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The Use of Negative Bias Potential for Structural Engineering of Vacuum-Arc Nitride Coatings Based on FeCoNiCuAlCrV High-Entropy Alloy

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The effect of negative bias potential ($U_b = -40$, -110, and -200 V) upon the deposition of multi-element coatings on their composition, structure, and mechanical properties was studied. It is shown that when using a high-entropy multi-element (of 7 elements) FeCoNiCuAlCrV alloy, it is possible to obtain a single-phase nitride (FeCoNiCuAlCrV)N. Nitride has an *fcc* crystal lattice (structural type NaCl). It has been established that with an increase in U_b in the structural state occurs transition from practically non-textured (polycrystalline) to the preferential orientation of the growth of crystallites with the [111] texture axis (at $U_b = -110$ V) and [110] (at $U_b = -200$ V). This is accompanied by a decrease in the lattice period, as well as a decrease in hardness and modulus of elasticity. For coatings (FeCoNiCuAlCrV) N, the highest hardness of 38 GPa is achieved by using the smallest (– 40 V) bias potential during the deposition process. It is shown that to achieve high hardness at high U_b it is necessary to increase the content in the high-entropy alloy of elements with high nitride-forming ability.

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

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1. INTRODUCTION

Structural engineering is the main method of creating new materials [1, 2]. Due to structural engineering, it is possible to achieve high functional properties of materials [3]. This is associated with a significant expansion of the possibilities of managing the structural state due to the use of non-equilibrium conditions in modern technologies. As a result, in recent years, several new classes of composite materials have been created. In most cases, such materials were created in order to achieve high mechanical properties [4]. These are systems "nanocrystallite - amorphous layer" [5], new structural forms of carbon (fullerene [6], nanotubes [7], graphene [8]), β stabilized states [9] or a combination of β and α states [10].

Especially high mechanical properties were obtained when creating multi-element high-entropy alloys [11]. High-entropy alloys have a simple crystal lattice [12]. However, in most cases, high-entropic alloys are in a two-phase state [13]. This complicates the determination of the contribution of these phases to the functional characteristics. In addition, in materials based on a cubic fcc lattice, an increase in the number of elements may not lead to an increase in the stability of the solid solution and an increase in functional properties. So the triple CrCoNi alloy has a higher yield strength and hardness compared to the CrMnFeCoNi alloy (consisting of five elements) [14]. However, as was shown in [15], an alloy based on CoNi has high properties with a different combination of elements. So the addition of Cu to the alloy allows (while maintaining the single-phase state) to significantly increase the ductility of the alloy by tensile strength (about 18 %) [16, 17]. As follows from [18, 19], the addition of Al should lead to a significant increase in the thermal stability of the alloy. In addition, the addition of Cr and V contributes to the formation of stable nitrides and leads to an increase in wear resistance. In such a combination of elements, one can expect a significant increase in mechanical properties during the formation of nitride coatings [20].

In this case, as was shown in [21], the use of ion-plasma methods for the production of materials contributes to the atoms ultrafast thermalization. This substantially limits the diffusion mobility of atoms and leads to the formation of a disordered solid solution [22]. Therefore, the use of ion-plasma methods allows to obtain materials in a wide range of structural states.

In this work, we studied the effect of the negative constant bias potential (supplied to the substrate during deposition) on the composition, structure, and mechanical properties of ion-plasma nitride coatings based on the FeCoNiCuAlCrV alloy.

2. SAMPLES AND METHODS OF EXPERIMENTS

Coatings were deposited by the vacuum-arc method on a modernized "Bulat-6" installation [21].

A cathode of the required composition was prefabricated 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.

After ten-time remelting, the high-entropy alloys crystallized at a rate of 20 K/s. It was melted composition used to produce cathode. In the initial state after remelting, the composition of the cathode was two-phase. It consisted of a bcc solid solution (content close to 85 vol. %) and a Laves phase (content close to 15 vol. %).

Samples of the size (15 × 15 × 2.5 mm) of 12X18H9T steel ($R_a = 0.09$ μm) were chosen as substrates for the deposition of coatings. The coating thickness was about 8.0 μm. The deposition was carried out at a pressure of nitrogen atmosphere $P_N = 5\ 10^{-3}$ Torr. In the deposition process, a constant negative bias potential $U_b = -40$, -110 and -200 V was applied to the substrate. The deposition parameters, as well as hardness (*H*) and elastic modulus (*E*) are presented in Table 1.

Table 1 – Parameters of deposition of high-entropy alloys (FeCoNiCuAlCrV) and the results of indentation

№ series	I_a, A	U_b, V	*P*, Torr	*H*, GPa	*E**, GPa
1	140	40	$5 \cdot 10^{-3}$	38	311
2	140	110	$5 \cdot 10^{-3}$	18	261
3	135	200	$5 \cdot 10^{-3}$	17	200

The phase-structural state was studied on a DRON-4 diffractometer in Cu-Kα radiation. For monochromatization of the detected radiation, a graphite monochromator was used, which was installed in the secondary beam (in front of the detector). The shooting was carried out in the angle range 2Theta from 20 to 80 degree. All diffraction peaks from the planes with the highest reticular density of atoms fall into this angular range. Scan step of 0.02 degree.

The study of the morphology of the coating cross-section was carried out on JEOL JSM840 scanning electron microscope. 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 [23] with a load up to $F = 0{,}5$ N. Berkovich diamond pyramid with an angle of 65 was used.

3. RESULTS AND DISCUSSIONS

Material studies are based on data on the elemental composition, structure and properties of materials. In multi-element materials, the elemental composition is the most important parameter [5]. This is due to the difference in the constituent elements of a complex of properties. The main ones (atomic radius, shear modulus, fillable sublevels, Pauling electronegativity, concentration of valence electrons) are listed in Table 2.

Table 2 – Parameters of the elements constituting of high-entropy alloys (FeCoNiCuAlCrV)

Element	Fe	Co	Ni	Cu	Al	Cr	V
Atomic radius, pm	126	125	124	128	143	128	134
Shear modulus, GPa	82	75	76	45	26	115	47
Filled sublevels	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3s^1$	$3d^4$	$3d^3$
Poling electro-negativity	1.83	1.88	1.91	1.90	1.61	1.66	1.63
Concentration of valence elec-trons, el/atom	8	9	10	11	3	6	5

As follows from various studies [24, 25], one of the most important parameters is the concentration of valence electrons (CVE). There are two main definitions of electron concentration: the average number of free electrons per 1 atom and the total number of electrons, including d-level electrons, located in the valence band, CVE. CVE for a multicomponent alloy can be defined as the weighted average CVE components:

$$CVE = \sum_{i=1}^{n} C_i (CVE)_i$$

This value is the basis for determining the possible type of alloy crystal lattice. It has been shown that, when CVE ≥ 8.0, a single-phase fcc structure is mainly formed; at 6.87 ≤ CVE < 8.0 – the bcc and fcc phases coexist, and at CVE < 6.87, the single-phase BCC structure is mainly formed.

The value of CVE also determines the properties of high-entropy alloys, for example, the modulus of elasticity (Fig. 1).

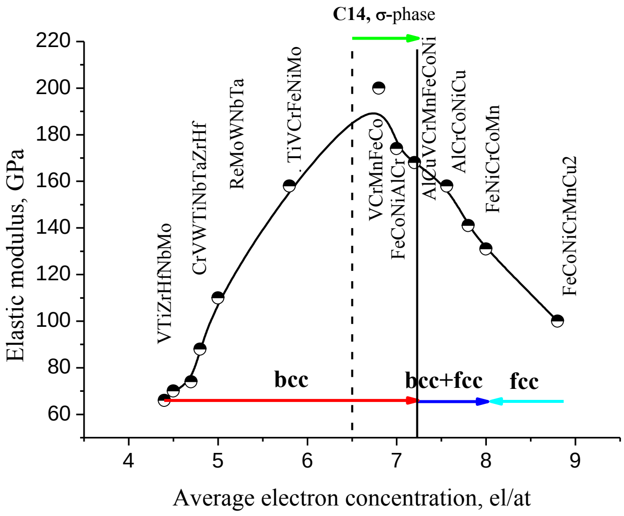


Fig. 1 – Dependence of the elastici modulus of high-entropy alloys on CVE

Analysis of the elemental composition was carried out according to energy dispersive spectroscopy. In the initial state, the cathode for evaporation had the elemental composition: Fe – 15 wt. %, Co – 15 wt. %, Ni – 13 wt. %, Cu – 22 wt. %, Al – 6 wt. %, Cr – 19 wt. %, V – 10 wt. %. The elemental composition of the deposited coatings are shown in Table 3 (only for the metal component) and Table 4 (including nitrogen).

Table 3 – The composition of metallic elements (wt. %) in coatings of 3 series, obtained at different potential bias

№ series	Fe	Co	Ni	Cu	Al	Cr	V
1	15.99	16.1	13.74	21.67	4.28	18.48	9.73
2	17.93	18.83	16.3	12.7	4.01	18.82	11.41
3	20.87	22.09	17.52	8.69	4.07	15.09	11.67

As can be seen from the obtained results, with increasing bias potential in the coating, the content of Fe, Co, Ni, V atoms increases and the content of Cu (to the greatest extent), Cr, and Al decreases. Thus, during

Table 4 – Elemental composition of coatings (wt.%) With regard to nitrogen content

№ series	Fe	Co	Ni	Cu	Al	Cr	V	N
1	14.35	14.47	12.33	19.44	3.71	16.67	8.76	10.27
2	16.21	17.04	14.73	11.47	3.51	17.11	10.36	9.58
3	19.49	20.65	16.35	8.1	3.72	14.14	10.92	6.62

the deposition of coatings in a nitrogen atmosphere, the relative content of nitride-forming elements increases. At the same time, the relative content of copper atoms (having a low binding energy with nitrogen) is greatly reduced. Thus, the most significant factor in the formation of the elemental composition is the bond strength between metal atoms and nitrogen atoms (in the formation of nitride). This fact indicates that elements with different masses, but high bonding energy with nitrogen is retained in the coating, and elements with a large mass but low binding energy are removed from the coating. This can be only during sputtering, when the bound metal-nitrogen complexes have a low sputtering coefficient [5, 20]. Such nitrogen-related complexes are mainly formed (by vacuum-arc evaporation) in the near-surface region upon deposition on a substrate. Therefore, the change in the elemental composition can be considered to be largely due to the sputtering of ions during the bombardment of the growing coating (secondary sputtering).

To study the phase composition and structural state of the coatings, an X-ray diffraction analysis method was used. Figure 2 shows parts of the diffraction spectra of coatings obtained at pressures of $P_N = 5 \times 10^{-3}$Torr and $U_b = -40$ V (Fig. 2, spectrum 1), $U_b = -110$ V (Fig. 2, spectrum 2) and $U_b = -200$ V (Fig. 2, spectrum 3).

An analysis of the diffraction spectra shows that with the smallest $U_b = -40$ V a polycrystalline structure is formed with a preferential orientation of a part of the crystallites with the [111] axis perpendicular to the growth surface (texture of the axial type with low perfection). An increase in U_b to – 110 V leads to an increase in the perfection of the texture with the [111] axis (manifested in an increase in the relative intensity of the {111} peaks). At the highest $U_b = -200$ V, a fundamental change in the type of texture is observed. In this case, the preferential crystallite growth axis is [110] (Fig. 2, spectrum 3).

It should be noted that in the coatings obtained at $U_b = -110$ V a peak was found from the bcc phase (less than 5 vol. %). This may be due to a decrease in the nitrogen content in the coating under the action of secondary spraying.

Important structural characteristics of the coatings are the lattice period and the average size of crystallites. Table 5 shows the corresponding data for 3 series of coatings.

It is seen that with increasing U_b (transition from 1 to 3 series) the lattice period decreases. The crystallite size does not change monotonically. However, a tendency to a decrease in crystallite size with increasing U_b is also visible.

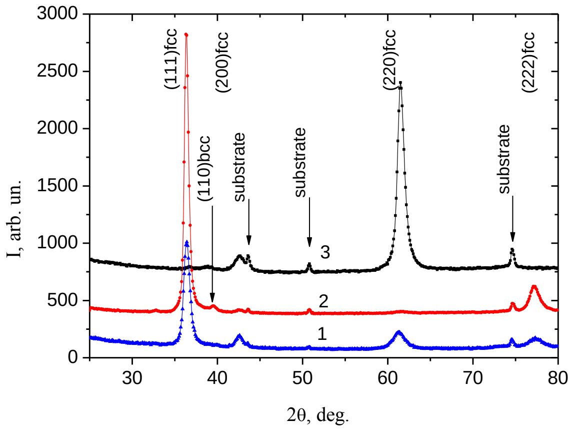


Fig. 2 – XRD-spectra of coatings (different series indicated in Table. 1): 1 – $P_N = 5 \times 10^{-3}$Torr, $U_b = -40$ V (series 1), 2 – $P_N = 5 \times 10^{-3}$Torr, $U_b = -110$ V (series 2), 3 – $P_N = 15 \times 10^{-3}$Torr, $U_b = -200$ V (series 3)

Table 5 – The period of the fcc lattice and size of crystallites

№ series	Lattice period, nm	The crystallite size, nm
1	0.42764	11.8
2	0.42745	13.7
3	0.42589	10.5

The final stage of structural engineering is the establishment of regularities of the influence of structural states on functional properties [9]. The most expressive and universal is the study of mechanical properties. This makes it possible qualitatively (and with the required data set - quantitatively) to determine the most important physical properties of materials (for example, the binding energy or the energy of plastic deformation).

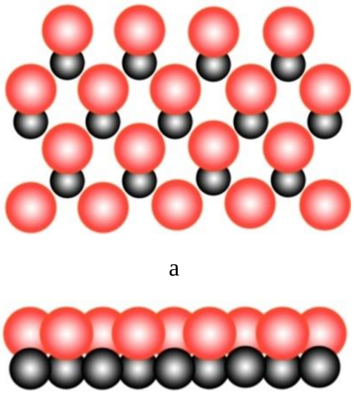
A universal method for determining the mechanical characteristics is the measurement of hardness. Table 1 shows the results of nanohardness termination by the method of [23]. It is seen that an increase in the bias potential leads not only to a decrease in hardness, but also to a decrease in the elastic modulus. The latter testifies to a significant weakening of the bond between atoms in the material.

Discussion of the results with the analysis of the possibility of structural engineering in multi-element alloys.

So despite the fact that the coatings were obtained on the basis of an alloy consisting of seven elements (FeCoNiCuAlCrV system), a single-phase state is formed in the coatings. At the same time, the hardness of such a coating does not exceed 38 GPa (table 1). Thus, the analysis of the mechanical properties of coatings from the multicomponent FeCoNiCuAlCrV alloy (in which the number of nitride-forming elements with a strong bond is less than elements with a weak bond) showed that such compositions can have high functional properties only with a low radiation-stimulated exposure (secondary sputtering) during deposition.

A feature of the structure of nitride coatings on the basis of this alloy is that, with an increase in U_b, the structural state changes from practically non-textural (polycrystalline) to the preferential orientation of crystallites with the [111] axis (at $U_b = -110$ V) and 110] (with $U_b = -200$ V).

The [111] texture appears due to the determining contribution to the free energy of the deformation factor ($E_s \sim E\varepsilon^2$) [10], and also due to the minimization of the kinetic factor due to the highest growth rate in the [111] direction (by alternating layers of metal atoms (Fe-Co-Ni-Cu-Al-Cr-V) and nitrogen (Fig. 3) with the formation of a multilayer system with an angstromic period in the direction of the [111] axis).


a

b

Fig. 3 – The circuit arrangement of metal atoms (Fe-Co-Ni-Cu-Al-Cr-V) (big light circles) and nitrogen (small dark ones) in the {111} plane in the fcc lattice (structural type NaCl): a – top view, b – side view

The appearance of the texture with the [110] axis is determined by minimizing the free energy during radiation-stimulated defect formation in the coating [20].

Analysis of the obtained results of the structural state in comparison with the elemental composition and mechanical characteristics shows that with increasing U_b, the nitrogen content in the coating decreases. This indicates that, due to the relatively weak bond of the majority of the alloy elements with nitrogen, when the energy of the bombarding particles increases, it is knocked out and intensively removed from the coating. This leads to a decrease in the lattice period from 0.42764 nm to 0.42589 nm (Table 5) and is accompanied by a decrease in hardness and modulus of elasticity (Table 1).

If a comparison is made with the hardness of other types of vacuum-arc coatings with a large number of strong nitride-forming elements, the tendency to change the hardness of the composition is revealed. Fig. 4 shows the comparative histograms of hardness for three types of high-entropy alloys: from elements having a relatively high nitride-forming ability (FeCoNiCuAlCrV), from elements with a higher nitride-forming ability (AlCrTiZrNbV) and from elements with a high nitri-forming ability (HfTaTiZrNbV).

From the comparative data in Figure 4 it can be seen that for coatings based on (FeCoNiCuAlCrV), the highest hardness was obtained at $U_b = -40$ V. In this case, a polycrystalline practically non-textured structure is formed, which is characterized by obstruction of sliding along the planes of the crystallites (in this case, the material properties become close to the elastic limit). In this case, the level of the maximum achievable hardness is approximately the same for all types of coatings.

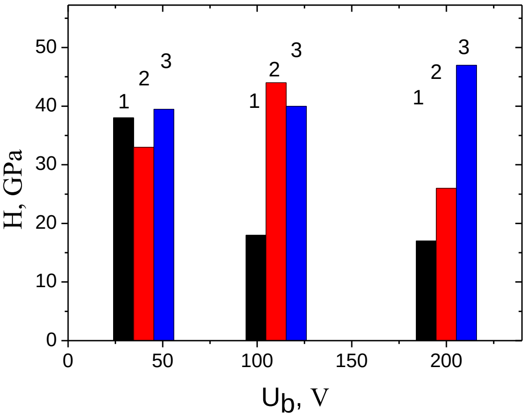


Fig. 4 – Dependence of hardness on U_b for vacuum-arc coatings based on nitrides of high-entropy alloys: 1 – (FeCoNiCuAlCrV) N, 2 – (AlCrTiZrNbV) N, 3 – (HfTaTiZrNbV) N

At a higher bias potential ($U_b = -110$ V), a relative increase in the hardness of coatings consisting of more powerful nitride-forming elements occurs. And with the largest $U_b = -200$ V, the highest hardness is achieved in (HfTaTiZrNbV)N coatings consisting of the strongest nitride-forming elements.

Thus, only in multi-element coatings consisting of elements with high nitride-forming ability (greater gain of free energy during the formation of nitride), an increase in the energy of the particles (due to an increase in U_b) can significantly increase the hardness.

4. CONCLUSION

1. When using a high-entropy alloy based on seven transition elements (FeCoNiCuAlCrV), it is possible to produce nitride in a single-phase (based on the fcc crystal lattice) state.
2. An increase in the negative bias potential during deposition leads to a depletion of Cu, as an element with the lowest bond energy with nitrogen.
3. With an increase in U_b in the structural state, occurs a transition from practically non-textured (polycrystalline) to the preferential orientation of crystallite growth with the [111] texture axis (at $U_b = -110$ V) and [110] (at $U_b = -200$ V).
4. For coatings (FeCoNiCuAlCrV) N, the highest hardness of 38 GPa is achieved by using the lowest (– 40 V) bias potential in the deposition process. This is due to the minimization of the effect of the radiation-stimulating factor (secondary sputtering) during the deposition of coatings.

Використання негативного потенціалу зміщення для структурної інженерії вакуумно-дугових нітридних покриттів на основі FeCoNiCuAlCrV високоентропійного сплаву

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Досліджено вплив негативного потенціалу зміщення (U_b = – 40, – 110 і – 200 В) при осадженні багатоелементних покриттів на їх склад, структуру і механічні властивості. Показано, що при використанні високоентропійного багатоелементного (з 7 елементів) FeCoNiCuAlCrV сплаву можна отримати однофазний нітрид (FeCoNiCuAlCrV)N. Нітрид має ГЦК кристалічну решітку (структурний тип NaCl). Встановлено, що при збільшенні U_b в структурному стані відбувається перехід від практично нетекстурованих (полікристалічне) до переважної орієнтації зростання кристалітів з віссю текстури [111] (при U_b = – 110 В) і [110] (при U_b = – 200 В). Це супроводжується зменшенням періоду решітки, а також зниженнем твердості і модуля пружності. Для покриттів (FeCoNiCuAlCrV)N найбільша твердість 38 ГПа досягається при використанні найменшого (– 40 В) потенціалу зміщення в процесі осадження. Показано, що для досягнення високої твердості при великих U_b необхідно збільшувати вміст в високоентропійном сплаві елементів з високою нітрідоутворюючою здатністю.

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

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