

Influence of the Bias Potential and the Pressure of the Nitrogen Atmosphere on the Structure and Properties of Vacuum-arc Coatings Based on the AlCrTiZrNbV High-entropy Alloy

O.V. Sobol¹, A.A. Andreev², V.F. Gorban³, A.A. Postelnyk¹, V.A. Stolbovoy², A.V. Zvyagolskiy¹

¹ National Technical University «Kharkiv Polytechnic Institute», 2, Kyrpychov Str., 61002 Kharkiv, Ukraine

² National Science Center Kharkov Institute of Physics and Technology, 1, Akademicheskaya Str., 61108 Kharkiv, Ukraine

³ Frantsevich Institute for Problems of Materials Science, Krzhizhanovsky str., 3, 03142 Kiev-142, Ukraine

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The effect of the constant bias potential (U_b) supplied to the substrate upon condensation and pressure of the nitrogen atmosphere (P_N) on the elemental composition, growth morphology, texture, and physical-mechanical characteristics of vacuum-arc (AlCrTiVZrNb) N_x coatings is studied. It is established that with increasing U_b from -110 V to -200 V, the axis of preferential growth of crystallites of the fcc phase from [100] to [110] changes. Such a change is accompanied by a decrease in the hardness (H) and the ratio H/E (where E is the modulus of elasticity). The conditions for the formation of the preferential orientation of the crystallites (axial texture) of vacuum-arc (AlCrTiVZrNb) N_x coatings and the influence of texture on mechanical properties are discussed. It was established that the change in P_N in the range $(1.7-5) \cdot 10^{-3}$ Torr basically allows to vary the degree of filling of the coating with nitrogen atoms. Based on the revealed regularities, the conditions for achieving high hardness for vacuum-arc coatings of nitrides AlCrTiVZrNb high-entropy alloy are substantiated. Because of the presence in the alloy of elements with a relatively low heat of nitride formation, in order to achieve high hardness, it is necessary to use deposition conditions with relatively low energy of bombarding atoms. The use of a low $U_b = -110$ V at the highest pressure $P_N = 5 \cdot 10^{-3}$ Torr allows achieving an superhard state with a hardness of 44 GPa.

Keywords: Vacuum arc, AlCrTiZrNbV, Bias potential, Pressure, Structural engineering, Phase composition, Texture, Hardness.

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1. INTRODUCTION

Determination of general patterns of technological parameters influence on the structural state with the aim of using such regularities to obtain specified operational characteristics is the most effective method not only for achieving the necessary properties [1], but also for predicting the possibilities for their further optimization [2, 3].

The traditional approach in creating new materials is to select one basic element as a matrix that is doped to obtain the desired combination of mechanical and/or operational properties [4, 5]. As a matrix-basis, Fe, Cu, Al, Ni, Mg, etc. were used. However, in recent years, thanks to structural engineering in the nonequilibrium conditions of formation, it has been possible to develop new mechanisms for the formation of composite materials [6] and to stabilize metastable phase-structure states [7].

Also in recent years, structural engineering has been actively used to obtain new states in multicomponent alloys. Particular attention is paid to multicomponent alloys having as a matrix five or more elements in equal (equiatomic) proportions and which form a disordered solid solutions [8, 9]. This is due to the possibility of creating structural states in them, thanks to which various mechanisms of their hardening can be used, such as solid-solution, dispersion, deformation, etc. [10]. Such alloys are called high-entropic alloys [11, 12] and under certain combinations of elements in these alloys it is possible to obtain high strength, plasticity, wear resistance, corrosion

resistance, etc. [13, 14]. This is due to the fact that highly entropic alloys have a unique property of ordering in a metal lattice under extreme influences and high temperatures [15, 16]. The ordering is due to the fact that in the highly 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 [17] and high physical-mechanical characteristics [18].

The high-temperature alloy of the HfNbTaTiZr system has a small difference in the heat of mixing between different atomic pairs [19] and can form a solid solution based on the bcc lattice in the cast state [20] it has been developed in recent years. Also all components of this alloy have a high binding energy with nitrogen. This served as the basis for the creation of high-hard nitride coatings based on the TiZrNbVHfTa high-entropy alloy [21, 22].

One of the main disadvantages of the TiZrNbVHfTa alloy is the high specific gravity of the constituent elements. In order to reduce the specific gravity, it is proposed to use Al and Cr instead of the heaviest components - Hf and Ta. Note that although the Al and Cr elements also have a relatively high binding energy with nitrogen, but compared with Hf and Ta, their binding energy with nitrogen is much lower [14, 23]. In this connection, one can expect a great influence of the pressure of the nitrogen atmosphere and the bias potential (which determine the efficiency of nitride formation during condensation) on the structural state and mechanical properties of vacuum-arc coatings formed on their basis. Investigation of the

influence of these technological parameters was the goal of this work.

2. SAMPLES AND METHODS OF EXPERIMENTS

The coatings were deposited by the vacuum-arc method on a modernized "Bulat-6" installation.

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 at least 99.9% were used. The alloys were smelted in an MIFI-9-3 arc furnace in an atmosphere of high-purity argon, and the atmosphere was further refined by the reuse of the Zr-Ti getter. To remove the shrinkage cavity, the surface of the ingot was melted with an arc of low power. The time of heating of the upper part of the ingot was selected in such a way as to create and feed the crystallization front with liquid metal, but as little as possible to influence the speed of its advance.

After a ten-time remelting, the highly entropy alloys crystallized at a rate of 20 K/s. Structure of ingot-billet for the cathode is shown in Fig. 1. In the initial state after smelting, the cathode composition is a biphasic bcc solid solution (content close to 70 vol.%) and Laves phase (content close to 30 vol.%).

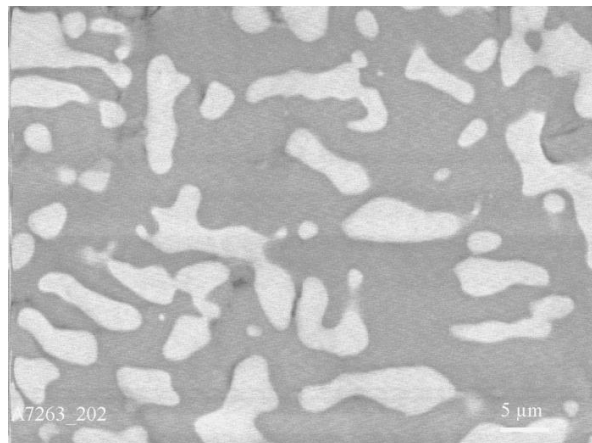


Fig. 1 – The structure of two-phase (dark – bcc phase, light – Laves phase) high-entropy alloy (TiZrAlVNbCr)

During deposition of the coating, a constant negative bias potential (U_b) of -110 or -200 V was fed to a substrate to achieve good adhesion of the coating to the substrate. The pressure of working atmosphere (nitrogen) during the deposition was $P_N = (1.7-5) \cdot 10^{-3}$ Torr. As samples for the deposition of coatings, samples of the size $(15 \times 15 \times 2.5)$ mm made of 12X18H9T steel ($R_a = 0.09 \mu\text{m}$) were chosen. The deposition time was about 90 minutes. Coating thickness was achieved $\sim 8.0 \mu\text{m}$. The deposition parameters, as well as the hardness (H) and the ratio of hardness to the modulus of elasticity (H/E) are shown in Table 1.

The phase-structure state was studied on a DRON-4 diffractometer in $\text{Cu-K}\alpha$ radiation. For monochromatization of the recorded radiation, a graphite monochromator was used, which 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 profiles.

Table 1 – Deposition parameters and microindentation results

No series	I_a , A	U_b	P_N , Torr	H , GPa	H/E , GPa
1	85	200	$5 \cdot 10^{-3}$	26	0.077
2	135	110	$5 \cdot 10^{-3}$	44	0.110
3	135	110	$1.7 \cdot 10^{-3}$	35	0.121
4	135	200	$2 \cdot 10^{-3}$	20	0.087

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

Microindentation was carried out on the «Micron-gamma» installation [24] with a load up to $F = 0.5$ N. Berkovich diamond pyramid with an angle of 65° was used.

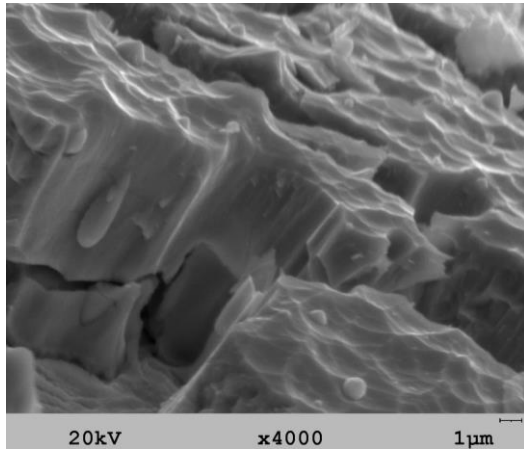
3. RESULTS AND DISCUSSIONS

The study of the cleavage surface (in the case of brittle fracture at a low nitrogen temperature) showed (Fig. 2) that the supply of a relatively small negative bias potential at deposition $U_b = -110$ V (Fig. 2a) is accompanied by the formation of coatings with a homogeneous structural state in thickness (without pronounced columnar formations). With a large potential $U_b = -200$ V, the structure of the coatings has a pronounced columnar component (Fig. 2b).

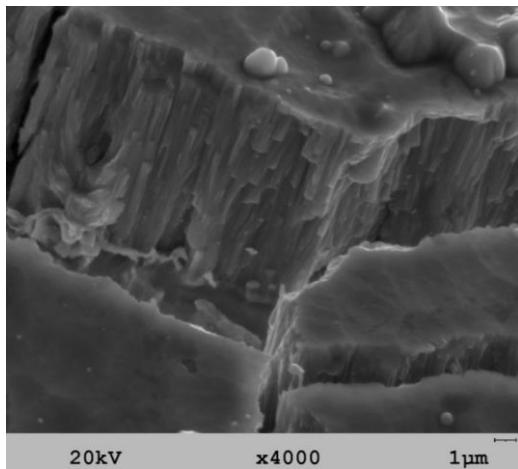
The results of energy-dispersive elemental analysis showed that the deposition of coatings with the supply of a large bias potential $U_b = -200$ V leads to a decrease in the relative content of light nitrogen atoms in them and an increase in the relative content of heavy Zr and Nb atoms. For $P_N = 5 \cdot 10^{-3}$ Torr at $U_b = -200$ V the following elemental composition is obtained: Ti – 11.29 at.%, Zr – 15.4 at.%, Al – 2.76 at.%, V – 11 at.%, Nb – 18.7 at.%, Cr – 16.25 at.%, N – 24.61 at.%. In the coatings deposited at $U_b = -110$ V, the following composition was obtained: Ti – 12.38 at.%, Zr – 11.62 at.%, Al – 4.3 at.%, V – 9.2 at.%, Nb – 14.7 at.%, Cr – 11.7 at.%, N – 36.1 at.%.

The change in pressure during deposition has the greatest effect on the relative content of nitrogen atoms in the coating. At a pressure $P_N = 2 \cdot 10^{-3}$ Torr, the content of nitrogen atoms is 22.82 at.%, and at $P_N = 1.7 \cdot 10^{-3}$ Torr, the relative content of nitrogen atoms decreases to 19.87 at.%.

To study the phase composition and the structural state of the coatings, the X-ray diffraction analysis method was used. Fig. 3 shows the areas of the diffraction spectra of the coatings obtained at the highest pressure $P_N = 5 \cdot 10^{-3}$ Torr and $U_b = -200$ V (Fig. 3, spectrum 1 $U_b = -110$ V (Fig. 3, spectrum 2) and at $P_N = 1.7 \cdot 10^{-3}$ Torr and $U_b = -110$ V (Fig. 3, spectrum 3).



a



b

Fig. 2 – Morphology of fracture of coatings of nitrides of AlCrTiZrNbV high-entropy alloy, obtained at a pressure of $5 \cdot 10^{-3}$ Torr and the bias potential U_b , V: a – -110, b – -200

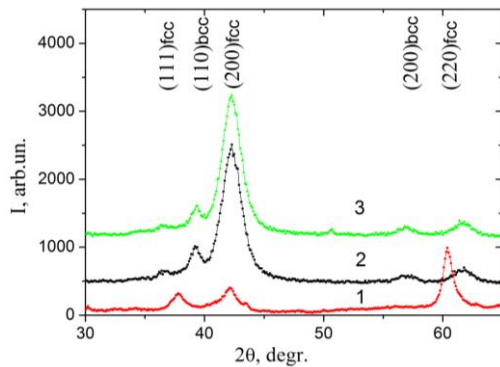


Fig. 3 – XRD patterns of different series of coatings (indicated in Table 1): 1 – $P_N = 5 \cdot 10^{-3}$ Torr, $U_b = -200$ V (series 1), 2 – $P_N = 5 \cdot 10^{-3}$ Torr, $P_N = 5 \cdot 10^{-3}$ Torr, $U_b = -110$ V (series 2), 3 – $P_N = 1.7 \cdot 10^{-3}$ Torr, $U_b = -110$ V (series 3)

The analysis of the obtained diffraction spectra showed that for all deposition regimes, characteristic the formation of two-phase coatings consisting of phases with bcc and fcc crystal lattices. A feature of coatings obtained with a smaller $U_b = -110$ V is the crystallite texture of the fcc phase with the [100] axis

perpendicular to the growth plane (Fig. 3, spectra 2 and 3). For coatings obtained at large $U_b = -200$ V, observed formation of a texture with the [110] axis perpendicular to the surface (Fig. 3, spectrum 1). The crystallite size for all types of coatings was nanometer (7-15 nm). It should be noted that in the magnetron sputtering of targets of similar composition for large U_b , besides texture [110] texture is observed [111] [25].

For crystallites of the bcc phase, as a result of their small volume content in the coating (up to 8%), only the most intense peaks from the (110) and (200) planes appear on all the diffraction spectra.

An important parameter of the crystallites is the lattice period. Table 2 shows the values of the lattice parameters for different series of coatings.

Table 2 – Periods of crystallite lattices for different series of coatings

No series	fcc lattice	bcc lattice
1	0.42638 nm	0.32418 nm
2	0.42578 nm	0.32417 nm
3	0.42597 nm	0.32417 nm
4	0.42740 nm	0.32419 nm

Table 2 shows that the largest lattice period is inherent in coatings with a [110] texture of the fcc phase obtained at the largest $U_b = -200$ V. The same trend is observed for the bcc component. The relative decrease in the lattice period at $U_b = -110$ V may indicate a stronger bond in it between the atoms [7].

Analysis of the obtained results of the structural state is expedient to be carried out in comparison with the elemental composition and mechanical characteristics. Fig. 4 shows the hardness versus the supplied constant bias potential U_b at different P_N pressures.

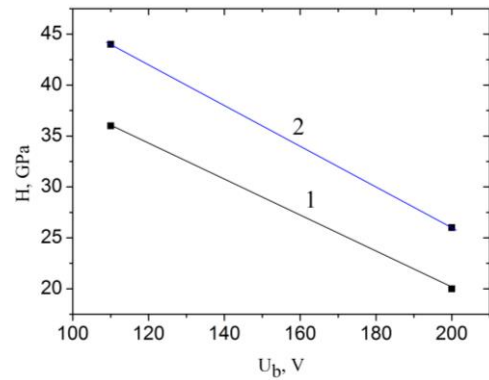


Fig. 4 – Dependence of hardness on U_b at different P_N , Torr: 1 – $1.7 \cdot 10^{-3}$, 2 – $5 \cdot 10^{-3}$

It can be seen that the hardness of coatings obtained with $P_N = 1.7 \cdot 10^{-3}$ Torr is less than at $P_N = 5 \cdot 10^{-3}$ Torr. When analyzing the influences P_N on hardness necessary to carry out a comparison with the data of the elemental composition of [17, 18]. Such an analysis shows that in coatings with the lowest hardness obtained with $P_N = 1.7 \cdot 10^{-3}$ Torr a nitrogen content of about 20 at.%, while at $P_N = 5 \cdot 10^{-3}$ Torr, the content of nitrogen atoms exceeds 36%. Thus, a significant decrease in the relative content of nitrogen atoms in the coating can explain the observed decrease in

hardness for different series obtained with the same U_b .

At the same time, the change in U_b leads to a change in the axis of the preferential orientation of crystallite growth from [100] at $U_b = -110$ V to [110] at $U_b = -200$ V. The plane (110) has a less dense packing of atoms in comparison with (100), and therefore this should lead to a decrease in the binding strength between atoms and a drop in hardness, which is observed experimentally.

The dense state of the coatings obtained at $U_b = -200$ V is also indicated by the relatively small value of the H/E parameter. For coatings obtained at $U_b = -200$ V, the value of this parameter is in the range 0.77-0.87, and for coatings deposited at $U_b = -110$ V, the parameter H/E is 0.11-0.12 (Table 1).

4. CONCLUSION

1. The elemental composition, structure and mechanical properties of nitride vacuum-arc coatings

based on the TiZrAlVNbCr highly entropy alloy can be substantially modified by supplied U_b and changing the pressure of the nitrogen atmosphere during deposition.

2. An increase in P_N in the interval $(1.7-5) \cdot 10^{-3}$ Torr leads to an increase in the nitrogen content in the coating with an almost unchanged structural state and a slight increase in hardness, as well as a decrease in the H/E parameter.

3. The change in U_b from -110 V to -200 V in the determining measure affects the structural state, accompanied by a change in the texture axis from [100] to [110]. Such structural changes are accompanied by a decrease in hardness and a decrease in the parameter H/E .

4. The highest hardness of 44 GPa of vacuum-arc nitride coatings based on the AlCrTiZrNbV high-entropy alloy is achieved by supplied a relatively low $U_b = -110$ V during the condensation process at the highest pressure $P_N = 5 \cdot 10^{-3}$ Torr.

Вплив величини потенціалу зміщення і тиску азотної атмосфери на структуру і властивості вакуумно-дугових покриттів на основі AlCrTiZrNbV високоентропійного сплаву

О.В. Соболю¹, А.О. Андреев², В.Ф. Горбань³, Г.О. Постельник¹, В.О. Столбовий², О.В. Звягольський¹

¹ Національний технічний університет «Харківський політехнічний інститут», вул. Кирпичова 2, 61002 Харків, Україна

² Національний науковий центр Харківський фізико-технічний інститут, вул. Академічна, 1, 61108 Харків, Україна

³ Інститут проблем матеріалознавства ім. Францевича, вул. Кржижановського, 3, 03142 Київ-142, Україна

Досліджено вплив постійного потенціалу зміщення (U_b) якій подається на підкладку при конденсації і тиску азотної атмосфери (P_N) на елементний склад, морфологію росту, текстуру і фізико-механічні характеристики вакуумно-дугових (AlCrTiVZrNb) N_x покриттів. Встановлено, що зі збільшенням U_b від -110 В до -200 В відбувається зміна осі переважного зростання кристалітів ГЦК фази від [100] до [110]. Така зміна супроводжується зменшенням твердості (H) і відношення H/E (де E – модуль пружності). Обговорено умови формування переважної орієнтації кристалітів (аксильної текстури) вакуумно-дугових (AlCrTiVZrNb) N_x покриттів і вплив текстури на механічні властивості. Встановлено, що зміна P_N в діапазоні $(1.7-5) \cdot 10^{-3}$ Торр в основному дозволяє варіювати ступінь наповнення покриття атомами азоту. На основі виявлених закономірностей обґрунтовані умови досягнення високої твердості в вакуумно-дугових покриттів нітриду високоентропійного сплаву AlCrTiVZrNb. Через наявність в сплаві елементів з відносно низькою теплою утворення нітриду для досягнення високої твердості необхідно використовувати умови осадження при відносно невисокій енергії бомбардуючих атомів. Використання в роботі невисокого $U_b = -110$ В при найбільшому тиску $P_N = 5 \cdot 10^{-3}$ Торр дозволяє досягти надтвердого стану з твердістю 44 ГПа

Ключові слова: Вакуумна дуга, AlCrTiZrNbV, Потенціал зміщення, Тиск, Структурна інженерія, Фазовий склад, Текстура, Твердість.

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