PHYSICS OF RADIOTECHNOLOGY AND ION-PLASMA TECHNOLOGIES

UDC 621.793:548.73

THE INFLUENCE OF NITROGEN PRESSURE ON THE STRUCTURE OF CONDENSATES, OBTAINED AT VACUUM-ARC DEPOSITION FROM HIGH ENTROPY ALLOY AlCrTiZrNbY

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The possibilities of structural engineering of vacuum-arc coatings based on the high entropy alloy AlCrTiZrNbY have been studied by means of electron microscopy with energy dispersion element analysis, X-ray diffractometry and microidentation methods. It was found, that the coatings formed by means of vacuum-arc method are two-phase objects. The change of nitrogen pressure from $2.0 \cdot 10^{-4}$ to $5.0 \cdot 10^{-4}$ Torr during the deposition increases the contents of its atoms in the condensate from 2.7 to 21.62 %, and this is accompanied by the transfer from nanocrystallic and claster to nanocrystallic two phase state (combination of bcc and fcc structures) and leads to hardness increase from 6.7 to 7.6 GPa. The observed structure changes are explained by the formation of defects of packaging in fcc crystal lattice at low nitrogen content.

INTRODUCTION

Operational opportunities of materials in many cases are determined by the functional properties of its operational surface [1−6]. Among the developed options of modifying the surface, the important place is after the vacuum-arc-coatings. The possibility of increasing the characteristics of such coatings by means of a using new materials − high entropy alloys (HEA) − during their deposition has been actively studied in the recent years. [7−9].

The main feature of HEAs is a large range of heterogeneous atoms (no less than 5 different elements) in the lattice of the solid solution. The atoms that make up the multi-element high entropy alloy are significantly different in electronic structure, sizes and thermodynamic properties. Disordered arrangement of atoms in the crystal lattice of solid solution leads to its significant distortion, which contributes in a significant solid-solution strengthening. [10] Reduced free energy of HEAs provides stability of a solid solution at its subsequent thermal treatment, which has been confirmed by the different authors [11−12].

Currently, among the nitride coatings, obtained on a basis of high entropy alloys, sufficiently high functional properties are by the coatings with the following composition: (AlCrTaTiZr)N [13]; (TiAlCrSiV)N [14]; (AlCrMoSiTi)N [15]; (AlMoNbSiTaTiVZr)N [16]; (AlCrNbSiTiV)N [17]; (TiVCrZrY)N [18]; (TiVCrZrHf)N [19]; (TiHfZrVNb)N [20]. It should be noted that the elements, which constitute such systems, are the elements with a significant difference in atomic radii.

The difficulty in different atoms configuration of HEA lattice is in most cases an unsolvable problem in the modeling the process of structure, however, extends the poss-formation, however, it widens the possibilities of experimental control of structure of such materials. The optimization of structural and phase state of HEA based materials can significantly improve their functional characteristics, and the important thing is finding the relation between the formed structures and the conditions of obtaining the materials (including the HEA based coatings) for directional control of the structural state (structural engineering).

As noted above, the alloys composed by the atoms with a large difference in the atomic radii are of great interest in this regard. It is in these structures the ordering processes progress in the most effective way [21].

The aim of this work was to establish a relationship between the deposition parameters (operating pressure of nitrogen in the chamber during the deposition and the bias potential), the structural state, and properties of vacuum-arc coatings based on HEA, which is required for structural engineering. The elements that constitute the alloy, selected for the study, are significantly (up to 45%) different in their atomic radii [22] (Table 1).

Table 1

The atomic radii R of the elements
of the alloy AlCrTiZrNbY

Element	Al	Cr	Ti	Zr	Nb	Y
R, nm	0.143	0.125	0.145	0.160	0.143	0.181

METHODS OF PREPARATION AND EXAMINATION OF THE SAMPLES

The coatings on the stainless steel 12X18H9T substrates were formed by means of vacuum-arc method on the "Bulat-6" installation [23]. The cathode of the composition Al+Cr+Ti+Zr+Nb+Y (Table 2) was previously manufactured by vacuum-arc remelting of a multi-component mixture of pure powders of these metals.

Table 2

The elemental composition of cathode made
of AlCrTiZrNbY alloy
(according to energy dispersive analysis)

Element	Al	Cr	Ti	Zr	Nb	Y
Wt. %	2.91	21.29	19.48	22.55	29.93	3.83
At. %	7.03	26.65	26.47	16.09	20.93	2.81

The reactive gas during the coatings deposition was nitrogen. To increase the adhesive bond and strengthening characteristics of the material of the coating, constant bias potential (U_b) of 200 V was applied to the substrate. Arc discharge current in the evaporator was 100...110 A. The pressure of nitrogen varied in the range of $5.0 \cdot 10^{-5}...5 \cdot 10^{-3} \cdot 10^{-5}$ Torr. The duration of deposition of 1 hour provided the thickness of the coatings of ~ 7 μm.

The surface morphology, fracture fractographs were investigated on a scanning electron microscope FEI Nova NanoSEM 450. The study of the element analysis of the coatings was conducted by analyzing the characteristic X-rays spectra generated by an electron beam in a scanning electron microscope. The spectra were obtained on the energy dispersion X-ray spectrometer of PEGASUS system by EDAX company, mounted in the microscope.

X-ray studies of phase and structural state were carried out on DRON-3M diffractometer in Cu-Kα radiation. To monochromize the registered radiation, the graphite monochromator, set behind the sample before the detector, was used. The study of phase composition, structure (texture, substructure) was carried out by means of traditional methods of X-ray diffraction by analyzing the position, profile shape and intensity of the diffraction reflections. The substructural characteristics were determined by the approximation [24]. The hardness of the coatings was measured on the hardness tester DM 8 by the method of micro-Vickers at a load on indenter of 0.2 N.

RESULTS AND DISCUSSION

The feature of evaporation the cathodes containing Al, is formation of a significant amount of droplet phase [25]. In the case of using the cathode made of multi-element HEA alloy, this leads to formation of two-phase coatings, formed by the droplet and multielement (high entropy) phases [26]. It was determined that the increase of nitrogen pressure during the deposition from $5.5 \cdot 10^{-4}$ up to $5.0 \cdot 10^{-4}$ Torr leads to reduction in the average size of the particles of the droplet phase on the surface from 2.4 to 0.8 μm (Fig. 1).

The elemental analysis of the coatings has shown that with the increase of operational pressure of nitrogen atmosphere, not only the saturation with nitrogen atoms takes place, but also the content of light Al atoms is increased in the coating (Fig. 2).
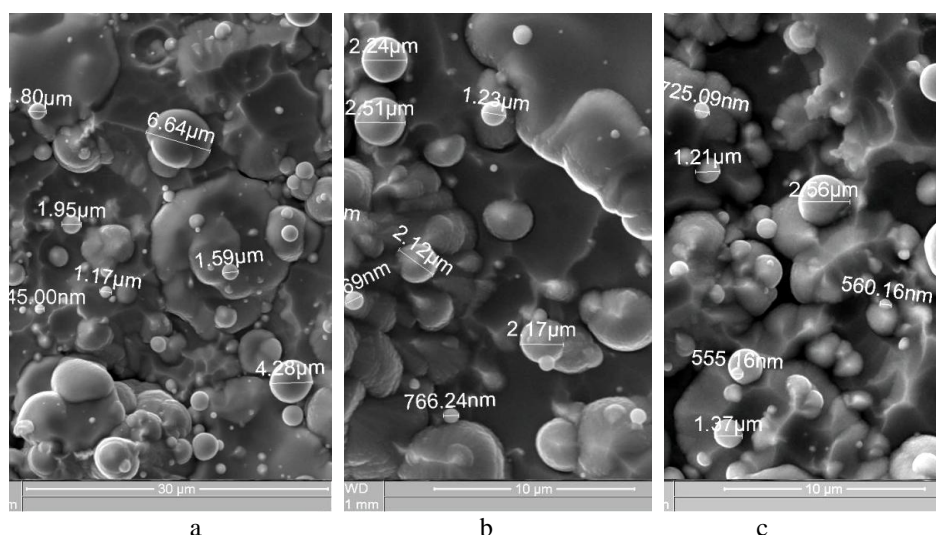
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Fig. 1. The surphace morphology of the coatings, deposited at different nitrogen pressure
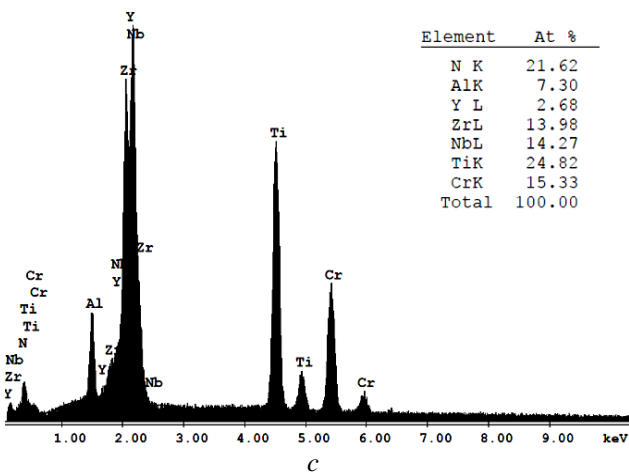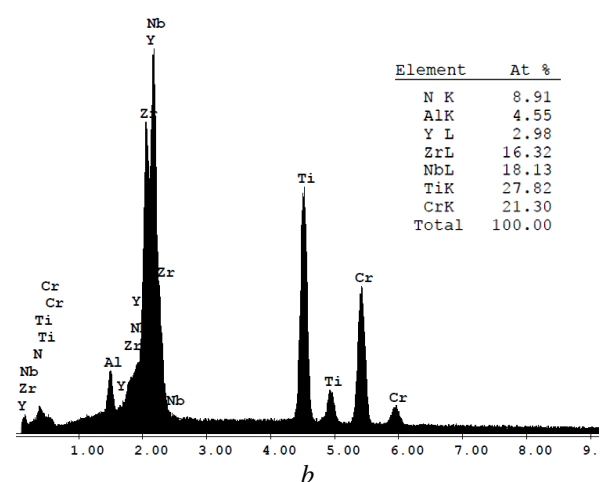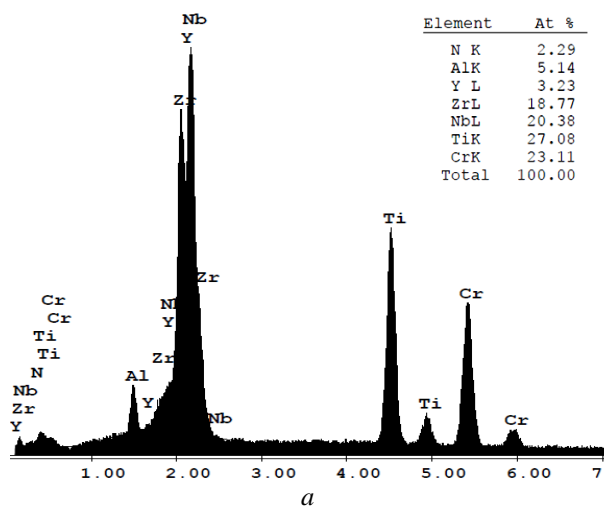(P_N, Torr) in the chamber: $a - 5.5 \cdot 10^{-4}$; $b - 1.2 \cdot 10^{-4}$; $c - 5.0 \cdot 10^{-4}$

Element	At %
N K	2.29
AlK	5.14
Y L	3.23
ZrL	18.77
NbL	20.38
TiK	27.08
CrK	23.11
Total	100.00

a

Element	At %
N K	8.91
AlK	4.55
Y L	2.98
ZrL	16.32
NbL	18.13
TiK	27.82
CrK	21.30
Total	100.00

b

Element	At %
N K	21.62
AlK	7.30
Y L	2.68
ZrL	13.98
NbL	14.27
TiK	24.82
CrK	15.33
Total	100.00

c

Fig. 2. Energy dispersion spectra and the composition of the coatings deposited at a nitrogen pressure P_N, Torr: $a - 5.5 \cdot 10^{-4}$; $b - 1.2 \cdot 10^{-4}$; $c - 5.0 \cdot 10^{-4}$

At high pressures (see Fig. 2,c), Al content in the coating approaches the value of its containing in the evaporating cathode. The content of nitrogen atoms in the coating increases non-monotonically with increasing pressure P_N (Fig. 3), the greatest increase is observed up to pressures $(1.2...3.0) \cdot 10^{-4}$ Torr.
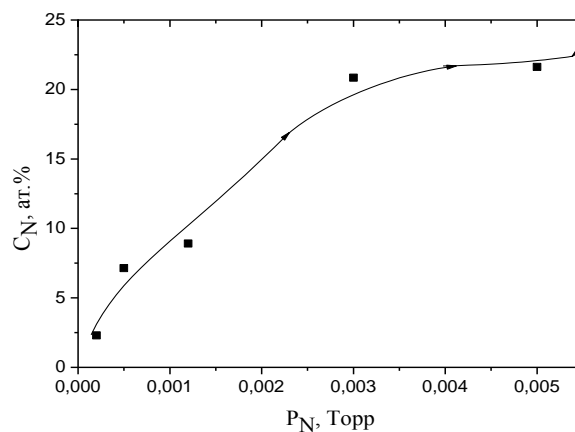

Fig. 3. The dependence of the nitrogen content in the coating C_N on pressure P_N of the operational atmosphere of nitrogen during the deposition

For the coatings obtained at the average pressure of nitrogen pressure $P_N = 1.2 \cdot 10^{-3}$ Torr, the elemental composition of droplets was determined (Figs. 4, 5), which was compared with the average composition of the coating. The obtained data show that the droplet phase is a clot of molten metal from the cathode material with somewhat increased content of heavy elements.
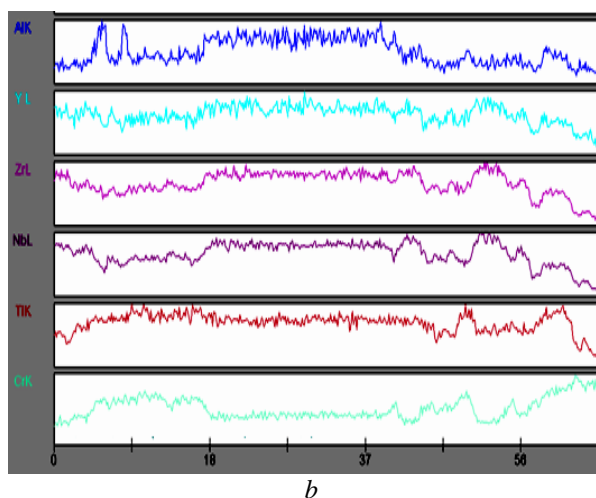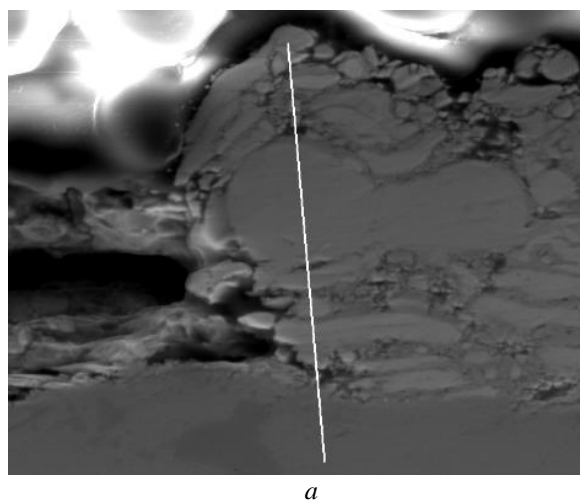

a

b

Fig. 4. The cross-section of a droplet (a) with a secant line, over which the concentration of the elements is defined (b)

For the coatings obtained on the basis of the studied multi-element system, the realization of various structural states is possible. During the deposition of condensate from the low-ionized flows, which are inherent to the magnetron method of obtaining the coatings, the amorphous-like structure is formed [27]. Using the vacuum-arc method with a high degree of
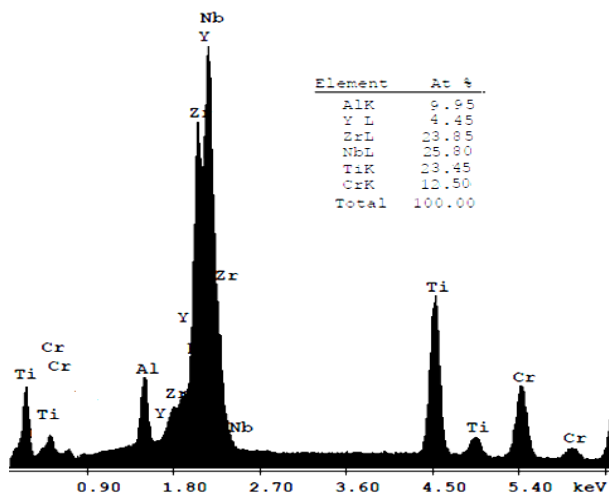
plasma ionization can largely increase the average energy of the deposited particles. It stimulates the processes of ordering in the coating, firstly, due to the increased mobility of the film-forming particles, and, secondly, due to the adjustment of structural states under the deforming influence of the accelerated particles, embedded on the nanometer depth.
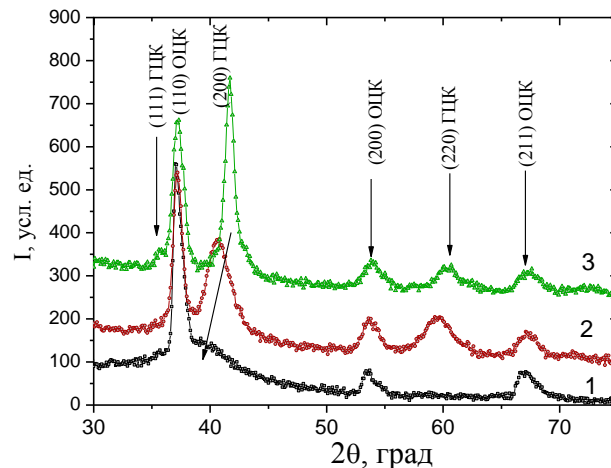
Fig. 5. Energy dispersion spectrum and elemental composition of a droplet (at.%), $P_N = 1.2 \cdot 10^{-4}$ Torr

Fig. 6. Areas of diffraction spectra f the coatings obtained at nitrogen pressures P_N, Torr:
1 − 5.0·10⁻⁵; 2 − 5.5·10⁻⁴; 3 − 5.0·10⁻³

The analysis of X-ray diffraction patterns (Fig. 6) shows that the pressure of nitrogen in the chamber $5.0 \cdot 10^{-5}$ Torr (the smallest of the used pressures), the deposited coating is a solid solution of metal atoms, characterized by bcc lattice with a medium size of crystallites of 15 nm (the lattice period of 0.342 nm).

The separation of the diffraction curve by the constituent profiles (Fig. 7,a) indicated on the formation of nanocrystalline structures with the size of ordering areas of about 2 nm (the cluster state [1]), which is manifested in the diffraction spectra in a form of a wide halo-like profile from the side of large angles.
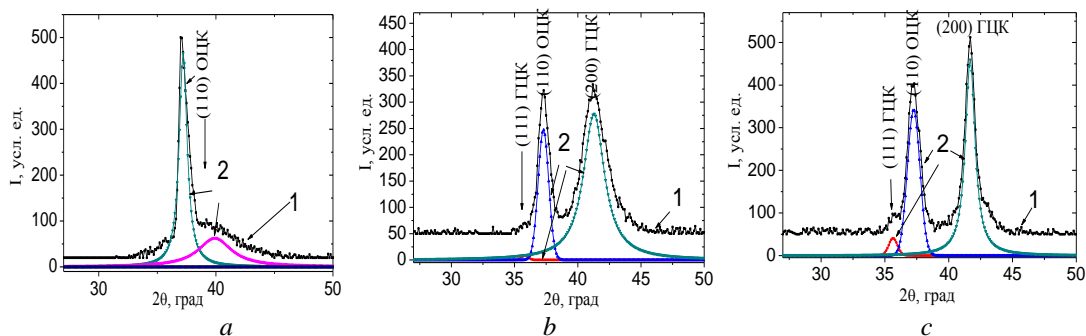
Fig. 7. The separation of diffraction spectra into the component profiles for the coatings obtained at P_N, Torr:
a − 5.0·10⁻⁵, b − 5.5·10⁻⁴, c − 5.0·10⁻³; 1 − the initial range, 2 − the selected profiles

On the diffraction spectrum from the coating obtained at a pressure of $5.0 \cdot 10^{-4}$ Torr (see Fig. 6, curve 2, and Fig. 7,b), the peak, corresponding to the bcc phase crystallites, both in the position and in the width is close to that considered earlier. There is a halo-like peak from the second component on this spectrum, which transforms in a more arranged (recalculation on reflex broadening gives a value of about 3.5 nm) and is shifed to the side of higher diffraction angles. The position of this peak, as well as the appearance of one more peak at around 60 degrees, confirm the formation of the nitride phase with NaCl-type lattice [28].

The diffraction spectrum of the coating containing more than 21 at.% nitrogen and obtained at a gas pressure of $5.0 \cdot 10^{-3}$ Torr in the chamber (see Fig. 3), two explicit diffraction peaks systems are observed: first one − from the bcc phase with the characteristic period of 0.342 nm, the second one − from the fcc phase (structural type NaCl) with a period of 0.437 nm (see Fig. 6, spectrum 3, Fig. 7,c) and the average size of crystallites of 7 nm.

Assuming that the second system of peaks in all three spectra belongs to the formed second fcc phase, the observed shift towards lower angles (indicated by

the arrow in Fig. 6) and blur of diffractional reflexes with the decrease of P_N can be associated with the formation of packaging defects at shifting of the lattice planes with unstabilized nitrogen saturation [29]. The reason for this is high energy of the metal particles, bombarding the coating at low pressure during applying negative bias potential U_b = -200 V A great difference in atomic sizes of HEA atoms (see Table 1) leads to deformation of the film both on the micro and macro levels, and stimulates the formation of packaging defects. At high pressures of the operational gas in the chamber, the decrease of the average energy of the deposited particles takes place (due to losses in collisions in the electrode gap), reducing the deformation of the coating, and the saturation of the coating with nitrogen atoms increases. The latter forms chemical bonds with the metal base and occupy the characteristic for the NaCl lattice type octahedral interstices, thereby preventing the shear movement of planes with the formation of packaging defects.

The listed structural changes lead to an increase in the hardness of the coating from 6.7 to 7.8 GPa (at a pressure of nitrogen of $5.0 \cdot 10^{-3}$ Torr – the highest of all, at which the coatings were deposited).

CONCLUSION

Two-phase structural state of bcc and fcc phases is formed in the coatings, obtained on the basis of AlCrTiZrNbY HEA by means of vacuum-arc deposition. Increasing the nitrogen pressure during the deposition of $2.0 \cdot 10^{-4}$ to $5.0 \cdot 10^{-3}$ Torr leads to an increase in the nitrogen content in the coating from 2.7 to 21.62%. The hardness of 7.8 GPa is reached at the highest nitrogen content. The structure of the coating is formed by two nanocrystalline phases with a bcc lattice (the average size of crystallits is ~ 15 nm, lattice period is 0.342 nm) and fcc lattice (average crystallite size is of 7 nm, the lattice period 0.437 nm).

REFERENCES

1. *Nanostructured coatings* / Edited by: Albano Cavaleiro, Jeff Th. M. de Hosson. Springer-Verlag, 2006, 648 p.

2. Ye.P. Zhilnikov, V.N. Samsonov. *Tribotechnology basics*. Samara: Publishing of the Samara state. erokosm. University, 2012, 136 p.

3. S.V. Lytovchenko, V.A. Chishkala, Ye.P. Nechiporenko, D.S. Matvienko, T.S. Maslova, V.I. Grytsenko. The use of eutectic compositions to create wear-resistant coatings // *Problems of Atomic Science and Technology. Ser. "Vacuum, pure materials, superconductors"*. 2002, N 1, p. 175-177.

4. S.V. Lytovchenko, V.M. Beresnev, V.A. Chy–shkala, A.Ye. Dmytrenko, U.S. Nyemchenko, V.V. Bu–rkovska. Silicide coatings structure optimization based on multiscale approach // *Physical Surface Engineering*. 2013, v. 11, N 3, p. 293-298.

5. O.V. Sobol, O.N. Grigorjev, Yu.A. Kunitsky, S.N. Dub, A.A. Podtelezhnikov, A.N. Stetsenko. Peculiarities of Structure State and Mechanical Characteristics in ion-Plasma Condensates of Quasibinary System Borides W_2B_5-TiB_2 // *Science of Sintering*. 2006, v. 38, p. 63-72.

6. Ping-Kang Huang, Jien-Wei Yeh. Effects of substrate bias on structure and mechanical properties of (AlCrNbSiTiV)N coatings // *J. Phys. D: Appl. Phys.* 2009, v. 41, p. 115401 (7 p.).

7. A.D. Pogrebnjak, A.A. Bagdasaryan, I.V. Yakushchenko, V.M. Beresnev. The structure and properties of high-entropy alloys and nitride coatings based on them // *Russ. Chem. Rev*. 2014, v. 83(11), p. 1027-1061.

8. U.S. Nyemchenko, V.M. Beresnev, O.V. Sobol, S.V. Lytovchenko, V.A. Stolbovoy, V.Ju. Novikov, A.A. Meylekhov, A.A. Postelnyk, M.G. Kovaleva. Structure and mechanical properties of nitride multi-layer systems on the basis of high entropy alloys and transition metals of group VI // *Problems of Atomic Science and Technology*. 2016, N 1(101), p. 112-120.

9. O.N. Senkov, J.M. Scott, S.V. Senkova, D.B. Miracle. Microstructure and room temperature properties of a high-entropy TaNbHfZrTi alloy // *Journal of Alloys and Compounds*. 2011, v. 509, N 20, p. 6043-6048.

10. S.A. Firstov, V.F. Gorban, N.A. Krapivka, E.P. Pechkovskiy New class of materials - High Entropy Alloys and coatings // *Bulletin of the University of Tambov . Series: Natural and Technical Sciences*. 2013, v. 18, N 4-2, p. 1938-1940.

11. N.A. Azarenkov, O.V. Sobol, V.M. Beresnev, A.D. Pogrebnyak, D.A. Kolesnikov, P.V. Turbin, I.N. Toryanik. Vacuum-plasma coatings based on the multielement nitrides // *Metallofizika i Noveishie Tekhnologii*. 2013, v. 35, issue 8, p. 1061-1084 (in Russian).

12. S.A. Firstov, V.F. Gorban, N.A. Krapivka, E.P. Pechkovskiy. The distribution of elements in multicomponent high entropy single-phase alloys with bcc lattice // *Composites and Nanomaterials*. 2012, N 3, p. 48-65.

13. C.H. Lai, S.J. Lin, J.W. Yeh, S.Y. Chang. Preparation and characterization of AlCrTaTiZr multi-element nitride coatings // *Surf. Coat. Technol*. 2006, v. 201, p. 3275-3280.

14. C.H. Lin, J.G. Duh, J.W. Yeh. Multi-component nitride coatings derived from Ti-Al-Cr-Si-V target in RF magnetron sputter // *J. Surf. Coat. Technol*. 2007, v. 201, p. 6304-6308.

15. H.W. Chang, P.K. Huang, A. Davison, J.W. Yeh, C.H. Tsau, C.C. Yang. Nitride films deposited from an equimolar Al-Cr-Mo-Si-Ti alloy target by reactive direct current magnetron sputtering // *Thin Solid Films*. 2008, v. 516, p. 6402-6408.

16. M.H. Tsai, C.H. Lai, J.W. Yeh, J.Y. Gan Effects of nitrogen flow ratio on the structure and properties of reactively sputtered (AlMoNbSiTaTiVZr)N_x coatings // *J. Phys. D*. 2008, v. 41, p. 235402-1.

17. P.K. Huang, J.W. Yeh. Effects of nitrogen content on structure and mechanical properties of multi-element (AlCrNbSiTiV)N coating // *J. Surf. Coat. Technol*. 2009, v. 203, p. 1891-1896.

18. D.C. Tsai, Y.L. Huang, S.R. Lin, S.C. Liang, F.S. Shieu. Effect of nitrogen flow ratios on the structure and mechanical properties of (TiVCrZrY)N

coatings prepared by reactive magnetron sputtering // *Appl.Surf. Sci.* 2010, v. 257, p. 1361-1367.

19. S.C. Liang, Z.C. Chang, D.C. Tsai, Y.C. Lin, H.S. Sung, M.J. Deng, F.S. Shieu. Effects of substrate temperature on the structure and mechanical properties of (TiVCrZrHf)N coatings // *Appl. Surf. Sci.* 2011, v. 257, p. 7709-7713.

20. A.D. Pogrebnjak, I.V. Yakushchenko, A.A. Bagdasaryan, et al. Microstructure, physical and chemical properties of nanostructured (Ti-Hf-Zr-V-Nb)N coatings under different deposition conditions // *Mat. Chem. Phys.* 2014, v. 147, p. 1079-1091.

21. O.V. Sobol'. Nanostructural ordering in W-Ti-B condensates // *Physics of the Solid State*. 2007, v. 49, p. 1161-1167.

22. *Physical encyclopedia: in 5 vol.* / Ch. Ed. A.M. Prokhorov: M.: "Soviet Encyclopedia–The Great Russian Encycl.", 1988-1998.

23. A.A. Andreev, L.P. Sablev, S.N. Grigoryev. *Vacuum arc coatings.* Kharkov: NSC KIPT, 2010, 318 p.

24. O.V. Sobol', A.A. Andreev, V.A. Stolbovoy, V.F. Gorban', N.V. Pinchuk, A.A. Meylekhov. The effects of nitrogen atmosphere pressure, constant and high-voltage pulse potentials of the substrate on the structure and properties of vacuum-arc ZrN coatings // *Problems of Atomic Science and Technology*. 2015, N 2(96), p. 105-110.

25. I.I. Aksenov, A.A. Andreev, V.A. Belous, V.Ye. Strel'nitskii, V.M. Khoroshikh. *Vacuum arc: plasma sources, coating deposition, surface modification.* Kiev: "Naukova Dumka", 2012, 727 p.

26. V.M. Beresnev, O.V. Sobol, I.N. Toryanik, A.A. Meylekhov, U.S. Nyemchenko, P.V. Turbin, I.V. Yakushchenko, M.O. Lisovenko. Formation of Biphasic State in Vacuum-Arc Coatings Obtained by Evaporation of Ti-Al-Zr-Nb-Y Alloy in the Atmosphere of Nitrogen // *Journal of nano- and electronic physics.* 2014, v. 6, N 1, p. 01030 (3 p).

27. M. Braic, V. Braic, M. Balaceanu, C.N. Zoita, A. Vladescu, E. Grigore. Characteristics of (TiAlCrNbY)C films deposited by reactive magnetron sputtering // *Surf. Coat. Technol.* 2010, v. 204, p. 2010-2014.

28. O.V. Sobol', A.A. Andreev, V.A. Stolbovoi, V.F. Fil'chikov. Structural-phase and stressed state of vacuum-arc-deposited nanostructural Mo-N coatings controlled by substrate bias during deposition // *Technical Physics Letters*. 2012, v. 38, issue 2, p. 168-171.

29. N.A. Azarenkov, O.V. Sobol', A.D. Pogrebnyak, V.M. Beresnev. Vacuum plasma coatings engineering. Kharkiv: Publishing of V.N. Karazin Kharkiv National University, 2011, 344 p.

ВЛИЯНИЕ ДАВЛЕНИЯ АЗОТА НА СТРУКТУРУ КОНДЕНСАТОВ, ПОЛУЧЕННЫХ ИЗ ВЫСОКОЭНТРОПИЙНОГО СПЛАВА AlCrTiZrNbY ПРИ ВАКУУМНО-ДУГОВОМ ОСАЖДЕНИИ

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Методами электронной микроскопии с энергодисперсионным элементным анализом, рентгеновской дифрактометрии и микроиндентирования изучены возможности структурной инженерии вакуумно-дуговых покрытий на основе высокоэнтропийного сплава AlCrTiZrNbY. Установлено, что сформированные вакуумно-дуговым осаждением покрытия являются двухфазными объектами. Изменение давления азота при осаждении покрытий от $2{,}0 \cdot 10^{-4}$ до $5{,}0 \cdot 10^{-4}$ Торр повышает содержание его атомов в конденсате с 2,7 до 21,62%, что сопровождается переходом от нанокристаллически кластерного к нанокристаллическому двухфазному состоянию (сочетание ОЦК- и ГЦК-структур) и повышением твердости от 6,7 до 7,6 ГПа. Наблюдаемые структурные изменения объяснены образованием дефектов упаковки в ГЦК-решетке при малом содержании азота.

ВПЛИВ ТИСКУ АЗОТУ НА СТРУКТУРУ КОНДЕНСАТІВ, ЩО ОТРИМАНІ З ВИСОКОЕНТРОПІЙНОГО СПЛАВУ AlCrTiZrNbY ПРИ ВАКУУМНО-ДУГОВОМУ ОСАДЖЕННІ

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Методами електронної мікроскопії з енергодисперсійним елементним аналізом, рентгенівської дифрактометрії та мікроіндентування вивчені можливості структурної інженерії вакуумно-дугових покриттів на основі високоентропійного сплаву AlCrTiZrNbY. Встановлено, що сформовані вакуумно-дуговим осадженням покриття є двофазними об'єктами. Зміна тиску азоту при осадженні покриттів від $2{,}0 \cdot 10^{-4}$ до $5{,}0 \cdot 10^{-4}$ Торр підвищує вміст його атомів у конденсаті з 2,7 до 21,62%, що супроводжується переходом від нанокристалічно кластерного до нанокристалічного двофазного стану (поєднання ОЦК- і ГЦК-структур) і підвищенням твердості від 6,7 до 7,6 ГПа. Зафіксовані структурні зміни пояснюються утворенням дефектів упаковки в ГЦК-гратці при малому вмісті азоту.