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Tribotechnical Properties of the Coatings (Ti-Zr-Nb)N

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Coatings based on (Ti-Zr-Nb)N were obtained by means of vacuum-arc deposition method. Their physical and mechanical properties, as well as tribotechnical characteristics have been studied. The coefficient of friction of the system "coating-Al_2O_3" is 1.1. The coatings are characterized by a columnar structure and their hardness reaches $HV_{0.05}$ = 44.57 GPa.

Keywords: Tribotechnical characteristics of coatings, Vacuum-arc deposition method, Refractory metal nitride, Coatings.

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1. INTRODUCTION

During the operation, the surface layer of machinery details and mechanisms is subjected to severe mechanical, thermal and chemical impact. The loss of performance occurs in majority of cases as a result of wear, erosion, corrosion, etc., of the surface layers. A significant resource to increase performance lies in material, from which the machine parts are manufactured. For this reason, tribotechnical materials science is getting more and more attention in modern engineering. Usage of space-doped materials for such applications is often not economically advantageous and in some cases is not technologically possible. However, the necessary results can be achieved by covering the working surfaces with multifunctional coatings, which combine high hardness, wear resistance and heat resistance simultaneously. A very promising method to provide a complex of high operational properties is to apply multielement coatings based on carbides, borides, nitrides and silicides of transition metals [1-4]. Stability of structure and composition, as well as high performance of multi-element nitride systems provide improvement of physical and mechanical characteristics of the surface and provide an opportunity to use them as protective films, which prevent penetration of harmful impurities into the surface layers of the products [5, 6]. Currently, ion-plasma methods, in particular, vacuum-arc and magnetron sputtering are the most commonly used for the deposition of coatings [7, 8].

Peculiarities of formation of ion-plasma coatings by means of spraying the multielement system based on Ti + Zr + Nb have been studied in the paper, and an analysis of physical and mechanical properties of the obtained coatings has been carried out.

2. EXPERIMENTAL PART

The coatings were formed by vacuum-arc deposition method. Unit-cast targets (cathodes) based on the system: 30 at. % Ti, 35 at. % Zr and 35 at. % Nb were used as sprayed materials. Molecular nitrogen was used as a working gas. The thickness of all the coatings in the experiment was 3.0 μm. Deposition parameters are listed in Table 1.

Table 1 – Physical and technological parameters of deposition of the coatings based on (Ti-Zr-Nb)N

Series No.	Deposited material	I_{arc}, A	U_b, V	P_N, Torr
a	Ti + Zr + Nb	95	100	4×10^{-3}
b	Ti + Zr + Nb	95	100	3×10^{-4}

Surface morphology of the fracture and wear tracks have been examined by means of SEM microscope by FEI - Nova NanoSEM 450. Elemental composition of the coatings was examined by analyzing the spectra of characteristical X-ray radiation, generated by electron beam in scanning electron microscope. The spectra have been taken with a help of energy dispersion spectrometer of X-ray radiation of PEGASUS system by EDAX company, built-in the microscope. X-ray structure studies of the coated samples were carried out on DRON-4 difractometer in Cu-k_α radiation. The hardness of the coatings was determined with a help of DM-8 hardness tester using micro Vickers method at a load of 0.05 N applied on indenter. Tribological tests were carried out on air using "ball-disc" scheme. "Tribometer" by CSM Instruments was used as a friction machine. In order to perform the tests, the coatings were deposited on the surfaces of polished cylindrical samples (R_a = 0.088 μm) made of steel 45 (HRC = 55) with diameter of 42 mm and a height of 5 mm. The thickness of the coatings was ~ 3.5-4.0 μm. A ball with diameter of 6 mm made of cast certified material – Al_2O_3 - was used as a counterbody. The load was 3.0 N and the sliding speed was 10 cm/sec. The structure of the wear track of the coating as well as the wear spot of the balls were examined after the tests by using optical inverted microscope Olympus GX 51 and scanning ion-electron microscope Quanta 200 3D. The quantitative estimate of wear resistance of samples and counterbodies was carried out by obtaining wear factor J [9]. The method for its calculation is presented in the work [10].

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3. RESULTS AND DISCUSSION

Investigation of surface morphology (Fig. 1) has shown that the increase of pressure of reaction atmosphere of nitrogen causes the decrease of number and size of microparticles as well as to reduction of roughness of the coating (Fig. 2). Elemental composition of the coatings, obtained by means of vacuum-arc deposition method, was analysed using energy dispersion method (see Table 2).

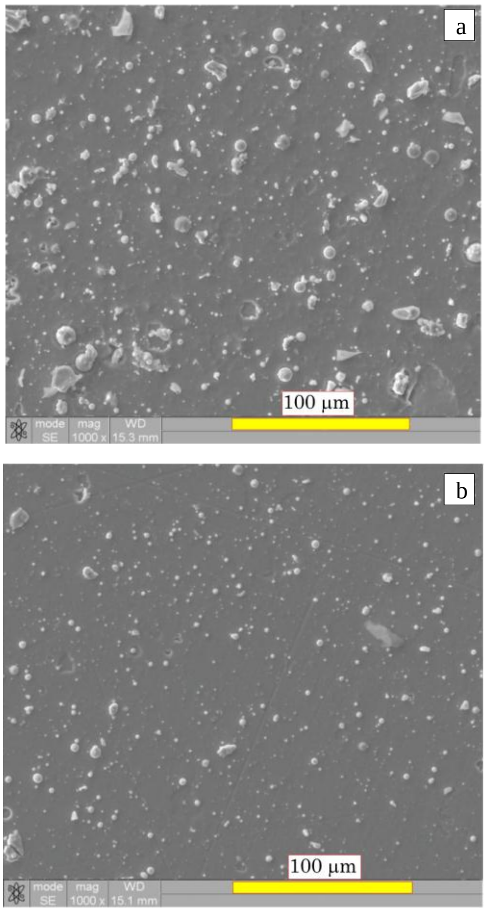

Fig. 1 – Image of the surface of the coatings (Ti-Zr-Nb)N, obtained under different partial pressures: a – $P = 3 \times 10^{-4}$ Torr ($R_a = 1.17$ μm); b – $P = 4 \times 10^{-3}$ Torr ($R_a = 0.42$ μm)

When comparing the elemental composition of the coatings of series a and b, we can see, that for the coatings of series a, the amount of titanium atoms is almost equal. For the coatings of series b the slight decrease of zirconia atoms is observed. Along with this, the content of niobium atoms for samples of both series remained practically the same.

Fractography investigations of the coatings (Fig. 2), obtained at different partial pressures of nitrogen, indicate formation of columnar structure (Fig. 2b), which is typical for the coatings obtained by vacuum-arc deposition method.

X-ray spectra analysis has shown that defining phase is a phase with face centered cubic crystal lattice. Low intensity peak in the area of $2\theta = 38°$ tells of slight inclusion of bcc lattice, which is typical for droplet phase at vacuum-arc deposition method [13].

Table 2 – Chemical composition of elements in the coating (Ti-Zr-Nb)N

Series No.	Elemental composition, at. %			
	N	Ti	Zr	Nb
a	38.72	20.91	20.38	19.99
b	40.86	20.52	19.36	19.26

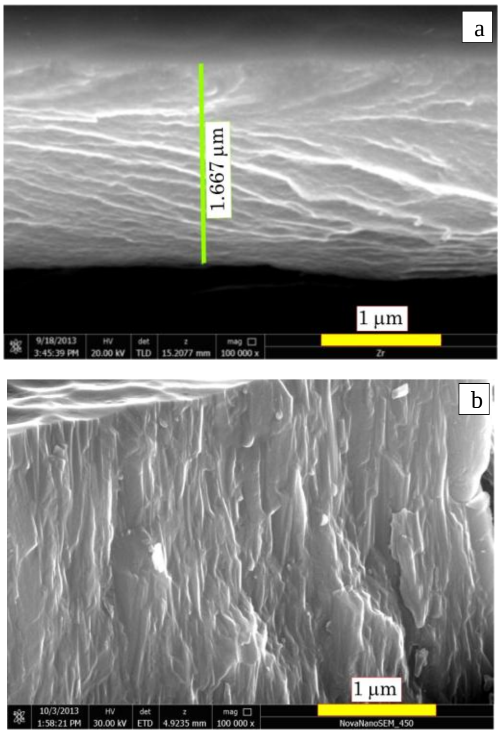

Fig. 2 – Image of the fractograms of the fracture of the coatings (Ti-Zr-Nb)N, obtained at different partial pressures of nitrogen: a – $P = 3 \times 10^{-4}$ Torr.; b – $P = 4 \times 10^{-3}$ Torr

The typical feature while increasing the pressure of reaction gas is the increase of peaks from the family of planes {111}, which is explained by the increase of perfection of growth of the crystallites with the preferred axis orientation [111], which is perpendicular to the plane of growth.

It is worth noticing, that with the increase of pressure, the intensity of this peak decreases (see spectra 1 and 3 on Fig. 3), which is apparently defined by significant decrease of droplet phase contents in the coating and correlates with the results of investigation of the surface (Fig. 1).

The sizes of the crystallites calculated by means of approximation method increase with the growth of pressure from 10 nm at the lowest pressure of $3 \cdot 10^{-4}$ Torr to 63 nm at the highest pressure of nitrogen atmosphere $4 \cdot 10^{-3}$ Torr.

The most important problem in the area of formation of protective coatings is increasing their physical and mechanical properties, in particular, hardness and wear resistance in order to increase performance characteristics of the products. The results of measuring mechanical characteristics, in particular, hardness of the obtained coatings (Zr-Ti-Nb)N, are shown in the Table 3.

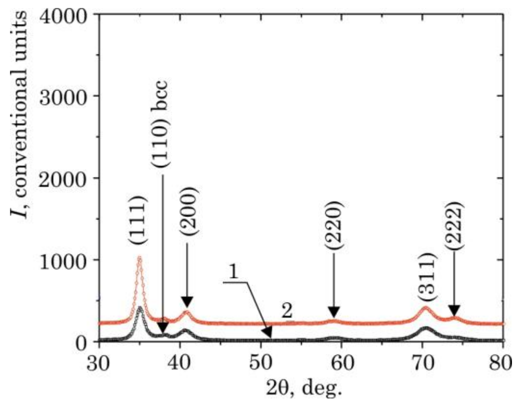

Fig. 3 – X-ray diffraction spectra parts of the coatings obtained at different partial pressures of nitrogen: curve 1 – $P = 3 \cdot 10^{-4}$ Torr; 2 – $P = 4 \cdot 10^{-3}$ Torr

Table 3 – Mean values of hardness of the coatings based on the system (Zr-Ti-Nb)N

Series No.	Hardness, $HV_{0.05}$ GPa	Remarks
a	37.21	direct flow
b	44.57	direct flow

As seen from the table, the maximal value of hardness is reached at the pressure of reaction gas $P = 4 \cdot 10^{-3}$ Torr, thus, this coating, according to the classification [11], can be determined as a superhard coatings with a hardness of $HV_{0.05}$ GPa. Profilogram of the surface of the steel disc before wear tests is shown at the Fig. 4.

Coating the polished surface of steel disc with the coatings of (Zr-Ti-Nb)N system results in increased roughness (Fig. 5) due to the droplet component of plasma flow.

The mean values of the friction coefficient (μ) of the system "coating-Al_2O_3" during the tests is 1.1.

As follows from the Table 6, the coatings of (Zr-Ti-Nb)N system, obtained at reaction gas pressure of $P = 4 \cdot 10^{-3}$ Torr have high hardness and wear resistance.

The results of tribological testing of the coated samples are shown in Table 5.

In conditions of friction, which are realized in our experiments, the coated sample is in much more severe load conditions in comparison with the counterbody. The surface of the counterbody – the ball – is constantly loaded and it experiences cyclical load, which is linked

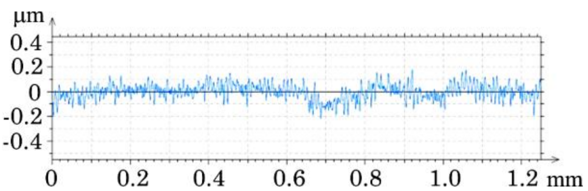

Fig. 4 – Profilogram of roughness of the surface of steel disc after polishing ($R_a = 0.088$ μm)

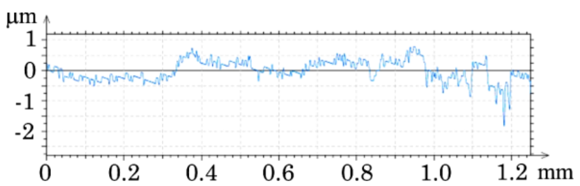

Fig. 5 – Profilogram of the surface of the coatings of b series, covered with the coating (Zr-Ti-Nb)N ($R_a = 0.42$ μm)

Table 5 – Tribotechnical characteristics of the coatings of the system "coating (Zr-Ti-Nb)N-Al_2O_3"

Series No.	Friction coefficient, μ		Wear factor, J, $mm^3 \times N^{-1} \times m^{-1}$	
	Initial	During the tests	Counterbody ($\times 10^{-5}$)	Sample ($\times 10^{-5}$)
a	0.61	1.95	0.391	9.69
b	0.491	1.05	3.21	2.4

only with the elastic contact and breaking of adhesive connections within the separate microareas of the actual contact of the same area. Elastic wave continuously appears along the circumference of the coated disc due to the interaction with the counterbody – the ball (every point of the surface of the coated disc with every rotation will go up and down), thus, involving significantly larger volume of material of the coated sample in the process of cyclical loading.

Figures 6-7 show the pictures of wear tracks on the surfaces of the coatings (Zr-Ti-Nb)N as well as the data for energy dispersion spectra.

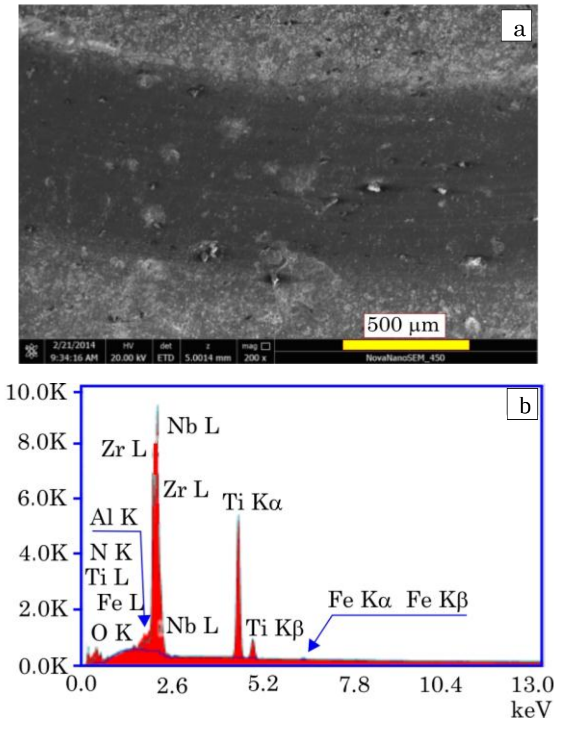

Fig. 6 – Image of the surface of the sample of a series of (Zr-Ti-Nb)N system after the tests: a – general view of the surface of the coating with the wear track, b – chemical composition of the wear track

The results of elemental composition of wear tracks are shown in Table 6.

Thus, all the conditions for development of adhesive fatigue failure of the coated disc surface are present. Tribotechnical characteristics of tribological system (sample-counterbody), but not the separate body, in particular, hard coating, need to be taken in account while predicting frictional characteristics and durability of the constructed friction unit. Structural and phase state of the coatings plays significant role during wear processes [12].

Table 6 – Elemental composition of wear tracks.

Sample No.	Elements, at. %							
	N	O	Al	Zr	Nb	Ti	Fe	Mn
a	41.5	11.58	0.28	11.86	12.57	22.54	–	–
b	–	41.98	0.64	1.7	1.73	3.32	50.37	0.27

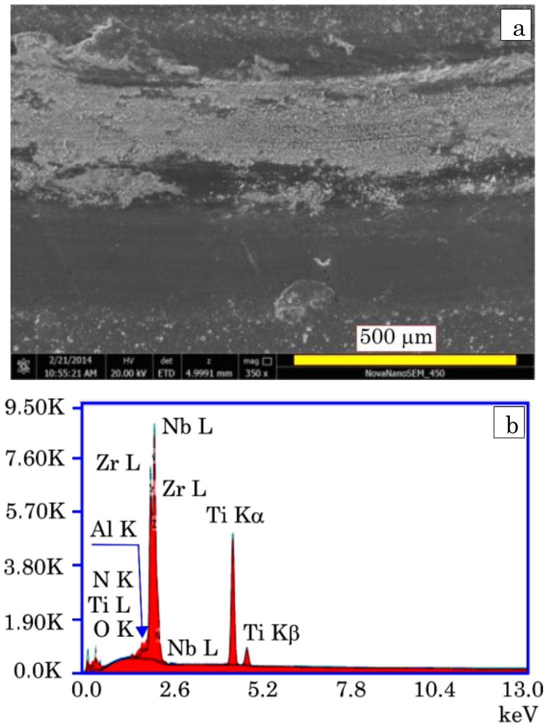

Fig. 7 – Image of the surface of the sample of b series of (Zr-Ti-Nb)N system after the tests: a – general view of the surface of the coating with the wear track, b – chemical composition of the wear track

4. CONCLUSIONS

1. Coatings of the system (Ti-Zr-Nb)N were obtained by means of vacuum-arc sputtering of unit-cast cathode in the medium of reaction gas - nitrogen. The obtained multicomponent films have clearly observed columnar structure.

2. It was shown that the elemental composition of the coatings, obtained by vacuum-arc deposition of the system (Ti-Zr-Nb)N, depends on physical and technological deposition parameters, in particular on the pressure of reaction gas - nitrogen.

3. X-ray diffraction spectra have shown that the main phase is the phase with face-centered cubic crystal lattice. The sizes of the crystallites, calculated by means of approximation method, increase with the growth of pressure from 10 nm at the lowest pressure of 3×10^{-4} Torr to 63 nm at the highest pressure of nitrogen atmosphere 4×10^{-3} Torr. With the increase of pressure of reaction gas, the amplification of peaks of {111} planes family is observed. This is explained by the increase of perfection of the crystallites growth with the preferred orientation of [111] axis, which is perpendicular to the plane of growth.

4. The influence of physical and technological deposition parameters on hardness of the coatings has been studied. The hardness of the coatings of (Ti-Zr-Nb)N system, which were obtained at partial pressure of nitrogen $P = 4 \times 10^{-3}$ Torr is $H_{0.05} = 44.57$ GPa, and at $P = 3 \times 10^{-4}$ Torr the hardness has values of $H_{0.05} = 37.21$ GPa.

5. Wear resistance of the coatings based on the system (Zr-Ti-Nb)N of series "b" is higher than wear resistance of the coatings based on (Zr-Ti-Nb)N system of series "a". The value of friction coefficient of the coatings (Zr-Ti-Nb)N while testing the system "coating-Al_2O_3" was $\mu \sim 1.1$.

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Триботехнические свойства покрытий (Ti-Zr-Nb)N

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Методом вакуумно-дугового осаждения получены покрытия на основе (Ti-Zr-Nb)N. Изучены их физико-механические свойства и триботехнические характеристики. Коэффициент трения системы "покрытие-Al_2O_3" составляет 1,1. Покрытия характеризуются столбчатой структурой, твердость покрытий достигает $HV_{0,05}$ 44,57 ГПа.

Ключевые слова: Вакуумно-дуговой метод осаждения, Триботехнические характеристики покрытий, Нитриды тугоплавких металлов, Покрытия.

Триботехнічні властивості покриттів (Ti-Zr-Nb)N

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Методом вакуумно-дугового осадження отримані покриття на основі (Ti-Zr-Nb)N. Вивчено їх фізико-механічні властивості та триботехнічні характеристики. Коефіцієнт тертя системи "покриття-Al_2O_3" складає 1,1. Покриття характеризуються стовпчастою структурою, твердість покриттів досягає $HV_{0,05}$ 44,57 ГПа.

Ключові слова: Вакуумно-дуговий метод осадження, Триботехнічні характеристики покриттів, Нітриди тугоплавких металів, Покриття.

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