CHANGES IN THE STRUCTURAL STATE AND PROPERTIES OF VACUUM-ARC COATINGS BASED ON HIGH-ENTROPY ALLOY TiZrHfNbTa UNDER THE INFLUENCE OF NITROGEN PRESSURE AND BIAS POTENTIAL AT DEPOSITION

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Complex studies have been carried out on the effect of nitrogen pressure and the negative bias potential on the structure and properties of vacuum-arc nitride coatings based on the high-entropy alloy TiZrHfNbTa. It is defined that the change in pressure during deposition (in the range 0.01...4 mTorr) mainly affects the nitrogen atoms content in the coating. The feed of a negative bias potential to the substrate (U_b = -50...-250 V) makes it possible to control the content of the metallic component using the effect of selective sputtering of atoms in the formation of coatings. Determined, that as the pressure increases the structural state associated with the predominant growth orientation (axial texture) of the crystallites changes. The texture changes in the sequence [311] → [311] + [111] → [111] with increasing pressure for a six-element (TiZrHfVNbTa)N nitride and the texture state changes in the sequence [110] → [110] + [111] → [111] for a five-element (TiZrHfNbTa)N nitride. It is shown that the presence of a bi-textured state in the coating makes it possible to achieve an ultrahard state with a hardness exceeding 50 GPa.

PACS: 81.07.Bc, 61.05.cp, 68.55.jm, 61.82.Rx

INTRODUCTION

Structural engineering has become a basic method for achieving the necessary functional properties of materials [1, 2]. Through the use of structural engineering, it was possible to create new materials [3, 4] or stabilize [5] metastable structural states. Separate direction of structural engineering is the creation of artificial materials (i. e., materials that are not identified in nature and are created by specially developed algorithms) based on multilayer [6] or multi-element composites [7]. For example, when creating multilayer composites, the algorithm determines the thickness of the layers, as well as the required elemental and phase composition. Such artificial materials have uniquely high functional characteristics [8]. A particularly large increase in the functional characteristics was observed in materials with a nanostructured state, when the formation was carried out under strongly nonequilibrium conditions [9]. Such materials include ion-plasma condensates [10]. Among methods for the formation of such materials, the greatest degree of ionization can be achieved by using the vacuum-arc method [11]. This made it possible to obtain high-density coatings with high hardness and wear resistance [12]. The highest mechanical properties were achieved for multilayer composites based on transition metal nitrides [13, 14].

In recent years, special attention has been paid to coatings based on multi-element (high-entropic) alloys [15]. This is due to the fact that high-entropy alloys have a unique ordering property in the metal lattice at high temperatures [16]. The ordering is due to the fact that in the high-entropic alloys, as a result of the intensive mixing effect, the contribution of the entropy factor increases, which stabilizes the formation of a solid solution with a simple crystal structure.

As is well known, using Boltzmann's conjecture on the relationship between entropy and system complexity [17], the configuration change in entropy, ΔS_{conf}, when forming a solid solution of n elements with equiatomous content, can be calculated by the following formula:

$$\Delta S_{conf} = -R \ln\left(\frac{1}{n}\right) = R \ln(n),$$

where R is the ideal gas constant, and n is the number of mixing elements. At $n = 5$, $\Delta S_{conf} = 1.61R$, which approaches the fusion entropy size of most intermetallides (in the range of values $R...2R$). This indicates that only a solid solution of the same type, namely a solid solution based on face-centered cubic (fcc), body-centered cubic (bcc), or fcc + bcc crystalline lattices, is formed mostly in high entropy alloys [18, 19].

In addition, large lattice distortions caused by the replacement of several metal elements with different atomic dimensions lead to a decrease in the diffusion rate of atoms increasing the effect of the formation and stabilization of the solid solution, and also contribute, due to large distortions, to a decrease in the crystallite growth rate, thereby causing the formation of a nanoscale and even an amorphous structure. As a result of high entropy of mixing of such alloys and deformation of the lattice, solid-solution phases with a simple face-centered cubic (fcc) or body-centered (bcc) structure, rather than double or triple intermetallic compounds, are formed.

Transition metals (Ti, Zr, Hf, Nb, Ta) with a high heat of nitride formation were used in this paper as base

elements of high-entropy alloys to obtain coatings with high hardness, low friction coefficient, good adhesion to the substrate. The aim of the paper is to determine the efficiency of using the vacuum-arc deposition method to obtain materials with high mechanical properties from composites containing strong nitride-forming components. The nitrogen atmosphere pressure and the bias potential were varied during deposition.

SAMPLES AND RESEARCH METHODS

The coatings were deposited by the vacuum-arc method using upgraded "Bulat-6" unit [11]. A cathode of the required composition was pre-fabricated by vacuum-arc remelting of a multicomponent mixture of pure metal powders. As initial components, metals with a purity of not less than 99.9% were used. A non-consumable tungsten cathode was used for remelting. The crystallized ingot was removed from the crystallizer, turned over and placed again in a crystallizer. The melt was melted again and the procedure was repeated 7 times to obtain the most homogeneous structure (The technology is developed at the Institute of Problems of Material Sciences NAS of Ukraine). The ingot in the form of a cylinder (diameter ~ 45 mm, height ~ 30 mm) was extracted from the crystallizer and soldered to a titanium cathode using solder. Thus, target cathodes based on the Ti+Zr+Nb+Hf+V+Ta system were fabricated (also five-element Ti+Zr+Nb+Hf+Ta target cathodes were fabricated), which were used to prepare nitride coatings. The average composition of the six-element cathode (at.%): Ti – 18, Zr – 18, Nb – 18, Hf – 15, V – 12, Ta –19. The composition of the five-element cathode (at.%): Ti – 27, Zr – 19, Nb – 20, Hf – 14, Ta – 20. The reactive gas was nitrogen. The deposition parameters are given in Table.

Samples with size (15x15x2.5 mm) made of 12X18H9T steel ($R_a = 0.09$ μm) were chosen as the base for the coatings deposition. The application time was 1.5 hours, coatings thickness was ~ 8.0 μm.

The morphology of the cross section of multi-period structures was studied with a scanning electron microscope JEOL JSM840. For electron-microscopic studies, coatings were deposited on copper substrates 0.2 mm thick. The study of the coatings elemental composition was carried out by analyzing the spectra of characteristic X-ray radiation generated by an electron beam in a scanning electron microscope.

The phase-structure state was studied on a DRON-3M diffractometer in Cu-K_α-radiation. A graphite monochromator was used to monochromatize the detected radiation and was installed in a secondary beam (in front of the detector). The study of the phase composition, structure (texture, substructure) was carried out using traditional X-ray diffractometry techniques by analyzing the position, intensity, and shape of the diffraction reflection profiles. The substructural characteristics (medium microdeformation <ε> and crystallite size, L) were determined by the two-order approximation of reflections from planes {111}.

Coatings hardness was measured by the microindentation method. Microindentation was carried out at the Micron-gamma unit [20–22] with a load up to $F = 0.5$ N using a Berkovich diamond pyramid with cutting angle of 65°, with automatic loading and unloading for 30 s.

Physico-technological parameters of coatings deposition

Se- rial No	Coatings	I_a, A	I_f, A	U_b, V	P, Torr
1	(TiZrHfVNbTa)N	90	0.4	150	$2 \cdot 10^{-4}$
2	(TiZrHfVNbTa)N	90	0.4	150	$5 \cdot 10^{-4}$
3	(TiZrHfVNbTa)N	90	0.4	150	$7 \cdot 10^{-4}$
4	(TiZrHfVNbTa)N	90	0.4	150	$2 \cdot 10^{-3}$
5	(TiZrHfVNbTa)N	90	0.4	150	$4 \cdot 10^{-3}$
6	(TiZrHfNbTa)N	110	0	50	$1 \cdot 10^{-5}$
7	(TiZrHfNbTa)N	110	0.5	150	$2 \cdot 10^{-4}$
8	(TiZrHfNbTa)N	110	0.5	150	$7 \cdot 10^{-4}$
9	(TiZrHfNbTa)N	110	0.5	150	$1 \cdot 10^{-3}$
10	(TiZrHfNbTa)N	110	0.5	150	$4 \cdot 10^{-3}$
11	(TiZrHfNbTa)N	110	0.5	50	$4 \cdot 10^{-3}$
12	(TiZrHfNbTa)N	110	0.5	100	$4 \cdot 10^{-3}$
13	(TiZrHfNbTa)N	110	0.5	200	$4 \cdot 10^{-3}$
14	(TiZrHfNbTa)N	110	0.5	250	$4 \cdot 10^{-3}$

RESULTS AND DISCUSSION

Fig. 1 shows that as the pressure of the nitrogen atmosphere increases, the content of the drop phase in the nitrides coatings of high-entropy alloys decreases. It should be noted that as it was stated earlier [23], the drop phase mainly consists of a metal alloy (in this case a high-entropy alloy TiZrHfNbTa with a bcc crystal lattice) with a predominant content of low-melting metallic constituents. It can be seen that at a low pressure of $2.5 \cdot 10^{-4}$ Torr (see Fig. 1,a), the drop phase is largely present both in the bulk and on the surface of the coating, and the size of the droplets varies in a wide range: from a micron fraction to several units micron. The increase in pressure leads to a qualitative change in the content of the drop phase. Fig. 1,b shows that the presence of a drop phase in the coating volume is not observed in coatings obtained at a pressure of $1.5 \cdot 10^{-3}$ Torr, and individual droplets of a small (submicron) size are detected on the surface.

The decrease in the content of the drop phase with increasing U_b can be explained by the fact that the droplet component, like any other cluster of atoms placed in the plasma, acquires a negative (floating) potential and is repelled by a surface on which a negative potential (in this case, the substrate surface) is fed.
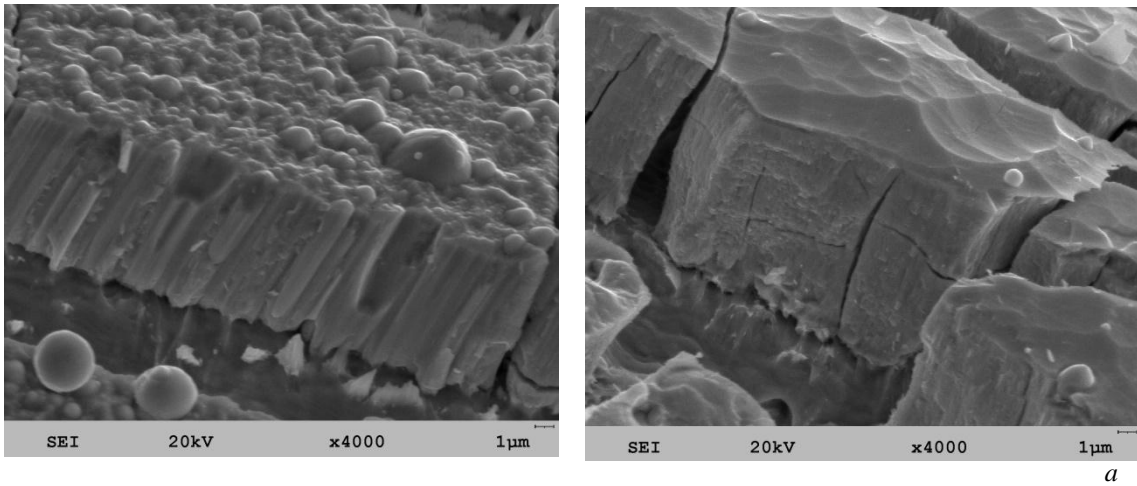
a   *b*

Fig. 1. Morphology of the coatings cross section and coatings surface obtained at pressures $2.5 \cdot 10^{-4}$ Torr (a)
and $1.5 \cdot 10^{-3}$ Torr (b)

To Energy-dispersive elemental analysis was carried out on the cross sections of the coatings. This made it possible to avoid errors while determining the elemental composition due to the inhomogeneous distribution of elements on the surface (droplets and other inhomogeneities). A typical EDX spectrum is shown in Fig. 2 and the distribution maps of the elements in Fig. 3.

a

b
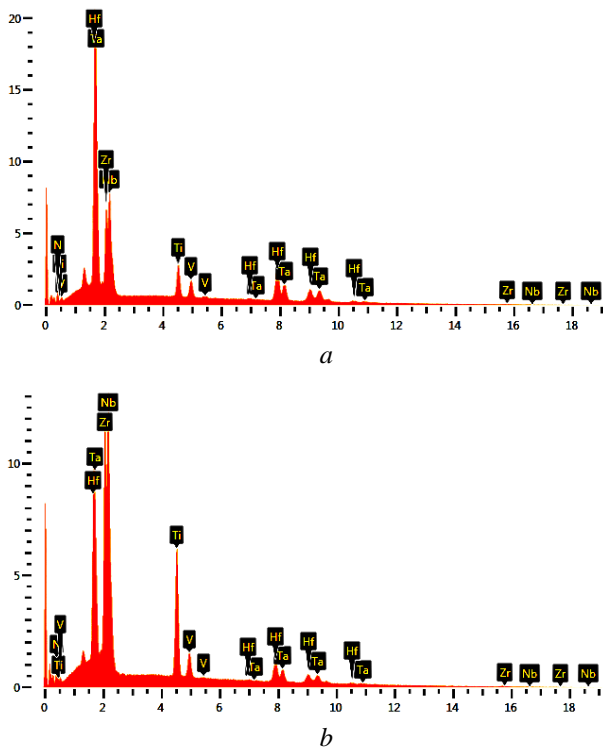
Fig. 2. Energy dispersion spectra of coatings obtained
at pressures $2.5 \cdot 10^{-4}$ Torr (a)
and $1.5 \cdot 10^{-3}$ Torr (b)

Fig. 3 shows that a uniform distribution of all elements constituting the high-entropic alloy nitride is observed on the coatings surface obtained at the nitrogen atmosphere pressure of $1.5 \cdot 10^{-3}$ Torr.
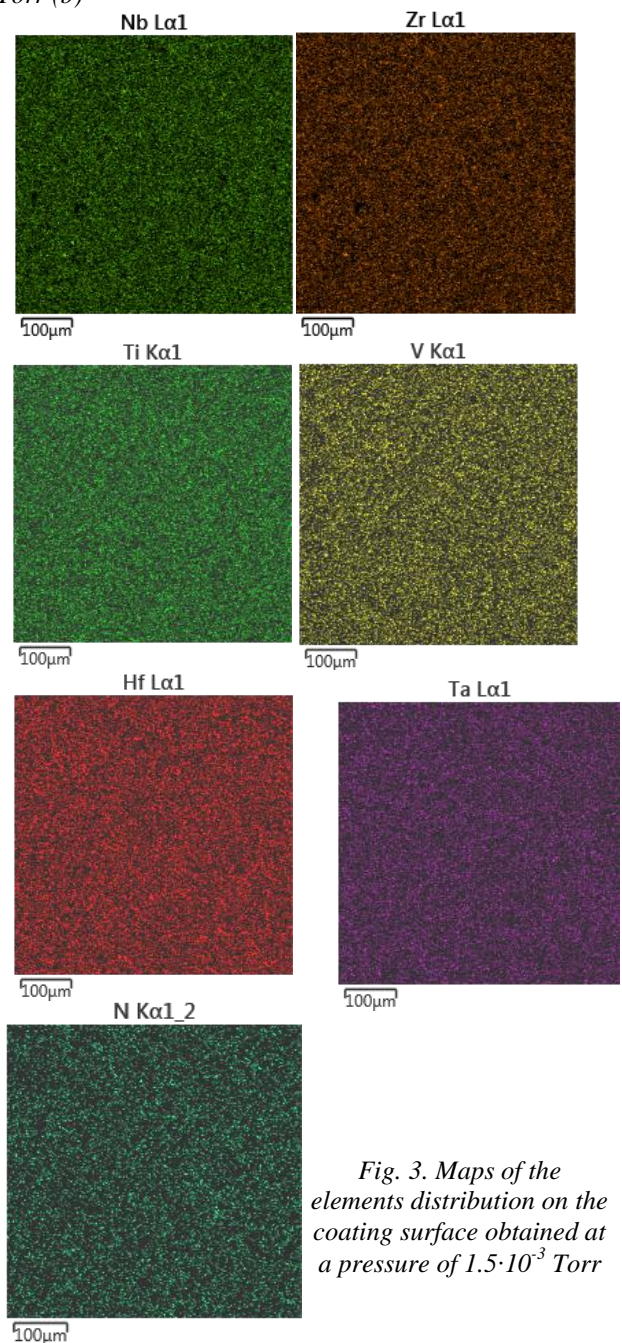

Fig. 3. Maps of the elements distribution on the coating surface obtained at a pressure of $1.5 \cdot 10^{-3}$ Torr

In this case, a microelement analysis of the nitrogen content in the coatings (Fig. 4) showed that the increase in the nitrogen content is especially seen at pressures 0.4...2.0 mTorr. It is to be noted that the atomic concentration of nitrogen in the coating, taking into account the mass composition of the metallic component, is in the range 37...52 at.%. Thus, according to the absolute value at the maximum pressure of 5.7 mTorr, the atomic nitrogen content exceeds the content of the metallic component making such coatings superstoichiometric considering the nitrogen component.
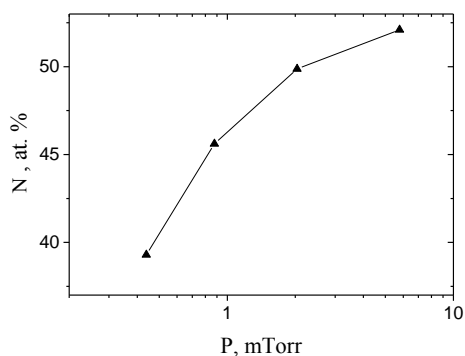

Fig. 4. Dependence of nitrogen content in coatings on the nitrogen atmosphere pressure for a six-component system (U_b = -150 V)

When the displacement potential is changed, the nitrogen content changes less significantly from 49.84 at.% and U_b = -50 V to 45.77 at.% and U_b = -250 V.
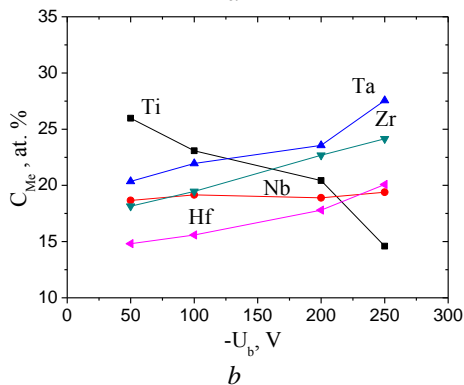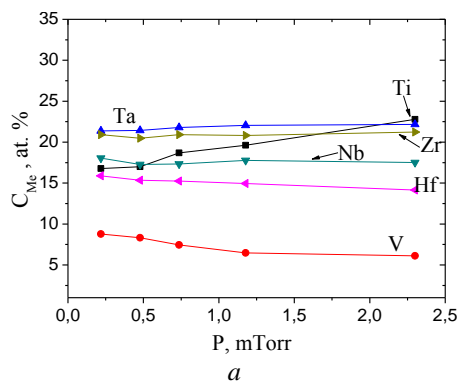

a

b

Fig. 5. Dependences of the metallic elements content in coatings obtained: a – at different pressures (U_b = -150 V) and b – at different bias potentials (P_N = 2 mTorr)

The influence of the nitrogen atmosphere pressure during deposition has a lesser effect on the ratio change

of the metallic elements in the coating (Fig. 5,a). With increasing pressure, a small redistribution of elements takes place. As a result of the redistribution in the coating, the content of strong nitride-forming elements increases (mostly Ti, less Ta) and the relative content of relatively weak (with the lowest gain of free energy during the formation of nitride) of nitride-forming elements (V, Nb) decreases. Note that for large P the content of Hf decreases. The reason for this, apparently, is the large scattering of the most heavy atoms of hafnium by their own atoms because of the most effective energy loss for particles of equal masses.

The feeding of a negative bias potential affects mostly the change in the elemental composition (see Fig. 5,b). At a pressure of 2 mTorr, an increase in the displacement potential leads to a decrease in the content of the lightest metallic element (Ti) and an increase in the heavy metal content (Ta and Hf). This clearly indicates that selective secondary sputtering of atoms is the determining factor in the formation of the elemental coating composition. This allows makes it possible to control the content of the metallic component using the effect of selective sputtering of atoms in the formation of coatings. Thus, the content of the lightest element of titanium decreases almost 2-fold with an increase in U_b from 50 to 250 V.

The revealed patterns in the elemental composition indicate that the secondary ballistic sputtering from the growth surface is the determining effect of the metal atoms considering feeding U_b [24]. The content of lightnitrogen gas atoms decreases with increasing U_b. Also, the content in the titanium atoms coating with a strong Ti–N bond decreases (the negative formation heat is 336 kJ/mol [25]). The results obtained make it possible to assert that the formation process of stable nitrides is carried out directly in the near-surface growth layers. In this case, the sputtering process is decisive in the formation of the composition.

It should be noted that the revealed patterns of elemental composition control with selective sputtering in the deposition process broadens the possibilities of structural engineering by feeding U_b.

The XRD method was used to study the phase composition and structure. Fig. 6 shows the XRD spectra of coatings obtained at different pressures of the working atmosphere (nitrogen gas).
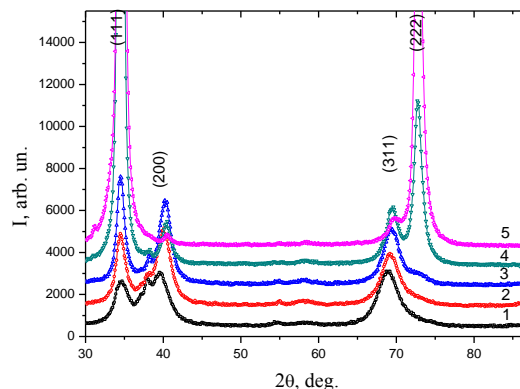

Fig. 6. XRD-spectra nitride coatings of a six-element alloy (TiZrHfVNbTa)N, obtained at U_b = -150 V and at pressure P_N, mTorr: 1 – 0.25; 2 – 0.5; 3 – 0.7; 4 – 2.0; 5 – 4.5

It can be seen that a texture [311] is formed at low pressure, which is sufficiently resistant to radiation defect formation [26]. This texture is maintained up to a relatively high pressure of 2 mTorr. At higher pressures, a bi-texture state with a basic growth texture [111] (see Fig. 6, spectrum 5) is formed. However, the degree of perfection of such a texture is not large, which can be associated with the disorienting effect of atoms of different sizes in the lattice sites of the metal components.

The appearance of the plane having preferential orientation of the crystallites (200) at a relatively low nitrogen atmosphere pressure (see curves 1–3, Fig. 6) indicate a mobility increase in the deposited particles [14] as a result of relatively low energy loss to collisions under reduced pressure.

An alloy on the basis of a simple bcc lattice (Fig. 7, spectrum 1) is formed in nitrile coatings based on a five-element alloy (the absence in the vanadium composition in contrast to the coatings, the spectra for which are shown in Fig. 6) at the lowest pressure of $1.5 \cdot 10^{-5}$ Torr.
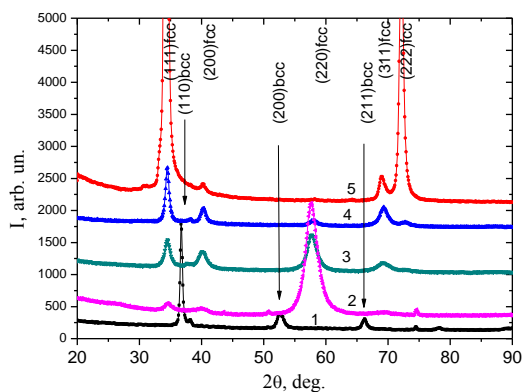

Fig. 7. XRD-spectra nitride coatings of a five-element alloy (TiZrHfNbTa)N, obtained at U_b = -150 V and at pressure P_N, mTorr:
1 – 0.01; 2 – 0.25; 3 – 0.7; 4 – 1.5; 5 – 4

Nitride is formed on the basis of the fcc metal sublattice (structural type NaCl) with increasing pressure. However, in contrast to the previous series, a texture with an axis [110] (see spectrum 2, Fig. 7) is formed in this series of coatings. The difference in the axis of the formed texture (from the series in Fig. 6) can be related to the increasing influence of the radiation factor due to the higher specific content of heavy elements. When the pressure $(2.5...7) \cdot 10^{-4}$ Torr is relatively low, then a range of particles without energy loss for collisions is small. This leads to high-energy bombardment and the formation of a radiation-stimulated texture with an axis [110]. Such a texture has a smaller reticular density in the plane of the surface (for example, in comparison with [111]).

At a pressure of more than 1 mTorr, as for the series in Fig. 6, the predominant orientation of crystallite growth with the axis [111] is observed.

The influence of the bias potential also affects the structural state. Fig. 8 shows the diffraction spectra of coatings obtained with different U_b (-50 to -250 V). It can be seen that in all cases a single-phase state is formed. Almost untextured state is formed at U_b = -50 V (see Fig. 8, spectrum 1). A noticeable intensification of

the diffraction peaks intensity from the plane {111} systems appears at U_b = -100 V (see Fig. 8, spectrum 2), which determines the preferential orientation of the crystallites with the axis [111] perpendicular to the growth surface. With an increase in U_b to -200 V (see Fig. 8, spectrum 3) and -250 V (see Fig. 8, spectrum 4), the relative intensity of the {111} peaks increases, indicating an increase in texture perfection [111]. In this case, the position of the peaks shifts toward smaller angles (as shown in Fig. 8 by an arrow) and at θ–2θ the imaging scheme corresponds to the increase in the macrostresses of compression in the coating [2].
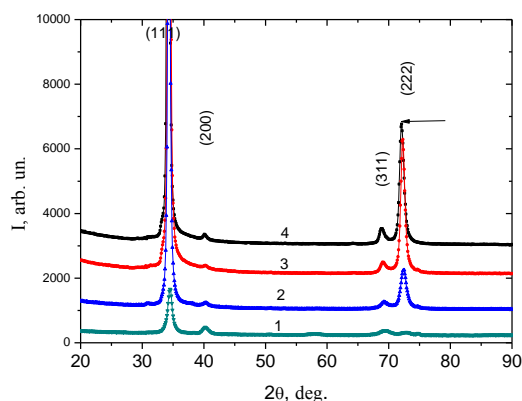

Fig. 8. XRD-spectra of coatings deposited at U_b, V:
1 – 50; 2 – 100; 3 – 200; 4 – 250

The most important mechanical characteristics for most application ranges of coatings is their hardness.

The results of microhardness measurements, generalized in Fig. 9 depending on pressure, show that coatings obtained at the pressure range 0.7...2 mTorr have the greatest hardness.
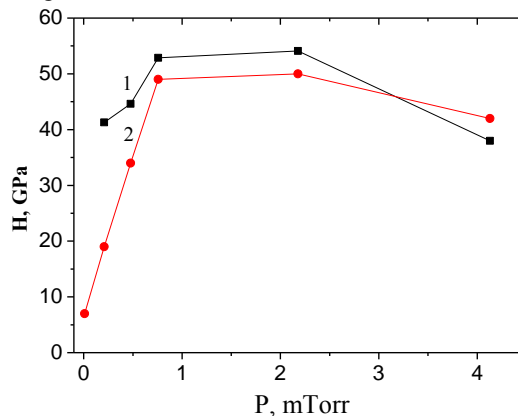

Fig. 9. Dependence of coatings microhardness on the pressure value during their deposition:
1 – for coating based on a six-element (TiZrHfVNbTa)N high-entropy alloy; 2 – for coating based on a five-element (TiZrHfNbTa)N high-entropy alloy

The structural state of such coatings is characterized by the presence of a bi-texture state ([311] + [111] for the first series and [110] + [111] for the second series). As can be seen, the appearance of the texture [110] results in a relatively lower hardness due to the radiation-stimulated effect.

The high hardness of coatings based on the 6-element alloy (compared to the 5-element alloy) which

precipitated at a low pressure of 0.2 mTorr is determined by the greater deformation of the crystalline fcc lattice (distortion). This effect is based on the overall greater discrepancy between the atomic radii for different elements in the 6-element alloy compared with the 5-element alloy. The deformation of the crystal lattice (caused by such a mismatch) makes it difficult to move dislocations and increases the strength.

The presence of monotexture [111] at a high pressure of 4 mTorr leads from 35 to 38 GPa typical for vacuum-plasma condensates of transition metal nitrides (for this texture type).

This is indicated by the hardness data for coatings obtained at a pressure of 4 mTorr (when the texture [111] is formed), but with different displacement potentials. With increasing U_b (and, correspondingly, at the structural level, an increase in the degree of texture perfection [111]), the hardness of coatings increases: 18.7 GPa ($U_b = -50$ V), 30.1 GPa ($U_b = -100$ V), 32.6 GPa ($U_b = -200$ V) up to a value of 40.2 GPa at $U_b = -250$V.

CONCLUSIONS

1. Vacuum-arc evaporation of high-entropy alloys in the nitrogen atmosphere makes it possible to obtain high-strength nitride coatings.

2. A single-phase state is formed based on the fcc metal sublattice (structural type NaCl) in (TiZrHfVNbTa)N and (TiZrHfNbTa)N coatings.

3. The change in pressure during deposition mainly affects the content of nitrogen atoms in coating, and the feeding of a negative bias potential to the substrate makes it possible to control the content of the metallic component.

4. As the pressure increases, the structural state associated with the predominant orientation of crystallite growth changes. The texture changes in the sequence $[311] \rightarrow [311] + [111] \rightarrow [111]$ with increasing pressure for a six-element (TiZrHfVNbTa)N nitride, and the texture state changes in the sequence $[110] \rightarrow [110] + [111] \rightarrow [111]$ for a five-element nitride (TiZrHfNbTa)N.

5. The presence of a bi-textured state in the coating makes it possible to achieve a superhard state of a hardness exceeding 50 GPa.

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ИЗМЕНЕНИЯ СТРУКТУРНОГО СОСТОЯНИЯ И СВОЙСТВ ВАКУУМНО-ДУГОВЫХ ПОКРЫТИЙ НА ОСНОВЕ ВЫСОКОЭНТРОПИЙНОГО СПЛАВА TiZrHfNbTa ПОД ВЛИЯНИЕМ ДАВЛЕНИЯ АЗОТА И ПОТЕНЦИАЛА СМЕЩЕНИЯ ПРИ ОСАЖДЕНИИ

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Проведены комплексные исследования по влиянию давления азота и отрицательного потенциала смещения на структуру и свойства вакуумно-дуговых нитридных покрытий на основе высокоэнтропийного сплава TiZrHfNbTa. Определено, что изменение давления при осаждении (в интервале 0,01…4 мТорр) в основном влияет на содержание атомов азота в покрытии, а подача отрицательного потенциала смещения на подложку (U_b= -50…-250 В) позволяет управлять содержанием металлической составляющей с использованием эффекта селективного распыления атомов при формировании покрытия. Установлено, что с увеличением давления происходит изменение структурного состояния, связанного с преимущественной ориентацией роста (аксиальной текстуры) кристаллитов. Для шестиэлементного нитрида (TiZrHfVNbTa)N с увеличением давления происходит изменение текстуры в последовательности [311] → [311] + [111] → [111], а для пятиэлементного нитрида (TiZrHfNbTa)N текстурное состояние изменяется в последовательности [110] → [110] + [111] → [111]. Показано, что наличие битекстурного состояния в покрытии позволяет достигнуть сверхтвердого состояния с твердостью, превышающей 50 ГПа.

ЗМІНИ СТРУКТУРНОГО СТАНУ І ВЛАСТИВОСТЕЙ ВАКУУМНО-ДУГОВИХ ПОКРИТТІВ НА ОСНОВІ ВИСОКОЕНТРОПІЙНОГО СПЛАВУ TiZrHfNbTa ПІД ВПЛИВОМ ТИСКУ АЗОТУ І ПОТЕНЦІАЛУ ЗМІЩЕННЯ ПРИ ОСАДЖЕННІ

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Проведено комплексні дослідження щодо впливу тиску азоту і негативного потенціалу зміщення на структуру і властивості вакуумно-дугових нітридних покриттів на основі високоентропійного сплаву TiZrHfNbTa. Визначено, що зміна тиску при осадженні (в інтервалі 0,01 ... 4 мТорр) в основному впливає на вміст атомів азоту в покритті, а подача негативного потенціалу зміщення на підкладку (U_b = -50...-250 В) дозволяє управляти вмістом металевої складової використовуючи ефект селективного розпилення атомів при формуванні покриття. Встановлено, що зі збільшенням тиску відбувається зміна структурного стану, пов'язаного з переважною орієнтацією зростання (аксіальної текстури) кристалітів. Для шестиелементного нітриду (TiZrHfVNbTa)N зі збільшенням тиску відбувається зміна текстури в послідовності [311] → [311] + [111] → [111], а для п'ятиелементного нітриду (TiZrHfNbTa)N текстурний стан змінюється в послідовності [110] → [110] + [111] → [111]. Показано, що наявність бітекстурного стану в покритті дозволяє досягти надтвердого стану з твердістю понад 50 ГПа.