

Regularity of Formation of Vacuum-arc Nitride Coating Based on Multi-component Alloys

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The physical factors, which influence on structural state and phase composition of nitride coatings based on multicomponent alloys obtained by means of vacuum-arc deposition method have been determined. It was shown that the increase in partial pressure of nitrogen ensures the formation of a single phase solid solution with fcc crystal lattice. Under the pressure of nitrogen atmosphere below 10^{-3} Pa, a single phase solid solution with a bclattice is formed; and within the pressure of nitrogen $P_N = 10^{-3} - 8 \times 10^{-22}$ Pa, a two-phase system of solid solutions with bcc and fcc lattices is observed. With an offset potential of -70 V, a texture [100] is observed; and within the alteration of bias potential of $(-70 \text{ V} - -90 \text{ V})$ texture [100] + [111] appears. In the range of U_b from -120 V to -150 V, a texture [111] is observed, and, with an increase of bias potential, a texture [111] + [110] is observed.

Keywords: Nitride coatings, Multi-component alloys, Pressure, Nitrogen content, Structure, Hardness.

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INTRODUCTION

Recently, considerable attention has been paid to the study of protective nitride coatings based on multi-component alloys, which are characterized by high mechanical properties (increased hardness and thermal stability) ([see, for example, 1-3]). Most of the scientific works are dedicated to the study of nitride coatings based on multi-component alloys, which are obtained by means of ion-plasma methods, such as magnetron sputtering and vacuum-arc deposition [4, 5].

The properties of nitride coatings based on high entropy alloys can be controlled by changing the conditions for obtaining them (e.g. by altering bias potential applied to the substrate, the temperature of the substrate or the concentration of nitrogen in the mixture of the operating gases).

Physical factors that influence the formation of structure of the nitride protective coatings obtained by means of vacuum-arc deposition of material based on multicomponent alloys have been analyzed and defined in this study.

1. MULTICOMPONENT (HIGH ENTROPY) ALLOYS

The results of the analysis of the literary data indicate that nitride coatings based on high entropy alloys can be obtained in a single phase substitutional solid solution, which, by its nature, is both highly firm and thermodynamically stable in comparison with multi-phase solid solution. The positive result is achieved by selecting such a number of components and the ratio of their concentrations in the alloy, at which an elevated values of mixing entropy are formed in design compositions, along with this, such a value of entropy is present not only in melted state, but also after solidification. Reduced free energy of the alloy determines stability of solid solutions during the subsequent heat treatment. High mechanical performance

at high temperatures is ensured owing to severe distortion of the crystal lattice (bcc, as a rule). At the same time, the higher entropy of mixing is, the more these characteristics of the alloy are manifested.

To predict the collective behavior of elements in a multi-component alloy, works [6-8] suggest using such physical parameters as difference in atomic radii, enthalpy of mixing (H^{mix}) and entropy of mixing (S^{mix}), the difference in electronegativity, concentration of valence electrons VEC.

When selecting alloying elements to produce multi-component coatings based on nitrides, the features of nitride formation need to be taken into account, as well as properties of components forming the alloy. The most stable nitride phases form metals groups IV-V (Table 1).

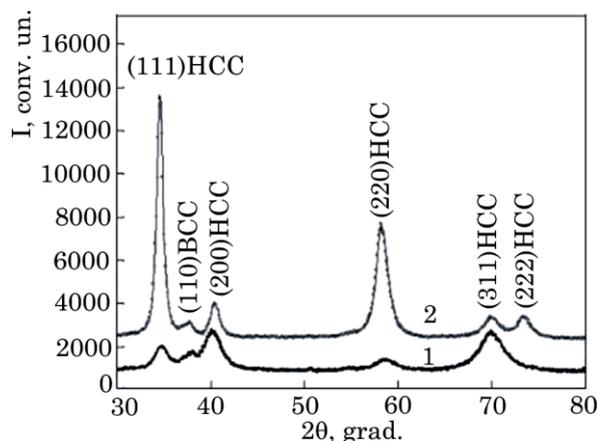
2. NITRIDE COATINGS BASED ON MULTI-COMPONENT ALLOYS

Nitride coatings based on high entropy alloys show high hardness, strength, and thermal stability [1, 2]. The main physical parameters that influence on formation of coatings by means of vacuum-arc deposition method, are partial pressure of the operational gas and bias potential, applied to the substrate, which allows to regulate energy of the deposited ions in a wide range [4].

Analysis of the diffraction spectra of nitride coatings formed based on high entropy alloys TiZrHfVNBa by means of vacuum-arc deposition method (Fig. 1) has shown that formation of monophasic state based on fcc metal lattice of NaCl type occurs in this structure, obtained both at a low pressure of 0.09 Pa and at a relatively high pressure of nitrogen atmosphere ($P_N = 0.4$ Pa). But the spectrum also contains low intensity bcc peaks (up to 7% of volume). This can be explained by the presence of a droplet phase in the coating.

Table 1 – Enthalpy of formation (ΔH) of Metals Nitrides [9]

Compound	TiN	ZrN	NbN	CrN	HfN	VN	AlN	TaN
(ΔH), kJ/mol	– 336.6	– 365.5	– 237.8	– 118.0	– 373.6	– 299.3	– 320.3	– 252.0

**Fig. 1** – Areas of the X-ray diffraction spectra of the coated samples $(\text{TiZrHfVNbTa})\text{N}$ obtained at $P_N = 0.4$ Pa (2) and $P_N = 0.09$ Pa (1) [10]

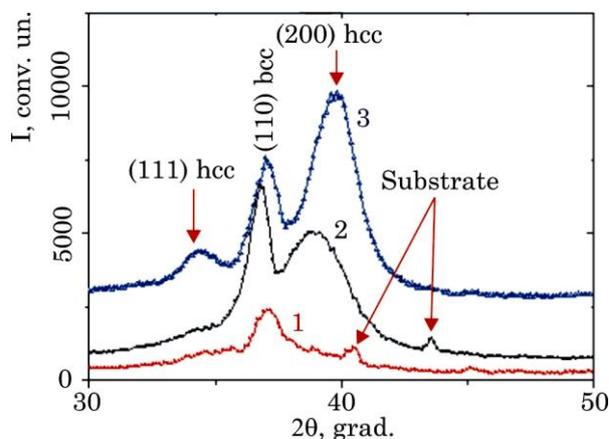
When studying the structural state of nitride coatings based in (TiAlZrNbY) system, obtained at the lowest pressure of (0.05 Pa), the phase with bcc lattice is also detected. This is inherent for the structure of high entropy alloy with no formation of own nitride lattice [111]. The size of the crystallites of the bcc phase is small enough and is 7,7 nm.

In the coatings obtained under the high pressure of the operating atmosphere of 0.3 Pa (curve 2 in Fig. 2), except for the constituent part with bcc crystal lattice, the nitride phase, corresponding to fcc lattice, is formed.

The size of the crystallites of bcc phase was about 11.5 nm, and of the nitride fcc phase it was about 5 nm. Lattice period, determined by the position of maximum of diffraction peak was 0.462 nm. The ratio of bcc and fcc phases is close to 1/2. The obtained results indicate the presence of bcc phase in the coating, which is mostly determined by the droplet phase, which has a crystal structure at all pressures of nitrogen used in the deposition process. A comparative analysis of the distribution of the elemental composition by cross section of droplets with an average composition of multi-component coating $(\text{TiZrNbAlYCr})\text{N}$ obtained by the vacuum-arc deposition method has shown that the droplet phase was mass of molten material of the cathode TiZrNbAlYCr with a slightly modified element composition to the side of heavy elements.

The closer to stoichiometric by nitrogen the composition of the nitride coatings is, the more often fcc phases are observed in the coatings. It should be noted that the formation of fcc lattice in multielement systems is confirmed by multiple literature sources [11, 12]. Along with this, such materials are more likely to form monophase solid solutions of the nitride phase rather than individual nitrides coexisting with each other.

The preferred texture of crystal growth of the coatings is the direction along the axis [111]. The presence of texture [111] in the coating indicates the preferred orientation of grains parallel to the surface of the sample with the

**Fig. 2** – Areas of diffraction spectra of the coatings of the system $(\text{TiZrNbAlY})\text{N}$, deposited at different pressures of nitrogen: curve 1 – $P_N = 0.05$ Pa; curve 2 – $P_N = 0.3$ Pa; curve 3 – $P_N = 0.5$ Pa

planes with a minimal surface energy. A comparison of the diffraction spectra of alloys indicates the strong influence of the bias potential of the substrate on the orientation of grain structure.

The study of the impact of the bias potential on the formation of nitride coatings based on high entropy alloy (TiZrHfVNb) [13] has shown that with the change of U_b from -50 V to -100 V (see Figure 3), a texture with the axis [111] (Spectrum 3) is observed in the direction of growth of the crystals of the coating.

Formation of texture with a plane [111] in the NaCl type lattice (metallic fcc lattice and non-metallic atoms in octahedral interstitials) is defined by the fact that such planes are the most compacted (with the highest reticular density), and are monotype by the elemental composition, i.e. consist only of atoms of metal and/or nonmetal by means of alteration of them. At a sufficiently high mobility of atoms this is enough for stratification and the formation of compacted planes [111] parallel to the growth surface during the condensation process. This process is enhanced with the increase of energy factor at the increase of bias potential and at a low pressure of the operating atmosphere, which helps to reduce the dissipation of energy in the inter-electrode gap due to collisions. By analyzing the data obtained during our research and the experimental data available in the literature, one can say that the preferential growth by the mechanism described above is inherent for implementation phases based on d -transition metals with NaCl type of lattice in the case of a strong covalent bond.

Thus, the analysis of the diffraction spectra of nitride coatings (Figure 1) obtained at a low pressure of $P_N = 0.09$ Pa and the bias potential of -150 V, is characterized by an almost untextured state (Spectrum 1 in Figure 1). Increasing the pressure of the nitrogen atmosphere during deposition to $P_N = 0.4$ Pa at the same bias potential leads to the appearance of bitextural state with the axes of axial texture [111] and [110]. The

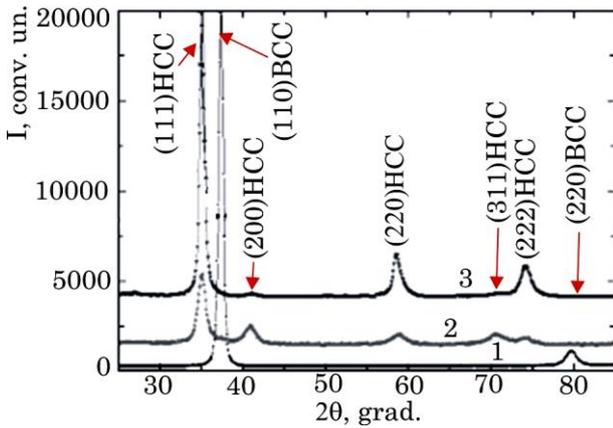


Fig. 3 – Areas of the X-ray diffraction spectra of the coated samples based on system (TiZrHfVNb)N: 1 – in vacuum with no Nitrogen; at $P_N = 0.3$ Pa; 2 – $U_b = -50$ V; 3 – $U_b = -100$ V

analysis of substructural characteristics, which was carried out by means of the approximation method, indicates that the increase of pressure of nitrogen atmosphere leads to an increase of the average size of the crystals in the coating from 11.9 nm to 41.6 nm, with the decrease of the value of microdeformation ε from 1.11 % to 0.86 %. This is particularly the case for deposition conditions with a negative bias potential of 70-200 V.

The analysis of the substructural characteristics of the nitride coatings showed the dependence of the sizes of crystallites on the bias potential. Table 2 shows the results of the investigation of (ZrTiCrNb)N coatings obtained by means of vacuum-arc deposition method.

Data shown in Table 2 indicate that the size of grain greatly depends on the bias potential applied to the substrate. Due to it, the energy of falling particles decreases, resulting in a higher radiation component of the plasma stream.

Table 2 – Alteration of the lattice period and RCS of nitride coatings

Parameters	$P = 0.3$ Pa		$P = 0.7$ Pa		$P = 0.7$ Pa Ion stimulation
	$U_b = -100$ V	$U_b = -200$ V	$U_b = -100$ V	$U_b = 200$ V	
RCS (L), nm	4.5	5.1	5.2	6.9	7.3
a , nm	0.4359	0.4365	0.441	0.4381	0.4371

The increase in strength is the result of the increase in strong Me-N bonds in the coatings. Along with this, high entropy state leads to higher values of hardness compared to simple TiN coatings ($H_{TiN} = 22-25$ GPa).

Figure 4 shows the graphs of the alteration of hardness and elastic modulus of the nitride multicomponent coatings (TiVCrZrHf)N depending on the applied bias potential [14]. There is an increase in hardness and elasticity modulus, with an increase of modulus of the negative bias potential up to -100 V. The values of hardness and elasticity modulus are $H = (32-33)$ GPa and $E = (268-276)$ GPa respectively.

This tendency can be explained, firstly, by the size of grains, which decreases by 30 % with the increase of the value of bias potential applied to the substrate. In

the polycrystalline material grain boundaries preventing the movement of dislocations. As a result of sliding, a gap in the plane of sliding from one grain to the other occurs in connection with different grain orientations. The smaller the grain, the higher the density of grain boundaries, the greater the hardness. Secondly, with the increase of bias potential, the consolidation of the coating occurs due to filling of intergrained emptiness, which also promotes the increase of hardness.

The factors promoting the increase of physical and mechanical properties of the coatings based on high entropy alloys were identified from the analysis of investigation results (see Figure 5).

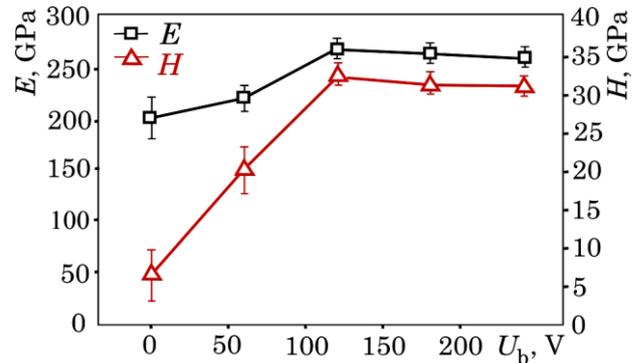


Fig. 4 – The change of the hardness H and elasticity modulus E of the coatings of system (TiVCrZrHf)N, deposited at different values of bias potential, applied to the substrate [14]

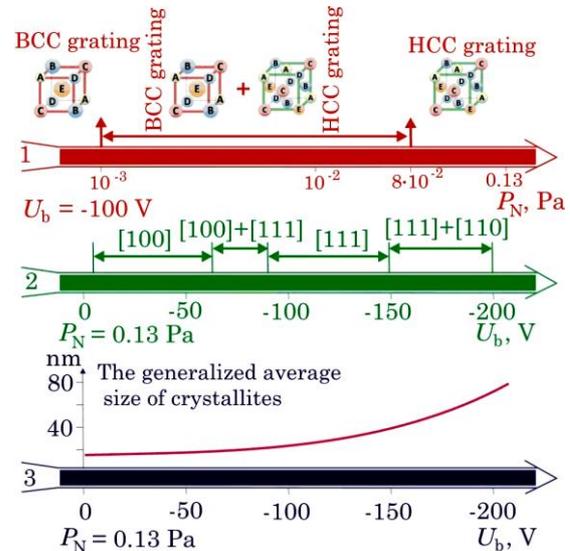


Fig. 5 – Laws of the influence of physical factors during the deposition on phase and structural state of vacuum-arc nitride coatings based on multi-component alloys

For example, if to carry out comparison of phase composition of nitride multicomponent coatings, one can make a conclusion that with the increase of pressure, saturation of the coating with nitrogen occurs, and the content of fcc phase increases.

At the pressure of nitrogen atmosphere P_N below 10^{-3} Pa, a monophasic solid solution with bcc lattice is formed. Within the limits of nitrogen pressure of $P_N = 10^{-3}-8 \times 10^{-2}$ Pa the two-phase system of a solid solution with bcc and fcc lattice is observed.

The texture of coatings changes depending on the bias potential. With the bias potential is of -70 V, a texture [100] is observed; and within the alteration of bias potential of $(-70$ V - -90 V), texture [100] + [111] appears. Further, in the range of alteration of bias potential from -120 V to -150 V, a texture [111] is observed, and, with an increase of bias potential, a texture [111] + [110] is observed.

CONCLUSION

The results of the studies, which were carried out, have shown that nitride multicomponent coatings have

fcc crystal lattice and are monophasic, which indicates of the effect of high entropy in the coatings.

With the increase in the negative bias potential on the substrate and during the deposition of nitride coatings based on multi-component systems, the texture [100] changes from -70 V to [111] at -120 V to -150 V. In this way, by alteration the deposition parameters at formation of nitride coatings based on multicomponent systems, one can set the structure and influence physical and mechanical properties of the studied coatings.

Закономерности формирования нитридных покрытий на основе многокомпонентных сплавов

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Определены физические факторы, влияющие на структурное состояние и фазовый состав нитридных покрытий на основе многокомпонентных сплавов, полученных методом вакуумно-дугового осаждения. Показано, что повышение парциального давления азота обеспечивает формирование однофазного твердого раствора с ГЦК кристаллической решеткой. При давлении азотной среды ниже 10^{-3} Па формируется однофазный твердый раствор с ОЦК решеткой, а в пределах давления азота $P_N = 10^{-3} - 8 \times 10^{-2}$ Па наблюдается двухфазная система твердых растворов с ОЦК и ГЦК решеткой. При потенциале смещения -70 В наблюдается текстура [100]; в пределах изменения потенциала смещения $(-70$ В - -90 В), появляется текстура [100]+[111]. В диапазоне U_b от -120 В до -150 В – наблюдается текстура [111] и, с повышением потенциала смещения, наблюдается текстура [111] + [110].

Ключевые слова: Нитридные покрытия, Многокомпонентные сплавы, Давление, Содержание азота, Структура, Твердость.

Закономірності формування нітридних покриттів на основі багатокомпонентних сплавів

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Визначено фізичні фактори, що впливають на структурний стан і фазовий склад нітридних покриттів на основі багатокомпонентних сплавів, отриманих методом вакуумно-дугового осадження. Показано, що підвищення парциального тиску азоту забезпечує формування однофазного твердого розчину з ГЦК кристалічною ґраткою. За умов тиску азотного середовища нижче 10^{-3} Па формується однофазний твердий розчин з ОЦК ґраткою, а в межах тиску азоту $P_N = 10^{-3} - 8 \times 10^{-2}$ Па спостерігається двофазна система твердих розчинів з ОЦК і ГЦК ґратами. При потенціалі зміщення -70 В спостерігається текстура [100]; в межах змінювання потенціалу зміщення $(-70$ В - -90 В), з'являється текстура [100] + [111]. В діапазоні U_b від -120 В до -150 В – спостерігається текстура [111] і, з підвищенням потенціалу зміщення, спостерігається текстура [111] + [110].

Ключові слова: Нітридні покриття, Багатокомпонентні сплави, Тиск, Вміст азоту, Структура, Твердість.

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