INFLUENCE OF THE THICKNESS OF THE BILAYER TiN / ZrN ON STRUCTURE AND PROPERTIES OF THE MULTILAYER COATING OBTAINED BY VACUUM-ARC EVAPORATION

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Phase composition, structure, substructure, hardness and elastic modulus of vacuum arc multilayer coatings of TiN/ZrN, obtained with different thicknesses bilayer periods at a constant negative bias potential (U_b) -140 V and -200 V, was investigated by X-ray diffraction, electron microscopy and microindentation. Found that that when applied to a substrate in forming the coating as U_b = -200 V well, as U_b = -140 V mononitrides layers TiN and ZrN are formed with the preferred orientation of the crystallites (texture) with [111] axis perpendicular to the plane of growth. Increasing the number of boundaries periods with decreasing thickness leads to increased hardness of 45 GPa, a hardness which is greater, than each of the layers of TiN and ZrN separately.

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INTRODUCTION

Work efficiency of the products in many industrial sectors is closely linked to developments in the field of surface engineering [1, 2]. The use of new technological solutions allowed us to obtain materials in the form of coatings effectively working under the action of aggressive environments and high temperatures [3]. Such materials include the multiperiod system that include two or more layers of different types in the period, among which the highest operational characteristics shows multilayer system based on nitrides of transition metals [1, 2, 4–8]. Such systems characterized by high mechanical and tribological characteristics that largely determined by large-surface interfaces associated with a periodic arrangement of the layers in the coating. In this paper, the influence of the period of the two-layer composition of TiN/ZrN on their structure and mechanical properties.

METHOD OF PRODUCTION AND RESEARCH OF SAMPLES

Multilayer two-phase nanostructured coatings TiN/ZrN deposited in vacuum-arc installation "Bulat-6". Fig. 1 shows the installations for reception multilayer coatings [2]. The vacuum chamber 1 was provided with an automatic maintain pressure nitrogen 2 and two evaporators. Vaporizer 3 contains zirconium and the evaporator 4 − titanium. In the rotary unit 8 housed substrate holder 5 in the form of stainless steel plates 300x300 mm. At its center on both sides of the samples were placed 6. Installation is equipped with a DC voltage source 7, the voltage which can be adjusted in the range of 20...1000 V. Slew system of the substrate holder 8 and 9 arc power source coupled to the automatic control of the deposition of multilayer coatings 10.

The control unit can operate in a continuous rotation of the substrate holder, or in a mode where the evaporators operate simultaneously for a predetermined time, unplug periodically at the time of reversal of the substrate holder with samples at 180°.As cathode materials used: VT1-0 titanium; zirconium (99.95%); active gas - nitrogen (99.999%). The coating was applied to the surface of the samples 20x20x2 mm of steel H18N10T prepared by standard methods of grinding and polishing. Procedure of depositing multilayer coatings comprising the following steps. The vacuum chamber was evacuated to a pressure of 10^{-3} Pa.
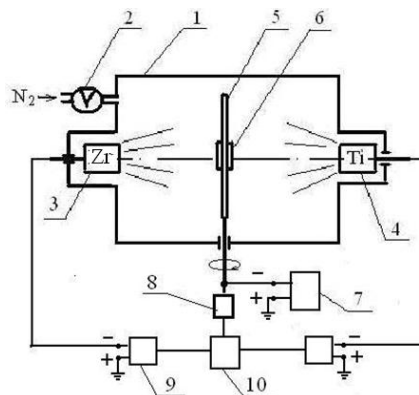

Fig. 1. Installation scheme for applying a multilayer coating TiN/ZrN

With continuous rotation of the rotator included evaporators titanium and zirconium and the substrate is cleaned by ion bombardment for 10…15 minutes at a constant potential of 1 kV. Then, the rotation was stopped, the potential of the substrate was set at -140 or -200 V, nitrogen was admitted into the chamber, and the layers of titanium nitride and zirconium was precipitated simultaneously from both sides of the plate (one side TiN, on the other side ZrN) for a predetermined time (10, 20, 40, 150 or 300 seconds). After a specified time, both the evaporator disconnected, turning plate substrates at 180° and again included both the evaporator. The resulting coating consisted of alternating layers of TiN and ZrN bilayer with periods of 50, 100, 200, 750 and 1500 nm.

Deposition modes: the arc currents in each evaporator 100 A, chamber pressure of 0.4 Pa, substrate temperature 350…450 °C. Total coating time was 120 minutes.

Phase composition, structure and substructural characteristics were studied by X-ray diffraction (DRON-4) using Cu-Kα-radiation. For monochromatisation detected radiation used graphite monochromator, which is set in the secondary beam (front of the detector). The study of the phase composition, structure (texture, substructure) produced using traditional methods by X-ray diffraction analysis of the position, intensity and shape of the profiles of the diffraction reflections. Diffraction patterns were used to decrypt tables International Centre for Diffraction Data Powder Diffraction File. Substructural characteristics were determined by approximation [10].

Microindentation performed on the "Microngamma" with a load of up to F = 0,5 N Berkovich diamond pyramid to automatically perform loading and unloading for 30 seconds.

RESULTS AND DISCUSSION

When using a negative potential bias in the range of values of $U_b = -100...-300$ V intensification due to at the same stirring interlayer thickness of the layers is critical to the performance coating [4–7]. The aim of this work was to study the influence of the thickness of layers formed with $U_b = -140$ and -200 V on the structure, substructure and mechanical properties of vacuum-arc coating system ZrN/TiN. Fig. 2 shows pictures of morphology of the fracture bilayer coating having a thickness of periods TiN/ZrN λ of about 1.5 μm (Fig. 2,a), λ = 0,8 mm (Fig. 2,b) and 0.2 μm (Fig. 2,c). ZrN layer thickness is about 1.5 times larger than the layer TiN.

To study the phase composition, structure and substructure able to use the method of X-ray diffraction. Fig. 3 shows plots of the diffraction spectra of multilayer coatings with different λ.

It can be seen that for all λ characterized by the formation of two-phase state (ZrN and TiN phase) with the preferred orientation of crystallites of both phases (in both layers) with the axis of the texture [111] perpendicular to the plane of growth. The degree of perfection of texture [111] for coatings with different λ is significantly different. Fig. 3 shows that the highest degree of perfection (the highest relative intensity of the peaks for the family of planes [111]) is inherent in the type of coatings with λ ≈ 100 nm (spectrum 2, Fig. 3). At a lower λ degree of perfection below that seen in the spectrum as a relative decrease in the intensity of the peaks of the planes of the [111]. With the smallest degree of perfection inherent texture coating with the highest λ, which corresponds to the range of 5 in Fig. 3. This behavior of the degree of texturing nitride layers can be explained by the difference in the interplanar distances at the atomic level between ZrN and TiN crystal lattices in which with increasing layer thickness increase growth misfit stresses lead to deformation at the interface and the loss of such a perfect texture.

Fig. 4 shows the substructural characteristics obtained in the approximation of the diffraction profiles of the two orders of reflections Cauchy function and graphing Hall. It is seen that with decreasing λ occurs reduction in the average size of the crystallites (see Fig. 4,a) and microdeformation changes nonmonotonically (see Fig. 4,b). So ZrN layers with decreasing λ microdeformation increases (see Fig. 4,b, dependence 1) while the TiN layers in its fall is observed (see Fig. 4,b, dependence 2). With the least number of layers and, accordingly, the largest decreases in λ microdeformation crystallites of both phases.
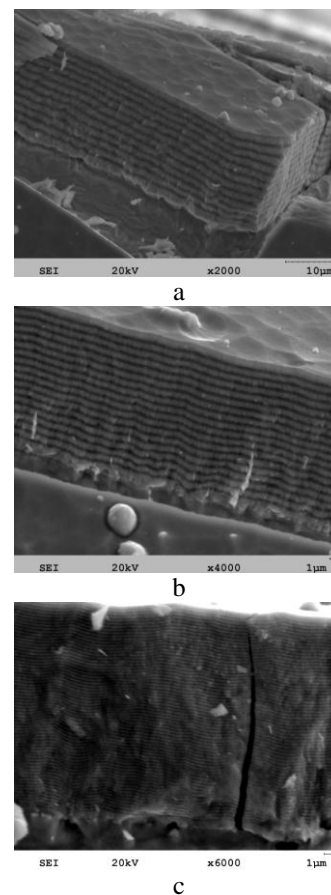

Fig. 2. Morphology of fracture coating with 26 layers (13 periods by two layer with an average λ = 1,5 μm) (a); 36 layers (18 periods by two layers with an average λ = 0,8 μm) (b) and 134 layer (67 periods by two layers with an average λ = 0,2 μm) (c)
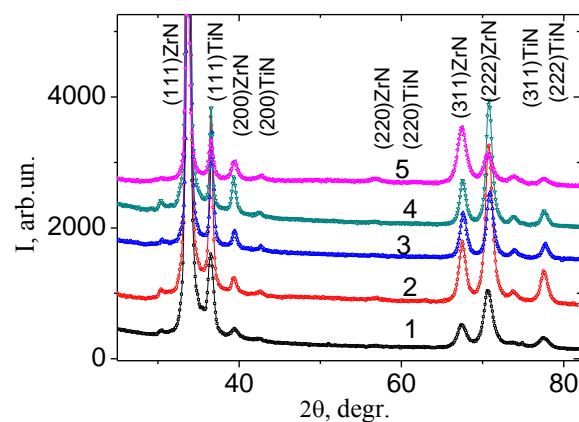

Fig. 3. Plots diffraction spectra of coatings TiN/ZrN, obtained at U_b = -200 V, with different λ: 1 – 50 nm; 2 – 10 nm; 3 – 200 nm; 4 – 750 nm; 5 – 1500 nm

The crystallite size (see Fig. 4,a) on their values close to the thickness of layers constituting phase (see. Fig. 2). It should be noted that in this case (when shooting by focusing Bragg-Brentano) size was determined in a direction perpendicular to the plane of the layer growth.

Fig. 5 shows the dependence of the change of the lattice parameter of λ. It can be seen that the smallest grating period value, for TiN, and ZrN layers tend to coatings with λ ≈ 200 nm. At a low value λ to the greatest degree change in the period of the lattice occurs in a layer of titanium nitride (curve 2 in Fig. 5), which may be associated with more intense state of compression and the formation of radiation defects in the layers of titanium nitride as the lighter component of the multilayer coating.
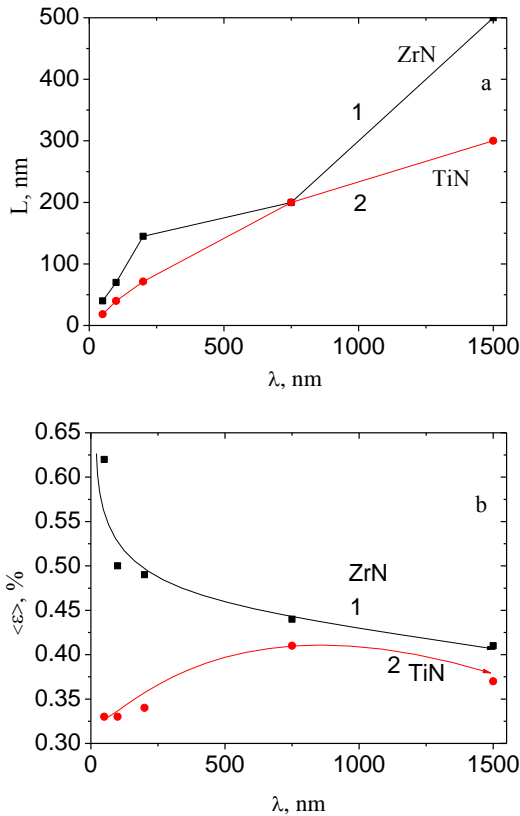

Fig. 4. Change the crystallite size L (a) and microstrain <ε> (b) of λ: 1 − to ZrN phase; 2 − for the TiN phase
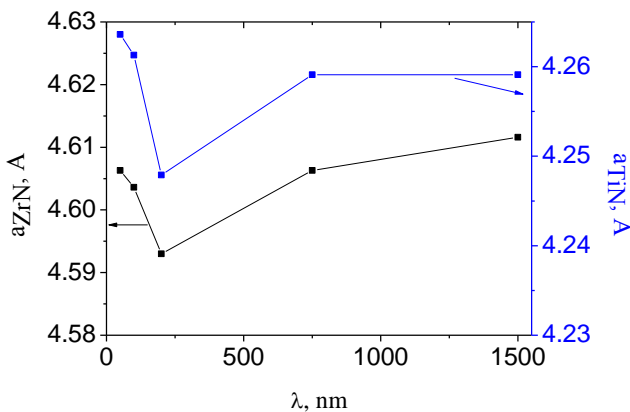
Fig. 5. The dependence of the change the crystallite size L (a) and microstrain <ε> (b) of λ; 1 − to ZrN phase, 2 − for the TiN phase

If we compare presented above structural data with the results of measurement of hardness (Fig. 6, curve 1) and elastic modulus (see Fig. 6, curve 2), it is seen that with decreasing λ observed increase in hardness and change of elastic modulus at small λ is nonmonotonic character.

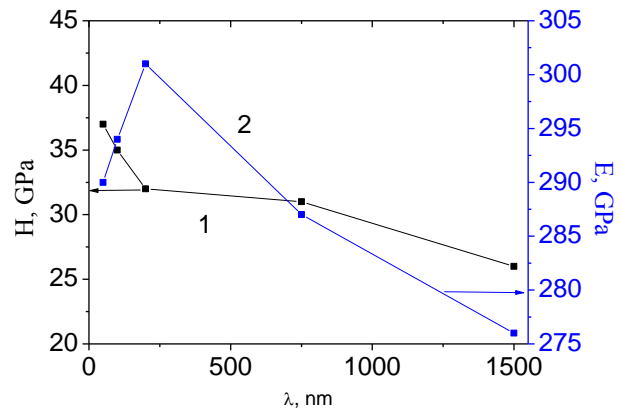*Fig. 6. The data measurement of hardness H (1) and elastic modulus E (2) coatings with different λ (Ub = -200 V)*

So the elastic modulus increases in the range of small thicknesses λ, and then decreasing with λ greater than 200 nm (see Fig. 6, curve 2). Note that the reduction of the modulus of elasticity for small λ, apparently due to a significant increase in the number of non-equilibrium phase boundaries [1].

The above results were considered to coatings obtained at a relatively high negative Ub = -200 V. When submitting smaller bias potential (magnitude Ub = -140 V) λ reduction leads to a decrease degree of perfection of texture with [111] axis perpendicular to the plane of growth, that is a decrease in the relative intensities of the peaks from the family of planes [111] (Fig. 7).
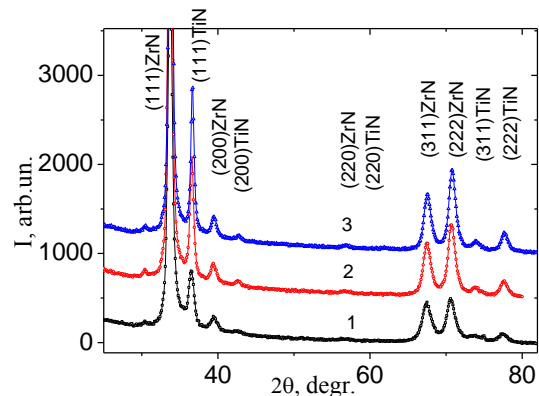

Fig. 7. Plots of the diffraction spectra coatings TiN/ZrN, obtained at Ub = -140 V with different λ: 1 − 100 nm; 2 − 200 nm; 3 − 750 nm

To determine the degree of texturing the most Illustrative is the construction of comparative dependences of the intensity with reference data (for ZrN − PDF 35-0753, and for TiN − PDF 38-1420). As seen from comparison the degree of texturing (according to the reference values divided by the intensity of the peaks of the planes, giving the reflexes in the range of diffraction

angles $2\theta=30\ldots65°$) in layers of titanium nitride and zirconium nitride texture [111] axis perpendicular to the plane of growth is determining (Fig. 8). But the degree of texturing above TiN and the ratio $I(111)/\Sigma I(hkl)$ reaches 97% (see Fig. 8,a), and layers ZrN $I(111)/\Sigma I(hkl)$ does not exceed 92% (see Fig. 8,b). Where $I(111)$ − the integrated intensity of the peak [111] and $\Sigma I(hkl)$ − the sum of integrated intensities of all the peaks. A lesser degree of texturing for ZrN may be associated with more intense bombardment by heavy atoms during the growth of Zr layers ZrN, which contributes to the creation of high defect density, enabling disorientation of crystallites.
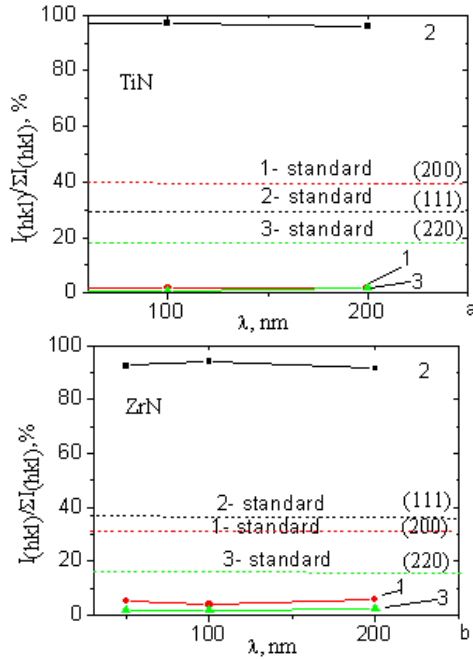

Fig. 8. The intensity distribution of the diffraction peaks at different thickness of periods to TiN (a) and the ZrN (b), coating system of TiN/ZrN, obtained at U_b = -140 V: 1 − (200); 2 − (111); 3 − (220) and the corresponding levels tabulated reference values

Substructural analysis characteristics presented in Fig. 9 shows that U_b = -140 V, as in the case U_b = -200 V (see Fig. 4) increase λ leads to a larger crystallites and microstrain in the layers ZrN. In this case, layers of TiN smaller crystallite size, which implies their crushing in the direction of growth under the action of compressive macrostresses accompanied discharge microstrain.

Confirmation of similarity of structure formation processes at a constant flow of negative potentials -140 V and -200 V can serve as similar as for U_b = -200 V (see Fig. 5), and for U_b = -140 V (Fig. 10), the increase of the lattice constant in the direction perpendicular the growth direction of the coating with a decrease in λ, the manifestation of which is more pronounced in the layers of TiN.
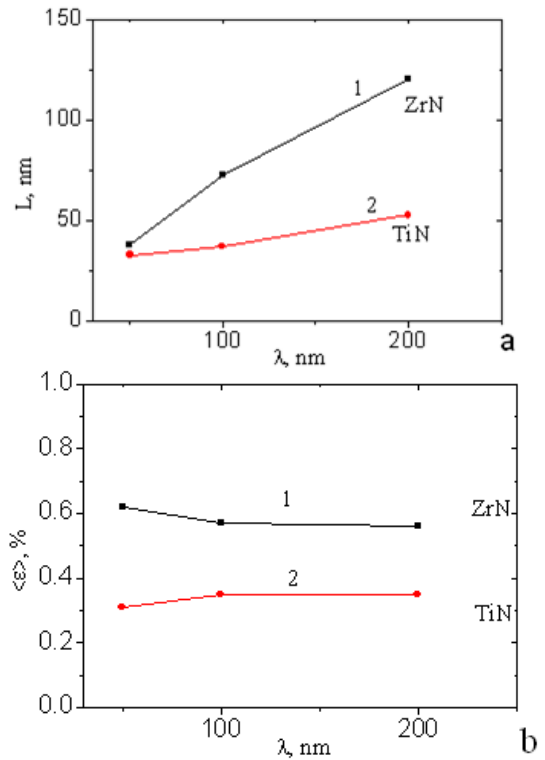

Fig. 9. Change of substructural characteristics (crystallite size L (a) and microdeformation <ε> (b)) of the λ in the coatings obtained with U_b = -140 V
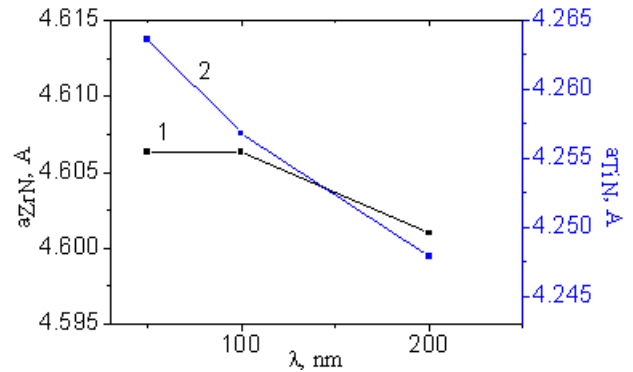

Fig. 10. Dependences of the variation of the lattice of periods thickness in the coatings obtained by U_b = -140 V

Analysis of the results of mechanical testing of coatings shows that in the case of the smaller in magnitude U_b = -140 V decrease the thickness of the layers leads to increase in hardness (Fig. 11, curve 1). However, the elastic modulus of coating increases with decreasing λ (Fig. 11, curve 2), in contrast to similar characteristics of the coating obtained with high U_b = -200 V. Also, it should be noted that in the case of smaller U_b = -140 V hardness and modulus of elasticity - higher in absolute value.
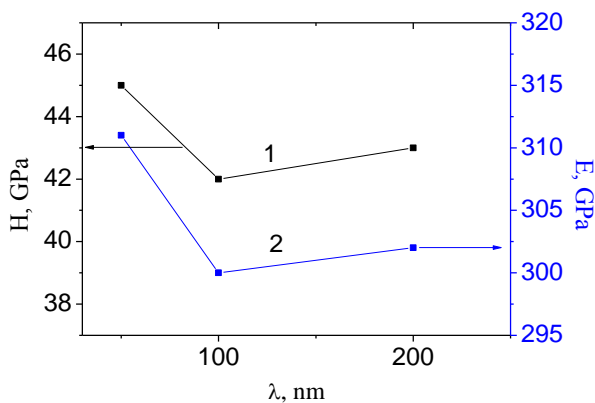
Fig. 11. The measurement data of hardness H (1) and elastic modulus E (2) coatings with different λ (U_b = -140 V)

The observed differences in the change of mechanical properties to λ at different U_b can be explained by the different levels of radiation exposure on the cross border stirring during the deposition of each layer. Indeed, if we assume that the increase in the average energy U_b increases with increasing density of defects at the interphase boundary of the irradiated layer during deposition (which promotes mixing and formation of solid solution), the increase in number of borders (with decreasing layer thickness) results in a greater volume of mixed defective areas interlayer regions. The latter causes the lowering of the modulus of elasticity and a decrease in absolute value of the hardness of the multilayer coating.

CONCLUSIONS

1. As used in the work modes of deposition of vacuum-arc coatings allow to receive by alternating layers of ZrN and TiN multilayer systems.

2. The coatings obtained at U_b = -140…-200 V characterized by a high degree of texturing, with texture axis [111], as in ZrN and TiN layers.

3. Decrease λ in a substructural level accompanied to increase of microstrain in ZrN layers and increase crystal lattice period, both ZrN and TiN.

4. Increasing the number of boundaries with decreasing λ leads to increasing the hardness to 45 GPa, both ZrN and TiN single-layer coatings.

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ВЛИЯНИЕ ТОЛЩИНЫ БИСЛОЕВ TiN/ZrN НА СТРУКТУРУ И СВОЙСТВА МНОГОСЛОЙНЫХ ПОКРЫТИЙ, ПОЛУЧЕННЫХ ВАКУУМНО-ДУГОВЫМ ИСПАРЕНИЕМ

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Методами рентгеновской дифрактометрии, электронной микроскопии и микроиндентирования исследованы фазовый состав, структура, субструктура, твердость и модуль упругости вакуумно-дуговых многослойных покрытий системы TiN/ZrN, полученных с разными толщинами двухслойных периодов при постоянных отрицательных потенциалах смещения (U_b) -140 и -200 В. Установлено, что при действии этих потенциалов в процессе осаждения покрытий слои мононитридов ZrN и TiN формируются с преимущественной ориентацией кристаллитов (текстурой) с осью [111], перпендикулярной плоскости роста. Увеличение числа границ при уменьшении толщины периодов приводит к увеличению твердости до 45 ГПа, что значительно превосходит твердость каждого из слоев ZrN и TiN в отдельности.

ВПЛИВ ТОВЩИНИ БІШАРІВ TiN/ZrN НА СТРУКТУРУ І ВЛАСТИВОСТІ БАГАТОШАРОВИХ ПОКРИТТІВ, ОТРИМАНИХ ВАКУУМНО-ДУГОВИМ ВИПАРОВУВАННЯМ

О.В. Соболь, А.О. Андрєєв, В.Ф. Горбань, В.О. Столбовий, Н.В. Пінчук, А.О. Мейлехов

Методами рентгенівської дифрактометрії, електронної мікроскопії та мікроіндентування досліджені фазовий склад, структура, субструктура, твердість і модуль пружності вакуумно-дугових багатошарових покриттів системи TiN/ZrN, отриманих з різними товщинами двошарових періодів при постійних негативних потенціалах зміщення (U_b) -140 і -200 В . Встановлено, що при дії цих потенціалів у процесі осадження покриттів, шари мононитридів ZrN і TiN формуються з переважною орієнтацією кристалітів (текстурою) з віссю [111], перпендикулярній площині зростання. Збільшення числа границь при зменшенні товщини періодів призводить до підвищення твердості до 45 ГПа, що значно перевершує твердість кожного з шарів ZrN і TiN окремо.