 V, 2) – 140 V, 3) – 200 V

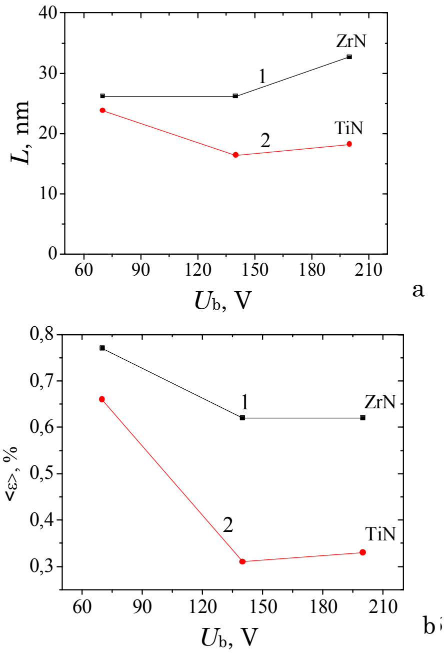

Fig. 4 – Change in the substructural (crystallite size, L (a) and microdeformation <ε> (b)) characteristics on the value of the applied bias potential U_b. 1 – refers to ZrN layers; 2 – to TiN layers

The reason of the observed non-uniform changes can be associated with more severe radiation damage of ZrN layers because of the large mass of Zr atoms bombarding the surface during the growth of these layers. Decrease in the microdeformation and increase in the average crystallite size at the highest $U_b = -200$ V can be associated with larger average energy of the deposited particles and surface heating temperature. Both the first and the second allow to increase the surface diffusion and, correspondingly, promotes more uniform filling of places that determines the increase in the average crystallite size. In this case, as seen from Fig. 5, lattice spacing decreases in both ZrN and TiN layers as a result of the coating compaction.

At that, average value of the bias potential of – 140 V, at which the smallest lattice spacing, crystallite size and microdeformation are reached, leads to the highest hardness of 43 GPa. We should note that in this case, hardness to modulus of elasticity ratio is equal to the value of $H/E = 0.14$. Such a large value corresponds to high elastic characteristics of the material and is almost unattainable in single-layer coatings.

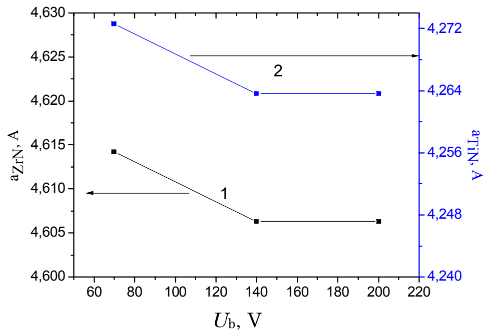

Fig. 5 – Change dependences of the lattice spacings on the value of the applied bias potential U_b. 1 – refers to ZrN layers, 2 – to TiN layers

Thus, supply of the constant negative bias potential in the range of the values $U_b = -30…-200$ V does not lead to a significant loss of planarity and mixing of the layers that allows to achieve high mechanical characteristics.

Supply of the pulsed high-voltage bias potential with the amplitude of – 2000 V leads to the changes on both the structural and substructural levels. On the structural level, it is manifested in the disorienting action during the formation of preferred orientation.

As seen from Fig. 6, there is no pronounced texture in the case of the supply of the pulsed high-voltage potential during deposition and relatively low $U_b = -70$ V. Comparison with the reference values for the corresponding powder X-ray diffraction patterns and determination of the relative intensity of peaks from different planes by the Harris method [8] shows (Fig. 7) that preferred orientation with the axis [110] perpendicular to the growth plane (Fig. 7, dependences 3 and 3-standard) is observed at small potential of – 70 V in both types of the layers. Increase in the potential leads to the development of the texture with the axis [111] typical for the coatings without a pulse action.

Decrease in the microdeformation and increase in the average crystallite size with increasing U_b, which are also typical for the samples without a pulse high-voltage action, occurs on the substructural level in this case. From which it follows that supply of a relatively high constant negative bias potential is the determining factor of influence on the substructural level. A substantial effect of the pulsed potential has an impact at a relatively low $U_b < 100$ B.

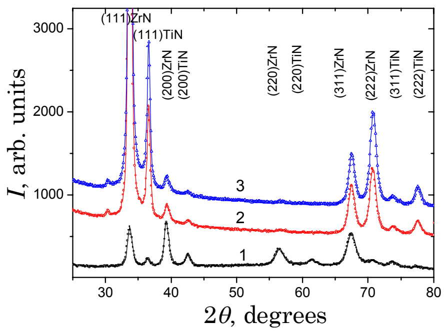

Fig. 6 – Diffraction spectral regions of TiN/ZrN coatings obtained at number of bilayers of 162 and pulse high-voltage stimulation with the amplitude of the supplied negative potential of 2000 V under the action of the constant bias potential U_b: 1) – 70 V, 2) – 140 V, 3) – 200 V

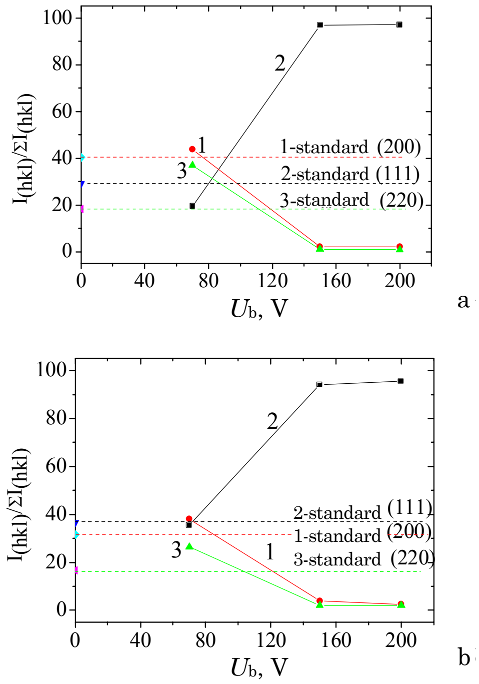

Fig. 7 – Diffraction peak intensity distribution at different bias potentials for TiN (a) and ZrN (b) in multilayer TiN/ZrN coatings: 1 – (200), 2 – (111), 3 – (220) and corresponding levels of the tabulated standard values

Lattice spacing for the TiN component varies similarly to the pulse-free mode, namely, it decreases with increasing U_b (Fig. 8). At the same time, change of the spacing for the ZrN component is not monotonic and differs from the similar parameter for the coatings obtained in the pulse-free mode (Fig. 8, dependence 1).

Dependence of the hardness on the constant bias potential with the pulse action has similar behavior with the same curve for the coatings without a pulse action. In the case of pulse action, maximum value of the hardness of 39 GPa is also achieved at U_b = – 140…– 150 V.

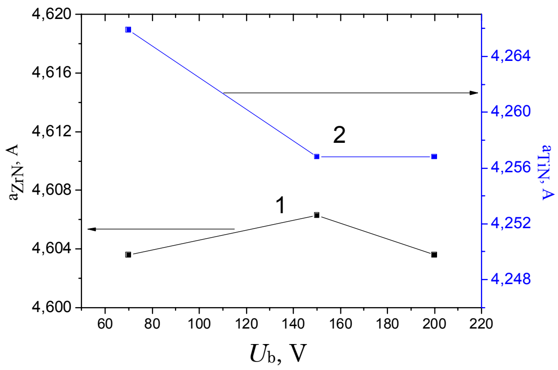

Fig. 8 – Change dependences of the lattice spacings on the value of the applied bias potential U_b. 1 – refers to ZrN layers, 2 – to TiN layers

4. CONCLUSIONS

1. Supply of a negative constant bias potential during the coating deposition in the whole range of values U_b = – 30…– 200 V does not lead to an appreciable mixing of layers leaving them planar that provides high mechanical characteristics of ZrN/TiN multilayer coatings.

2. Supply of a high-voltage (1200…2000) V negative pulsed potential during deposition is accompanied by the near-surface cascade-generation with the formation of the radiation-induced growth texture of crystallites with the axis [110] at the lowest U_b = – 30 V or disorientation of crystallites at U_b = –70 B.

3. At U_b more than 100 V, the effect of a pulsed high-voltage potential has an impact, mainly, on the change in the lattice spacing associated with the deflected mode.

4. Change in the hardness depending on U_b in multilayer ZrN/TiN coatings (with the bilayer thickness of 50-100 nm) has a non-monotonic behavior with the maximum for U_b = – 140…– 150 V, at which the highest hardness of 45 GPa is achieved. At that, in the hardest coatings *H*/*E* ratio is equal to 0.14 that corresponds to high relaxation characteristics of the material.

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