UDC 669.295.539.121

FRICTIONAL PROPERTIES OF MULTIELEMENT COATINGS (TiZrHfVNbTa)N

U.S. Nyemchenko[1], V.Ju. Novikov[2], V.A. Stolbovoy[3], V.M. Beresnev[1,4], O.V. Sobol'[5]
[1]V.N. Karazin Kharkiv National University, Kharkiv, Ukraine
E-mail: Ululkin@gmail.com;
[2]Belgorod National Research University, Belgorod, Russia;
[3]National Science Center "Kharkov Institute of Physics and Technology", Kharkov, Ukraine;
[4]Sumy State University, Sumy, Ukraine;
[5]National Technical University "Kharkiv Polytechnic Institute", Kharkiv, Ukraine

The influence of pressure of nitrogen atmosphere on the structural and phase state and properties of vacuum-arc nitride coatings Ti-Zr-Hf-V-Nb-Ta has been studied. The multi-element nitride coatings deposited in nitrogen, are single-phase with a cubic face-centered cubic lattice (structural type NaCl) excluding the dropping component. The maximum hardness (42.2 GPa) is achieved for the nitride coatings deposited by vacuum arc evaporation (Ti, Zr, Hf, V, Nb, Ta) of the alloy at the pressure of nitrogen of 0.3 Pa. The tribotechnical characteristics have been studied during high temperature tests. It was found that wear resistance of the coatings is higher at T = 500 °C and T = 700 °C due to formation of oxide tribofilms on the surface, which act as a solid lubricant during testing.

INTRODUCTION

The surface layer of structural materials is exposed to heavy mechanical, thermal and chemical resistance during the operation. The loss of performance of constructional materials in most cases is due to the damage caused to the surface, which is a result of wear, erosion, corrosion, and so on. N. One of the most effective methods ensuring the obtaining of predetermined complex of characteristics for surface hardness of material is hardening method, which allows to form a protective coating on the surface [1, 2]. By choosing a suitable material for the coatings and technological deposition regimes, one can vary basic surface properties of machine parts, such as hardness, friction coefficient, thermal conductivity, wear resistance and corrosion resistance within a wide range, while maintaining excellent properties of the substrate material.

Published data show that the coatings based on nitrides of various refractory materials are stable coatings with high physical and mechanical properties [3]. Recently, however, with an increase of specific loads, and, in some cases, poor lubrication conditions, increased requirements for reliability and durability of machine parts, these coatings are no longer justified.

Increased wear and durability of friction joints can be achieved by spraying multi-element materials and by creating multicomponent carbide or nitride coatings on their basis, which provide increased wear resistance, hardness, heat resistance, etc. [4, 5].

Modern perspective coatings to use in tool making industry, which protect the cutting tool working at high speeds (temperatures), as well as the coatings to use in heavy loaded friction units are multi-component systems based on nitrides of refractory metals - titanium nitride, hafnium, zirconium, and niobium [6, 7].

In connection with this, we investigated the tribological characteristics of multicomponent-component nitride coatings, obtained by means of vacuum-arc evaporation method of the material based on (TiZrHfVNbTa).

EXPERIMENTAL PART

The coatings were deposited by means of vacuum-arc method on the "Bulat-6" installation. The cathode of the desired composition was produced before the deposition by means of vacuum-arc melting of a multicomponent mixture of powders of pure metals. Non-diffusing tungsten cathode was used for melting. Crystallized ingot was removed from the crystallizer, turned over and placed back in the crystallizer. The flux was re-melted; the procedure was repeated 7 times to obtain the most homogeneous structure.

The ingot was in a shape of cylinder (diameter ~ 45 mm, height ~ 30 mm), which was removed from the crystallizer and soldered to the titanium cathode with a solid solder. Thus, the cathodes (targets) based on Ti+Zr+Nb+Hf+V+Ta system were fabricated. These targets were used to obtain the nitride coatings. The reactive gas was nitrogen. During deposition in order to improve the adhesion, a constant negative potential U_{cp} = -150 V was applied, and in some cases in order to increase the average energy of deposited particles without significant heating, pulsed negative potential U_{pp} = -800 and -1200 V was applied in pulsed mode with a duration of 10 μs and frequency ν = 7 kHz. The temperature during deposition did not exceed 450 °C. The deposition parameters are given in Table 1.

The substrates for the coatings deposition were the samples withthe size 15x15x2.5 mm made of 12X18H9T steel (Ra = 0.09 μm). The time of deposition was 1.5 hours, the thickness of the coating ~ 8.0 μm.

The surface morphology, fractograms of the fracture, friction tracks were investigated on a scanning electron microscope FEI Nova NanoSEM 450.

The study of the elemental composition of the coatings was carried out by analyzing the spectra of characteristic X-rays generated by an electron beam in a scanning electron microscope. The spectra were recorded by means of x-ray energy dispersive spectrometer of PEGASUS system by EDAX, installed in the microscope.

Table 1

Physical and technological parameters of coatings deposition

Series No.	Coatings	I_{arc}, A	$I_{foc. cat.}$, A	U_{cp}, V	U_{pp}, V	ν, kHz	P, Torr	$HV_{0.2}$ GPa	Ra, μm
1	(TiZrHfVNbTa)N	110	0.4	-150	–	–	$3\cdot10^{-3}$	40.1	1.26
2	(TiZrHfVNbTa)N	110	0.4	-150	-800	7	3×10^{-3}	42.2	1.32
3	(TiZrHfVNbTa)N	110	0.4	-150	-800	7	7×10^{-4}	36.3	1.62
4	(TiZrHfVNbTa)N	110	0.4	-150	–	–	7×10^{-4}	33.8	1.42
5	(TiZrHfVNbTa)N	110	0.4	-150	-1200	7	7×10^{-4}	38.3	1.55

The study of the elemental composition of the coatings was carried out by analyzing the spectra of characteristic X-rays generated by an electron beam in a scanning electron microscope. The spectra were recorded by means of x-ray energy dispersive spectrometer of PEGASUS system by EDAX, installed in the microscope.

Investigation of phase-structural state was carried out on a DRON-3M in Cu-Kα radiation. To monochromatise the detected radiation, the graphite monochromator, which is set in the secondary beam (in front of the detector) was used. The study of the phase composition, structure (texture, substructure) were carried out using traditional methods – by means of X-ray diffraction analysis of the position, intensity and shape of the profiles of the diffraction reflexes. Substructural characteristics were determined by means of approximation method [8].

Tribological tests were carried out on air by “ball-disk” scheme. High temperature “Tribometer”, CSM Instruments was used as a friction machine. The coatings were deposited onto the polished surface of the cylindrical samples (Ra = 0.088 μm) made of steel 45 (diameter 42 mm, height 5 mm). The thickness of the coating was ~ 4.5...5.0 μm. The ball with the diameter of 6.0 mm, made of sintered certified material – Al_2O_3 – was used as a counterbody. The load was 6.0 N, the sliding speed was 10 cm/s. The tests conform to the international standards ASTM G99-959, DIN50324 and ISO 20808. The roughness and the volume of the removed material of the coating was determined by the cross-section of the wear track on the surface of the sample using automated precession contact profilometer of the model Surtronic 25. The hardness of the coatings was measured using a hardness-testing machine DM 8 using micro-Vickers method, at a load of 0.2 N.

RESULTS AND DISCUSSION

Investigation of surface topography using a scanning electron microscope shows the presence of micron size droplets. The surface roughness varies from 1.26 to 1.62 μm depending on the deposition parameters (see Table 1).

The elemental analysis data are shown in Table 2. It can be seen that for all the operation modes used in a work there is a good correspondence between the elemental composition of the coating and the evaporated target (without taking nitrogen atoms into account).

The analysis of the diffraction spectra indicates, that for the coatings, obtained at a low pressure of $7\cdot10^{-4}$ Torr (Series No. 1) as well as for the coatings, obtained at relatively high pressure of nitrogen atmosphere $3\cdot10^{-3}$ Torr (Series No. 4), despite of the large number of constituent metal elements and different inclinations of the constituent elements to form the nitrides, the single-phase state on basis of the fcc metal lattice is formed. The lattice in the case of nitrides has a structural type of NaCl and a low content (up to 7 vol.%) component with a bcc lattice, apparently associated with the presence of droplet phase in the coating.It should be noted, that the formation of the fcc lattice by nitride coatingsof multielement systems is confirmed by many sources of literature [9–11]. This circumstance points to the fact that the formation of a single-phase solid solution of the nitride phase is more inherent for such material, rather than separate nitrides, coexisting with each other.

Table 2

Elemental composition of the coatings, at.%

Series No.	N	Zr	Nb	Ti	V	Hf	Ta
1	55.48	8.33	7.73	7.85	6.12	9.33	5.16
2	54.85	8.52	8.37	7.67	6.1	9.29	5.2
3	52.33	8.13	8.48	7.62	6.71	9.48	5.25
4	52.75	8.59	8.55	8.96	6.67	9.47	5.01
5	52.82	8.61	8.39	9.2	6.74	9.34	4.9

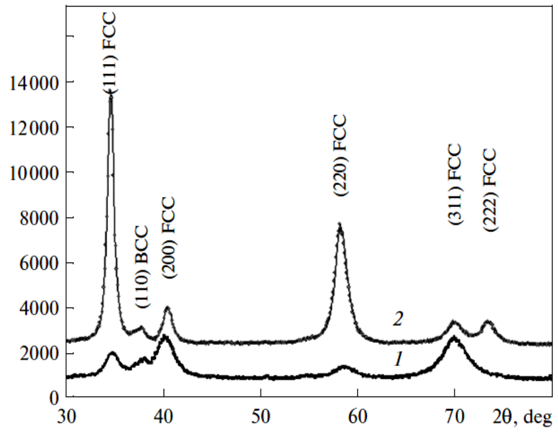


Fig. 1. The area of x-ray spectra of the coated samples (TiZrHfVNbTa)N; 1 – Series No. 4; 2 – Series No. 1

The coatings, produced at a low pressure of $7\cdot10^{-4}$ Torr, are characterized by almost untextured state (spectrum 1 in Fig. 1). The increase of the pressure of the nitrogen atmosphere up to $3\cdot10^{-3}$ Torr during the deposition leads to appearance of the state with the axial texture axes [111] and [110]. The investigation of the substructural characteristics by means of approximation method has shown that the bombardment of the growing coating by charged accelerated particles of the target at low pressureoccurs in almost collision-free mode (in the electrode gap), which leads to the development of high micro deformation of 1.09% at small and average crystallite size of about 10 nm.

The results of hardness measurement of the obtained coatings are given in Table 1. The hardness of the coatings according to the physical parameters of deposition lies in the range of 36 to 42.2 GPa. It should be noted, that the maximum values of hardness (40.1 and 42.2 GPa) are inherent to the coatings of Series No. 1 and Series No. 2, which are characterized by the strongest growth texture (111). It should be also noted, that the plane (111) is the most close-packed as for the fcc crystal lattice.

The image of friction tracks, as well as the results of tribotechnical tests are shown in Fig. 2 and in Table 3.

Table 3

Tribotechnical characteristics of the systems «coating (TiZrHfVNbTa)N – Al_2O_3»

Series No.	Coatings	Friction coefficient, µ		Wear, mm^3/N/m	
		Initial	While testing	Counter-body	Coating
Initial	Steel 45, polished.	0.318	0.498	$1.01\cdot10^{-6}$	$5.12\cdot10^{-5}$
1	(TiZrHfVNbTa)N	0.363	1.003	$3.29\cdot10^{-5}$	$5.44\cdot10^{-5}$
2	(TiZrHfVNbTa)N	0.683	1.063	$3.84\cdot10^{-6}$	$4.1\cdot10^{-5}$
3	(TiZrHfVNbTa)N	0.500	0.878	$2.03\cdot10^{-5}$	$5.94\cdot10^{-5}$
4	(TiZrHfVNbTa)N	0.607	0.942	$9.93\cdot10^{-6}$	$2.12\cdot10^{-5}$
5	TiZrHfVNbTa)N	0.409	0.974	$1.34\cdot10^{-5}$	$5.06\cdot10^{-5}$

Tables 4 and 5 show the results of energy-dispersive analysis of the elemental composition of the wear tracks and the wear products, respectively.

All the coated samples had a friction coefficient, which was higher than 0.9. Such high values can be explained by the high roughness (see Table 1) and the presence of the droplet fraction on the surface and in the coating (see Fig. 2), which are a consequence of the process of continuous-flow vacuum-arc deposition. However, the coatings perform good results in abrasion resistance. The images of the wear tracks (see Fig. 2), obtained by means of SEM, and the results of energy-dispersive analysis (Table 4) show that the coatingswere not erased to the substrate. During the test, there was no chipping, cracking or delamination of the coatings, they have good adhesion. During the abrasive wear, the material of the coatings was plastically deformed; the observed wear pattern is typical for soft metals. In order to obtain the information on the effect of temperature on the tribotechnical characteristics, the high-temperature tests were conducted. The sample of the coating obtained at $P = 3\cdot10^{-3}$ Torr (Series No. 2) with the hardness of H = 42.2 GPa was taken as a sample. The results of tribology tests at T = 500 and 700 °C are shown in Table 6.

Fig. 3 shows a photograph of the area of friction tracks for the coating of Series No. 2, their wear products and their elemental composition at a temperature of 500 °C test.

The oxygenation of the surface nanolayer of the coating increases (Table 7), and the presence of large amounts of oxygen in the products of wear, indicate the presence of ZrO_2, TiO_2, etc. oxides.

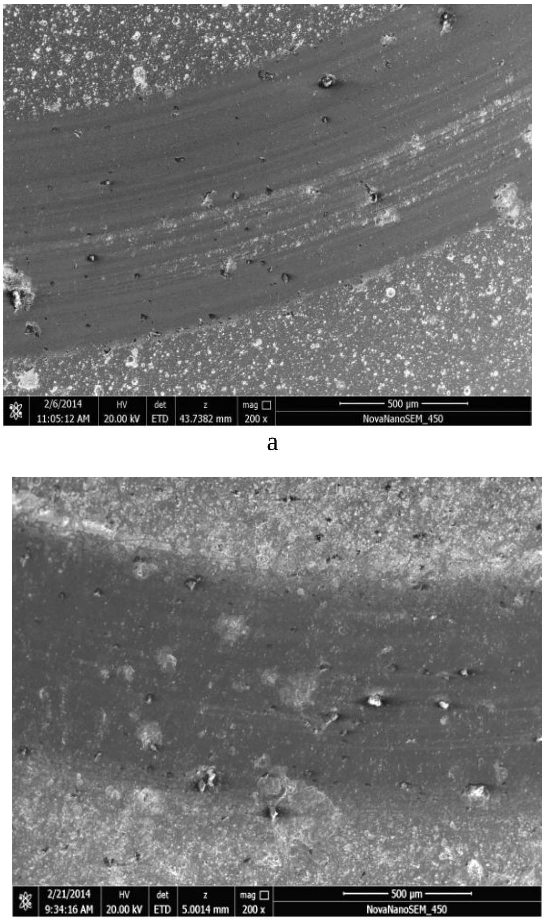


Fig. 2. Image of wear tracks of the coatings (TiZrNbHfVTa)N, obtained by means of SEM: a – Series 2; b – Series 4

Using the data of the energy dispersion analysis (Table 7), the identification of the results of X-ray structural analysis has been carried out. The diffraction patterns of the coatings after the tests revealed reflexes at small angles, which is associated with the formation of TiO_2 oxides (JCPDS 01-0562), ZrO_2 (JCPDS42-1164) and the oxide type $MeTiO_4$, where “Me” corresponds to the content of Zr and Hf.

According to the structural type, this oxide is similar to the isostructural $ZrTiO_4$ (JCPDS 07-0290) and $HfTiO_4$ (JCPDS 14-0103), as well as to the appearance of reflexes from NbO_2 (JCPDS 17-0212).

Table 4

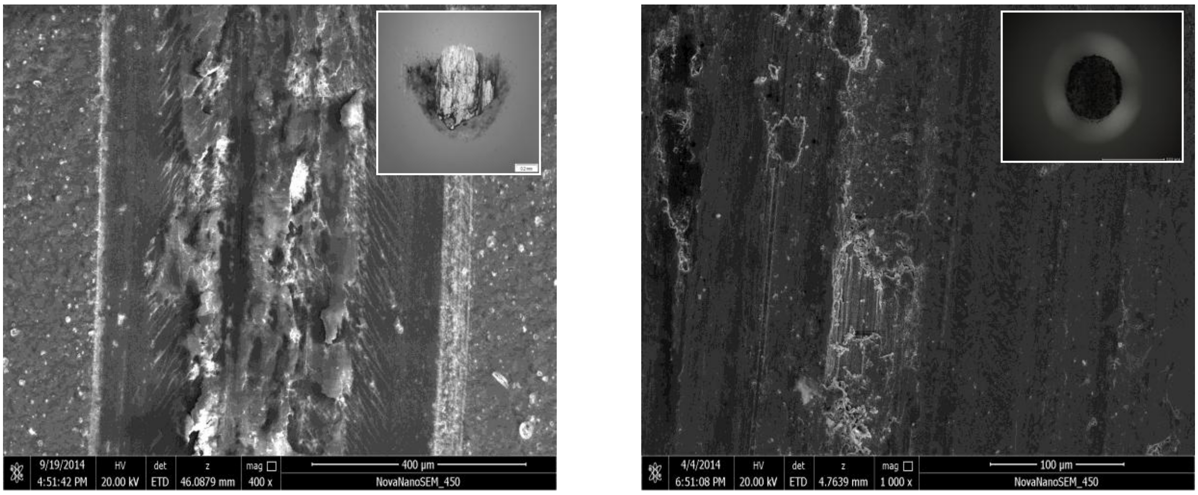
Elemental composition of wear tracks

Series No.	Elemental composition, at.%								
	N	Zr	Nb	Ti	V	Hf	Ta	O	Al
1	51.48	8.48	8.17	8.14	6.64	9.39	5.2	2.49	–
2	52.2	8.82	8.46	8.21	6.47	9.29	5.23	1.34	–
3	45.8	8.17	7.81	10.25	7.2	8.38	4.66	6.65	1.09
4	50.63	8.73	8.18	10.25	7.03	8.67	4.54	6.65	–
5	41.12	10.79	10.91	11.25	8.59	10.82	6.04	–	–

Table 5

Elemental composition of the wear product

Series No.	Elemental composition, at.%									
	N	Zr	Nb	Ti	V	Hf	Ta	Fe	O	Al
1	27.38	3.76	3.65	3.57	2.93	3.4	2.91	0.47	48.96	2.98
2	22.79	3.84	3.81	3.21	2.56	3.35	2.45	0.33	53.99	3.66
3	22.87	2.79	2.62	3.42	2.49	2.32	2.15	0.32	48.48	12.54
4	19.23	3.23	3.17	3.41	2.39	2.74	2.3	0.45	53.74	9.34
5	21.92	3.37	3.46	3.45	2.66	2.95	2.62	0.58	50.85	8.14



a b

Fig. 3 Image of wear tracks of the coatings and Al_2O_3 counterbodies at high temperature tests for the coatings of Series No. 2: a – 700 °C; b – 500 °C

Table 6

Tribological characteristics of the systems «coating (TiZrHfVNbTa)N – Al_2O_3»
under the testing temperatures 20, 500 and 700 °C

Testing temperature	Friction coefficient, µ		Wear intensity, $mm^3/N/m$	
	Initial	During the testing	Counterbody	Coating
T = 20 ºC	0.683	1.063	$3.84\cdot10^{-6}$	$4.1\cdot10^{-5}$
T = 500 ºC	1.15	0.827	$7.36\cdot10^{-6}$	$2.12\cdot10^{-5}$
T = 700 ºC	0.725	0.585	$2.47\cdot10^{-5}$	$2.71\cdot10^{-5}$

Table 7

Elemental composition of the surface of the coatings of Series No. 2 and their wear products at T= 500 °C

Elements	N, at. %	O, at.%	Al, at.%	Hf, at.%	Ta, at.%	Zr, at.%	Nb, at.%	Ti, at.%	Fe, at.%
Coatings	43.38	41.15	3.48	1.74	2.12	1.89	1.47	1.58	3.09
Wear products	–	49.96	6.46	5.26	5.32	6.07	4.82	4.06	21.04

It is known that the phase change in the active layers occurs respectively to the giventemperature and power conditions, and depends on the activity of diffusion processes.

As a result, the redistribution the of elements in the structural components, the dissolution of fine inclusions, the smoothing of heterogeneity degree over the depth of the active layer and the creation of the so-called layers, saturatedby chemical elements from the environment on the surface of the friction surface is possible [12–14].

It should be kept in mind, that the beneficial effect of the tribochemical processes on anti-friction properties takes place only up to a certain level of the friction characteristics. Wear cannot be associated with any of the properties of the oxide film. It is necessary to take the complex of characteristics, such as strength, brittleness, hardness, bonding strength of the oxide film with the surface of the basic metal into account.

Unlike the friction at room temperature, high temperature friction provides more intense oxidation and subsequent reduction of the damaged oxide films. Tribooxidation of the coatings (TiZrHfVNbTa)N results in structural adjustment of the surface layers to the difficult conditions of high temperature friction [15]. Oxygen-containing compounds based on a metal, which are formed in the friction process may act as a shield, which protects the surface from wear.

The study has been conducted in CCU, agreement No.14.594.21.0010 and the unique identifier for the works RFMEFI62114X0005 (under the support of the Ministry of Education)

The work was carried out as a part of complex state-funded scientific research works 0113U001079 and 0112U006974, funded by the Ministry of Education and Science of Ukraine.

SUMMARY

1. The nitride coating based on the multi-element material Ti-Zr-Hf-V-Nb-Ta was obtained by means of vacuum-arc deposition method. It is shown that the formation of single-phase solid solution with fcc lattice is inherent to such materials.

2. The coatings produced at a low pressure of nitrogen ($7\cdot10^{-4}$ Torr) are characterized by almost untextured state. Increasing the pressure of the nitrogen atmosphere during the deposition of up to 3×10^{-3} Torr leads to the appearance of bitextural state with the axial texture axes [111] and [110].

3. The maximum hardness values (40.1 and 42.2 GPa) are inherent to the coatings, obtained at the pressure of nitrogen $3\cdot10^{-3}$ Torr, which are characterized by the strongest growth of the texture (111).

4. It was found out, that the coatings, based on system (TiZrHfVNbTa)N have improved wear resistance at tribological tests when tested in air at T = 500 and 700 °C; this is due to the formation of surface stable oxides based on transition metals forming high entropy alloy, which act like a solid tribolubricant at high temperatures. The intensity of wear of the coatings is 2 times lower than in the case of tests at room temperature.

REFERENCES

1. E.N. Reshetnyak, V.E. Strel’nitskij. Synthesis of hardeningnanostructural coatings // *VANT. Series “Physics of radiation effect and radiation materials science”*. 2008, N 2(92), p. 119-130.

2. A.D. Pogrebnjak, V.M. Beresnev. Hard nanocomposite coatings, their structure and properties. Ch. 6. *Books «Nanocomposites new trends and developments»*. Croatia: NTECH, 2012, p. 123-160.

3. N.A. Azarenkov, O.V. Sobol, V.M. Beresnev, A.D. Pogrebnyak, D.A. Kolesnikov, P.V. Turbin, I.M. Torianyk Vacuum-plasma coatings based on the multielement nitrides // *Metal physics and modern Technologies*. 2013, v. 35, N 8, p. 1061-1084.

4. A.D. Pogrebnjak, A.V. Pshyk, V.M. Beresnev, B.R. Zhollybekov. Protection of specimens against friction and wear using titanium-based multicomponent nanocomposite coatings: A review // *J. of Friction and Wear*. 2014, v. 35, N 1, p. 55-66.

5. A.D. Pogrebnjak, A.P. Shpak, N.A. Azarenkov, et al. Structures and properties of hard and superhard nanocomposite coatings // *UFN*. 2009, v. 179, N 1, p. 35-64.

6. A.D. Pogrebnjak, I.V. Yakushchenko, A.A. Bagdasaryan, O.V. Bondar, R. Krause-Rehberg, G. Abadias, P. Chartier, K. Oyoshi, Y. Takeda, V.M. Beresnev, O.V. Sobol. 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.

7. A.D. Pogrebnjak, N.A. Azarenkov, V.M. Beresnev, S.V. Litovchenko. Influence of deposition parameters on the structure and properties of nitride coatings. Ch. 11 // *Books «Manufacturing Nanostructures»*. Manchester, United Kingdom: One Central Press, 2014, p. 294-320.

8. L.S. Palatnik, M.Ya. Fuksc, V.M. Kosevich. *Mechanism of formation and substructure of condensed films*. M.: “Science”, 1972, 320p.

9. Y. Zhang, T.T. Zuo, Z. Tang, M.C. Gao, K.A. Dahmen, P.K. Liaw, Z.P. Lu. Microstructures and properties of high-entropy alloys // *Progress in Materials Science*. 2014, v. 61, p. 1-93.

10. B.S. Murty, J.W. Yeh, S. Ranganathan. *High-Entropy Alloys*. Amsterdam, Boston: Elsevier, 2014, 169 p.

11. 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.

12. G.K. Dosbaeva, S.C. Veldhuis, K. Yamamoto, D.S. Wilkinson, B.D. Beake, N.J enkins, A. Elfizy, G.S. Fox-Rabinovich. Oxide scales formation in nanocrystalline TiAlCrSiYN PVD coatings at elevated temperature // *Int. J. Refract. Met. Hard Mater*. 2010, v. 28, N 1, p. 133-141.

13. R. Franz, C. Mitterer. Vanadium containing self-adaptive low-friction hardcoatings for high-temperature applications: A review // *Surf. Coat. Technol*. 2013, v. 228, N 7, p. 1-13.

14. H. Kato, K. Komai. Tribofilm formation and mild wear by tribo-sintering ofnanometer-sized oxide particles on rubbing steel surfaces // *Wear*. 2007, v. 262, N 1-2, p. 36-41.

15. S.A. Klimenko, I.A. Podchernjaeva, V.M. Beresnev, V.M. Panashenko, S.An. Klimenko, M.Yu. Kopeikina. AlN-(TiCr)B_2 ion-plasma coating for cutting tools of cBN-based polycrystalline superhard material // *Journal of Superhard Materials*. 2014, v. 36, N 3, p. 208-216.

Статья поступила в редакцию 15.01.2015 г.

ФРИКЦИОННЫЕ СВОЙСТВА МНОГОЭЛЕМЕНТНЫХ ПОКРЫТИЙ (TiZrHfVNbTa)N

У.С. Немченко, В.Ю. Новиков, В.А. Столбовой, В.М. Береснев, О.В. Соболь

Проведено исследование влияния давления атмосферы азота на структурно-фазовое состояние и свойства вакуумно-дуговых нитридных покрытий системы Ti-Zr-Hf-V-Nb-Ta. Без учета капельной составляющей, многоэлементные нитридные покрытия, осажденные в азоте, являются однофазными с кубической ГЦК-решеткой (структурный тип NaCl). Наибольшая твердость (42,2 ГПа) достигнута в нитридных покрытиях, осажденных вакуумно-дуговым испарением (Ti, Zr, Hf, V, Nb, Ta) сплава при давлении азота 0,3 Па. Изучены триботехнические характеристики при высокотемпературных испытаниях. Установлено, что при T = 500 и 700 ºC износостойкость покрытий выше за счет образования окисных трибопленок на поверхности, действующих в качестве твердой смазки в процессе испытаний.

ФРИКЦІЙНІ ВЛАСТИВОСТІ БАГАТОЕЛЕМЕНТНИХ ПОКРИТТІВ (TiZrHfVNbTa)N

У.С. Нємченко, В.Ю. Новіков, В.О. Столбовой, В.М. Береснєв, О.В. Соболь

Проведено дослідження впливу тиску атмосфери азоту на структурно-фазовий стан і властивості вакуумно-дугових нітридних покриттів системи Ti-Zr-Hf-V-Nb-Ta. Без урахування крапельної складової, багатоелементні нітрідні покриття, осаджені в атмосфері азоту, є однофазними, з кубічною ГЦК-решіткою (структурний тип NaCl). Найбільшої твердості (42,2 ГПа) досягнуто у нітридних покриттях, осаджених вакуумно-дуговим випаровуванням (Ti, Zr, Hf, V, Nb, Ta) сплаву при тиску азоту 0,3 Па. Вивчено триботехнічні характеристики при високотемпературних випробуваннях. Встановлено, що при T = 500 і 700 ºC зносостійкість покриттів вище за рахунок утворення окисних трібоплівок на поверхні, що діють в якості твердого змащувача в процесі випробувань.