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Tribotechnical Characteristics of Multielement Coatings Based on Nitrides of Ti, Zr, Cr, Nb, Si, Obtained by Means of Vacuum-arc Deposition Method

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Frictional properties of multi-element nanocomposite coatings by means of tribometry method have been studied. The obtained nitride nanostructured coatings include only a single phase of solid solution with the fcc lattice and NaCl structural type with (111) preferred orientation. The influence of annealing temperature on the tribological characteristics has been studied. It has been determined that the wear resistance (wear factor) of the coatings after annealing was 1.03×10^{-5} mm$^3 \times$ N$^{-1} \times$ m^{-1} which is higher than before the annealing 7.8×10^{-5} mm$^3 \times$ N$^{-1} \times$ m^{-1}.

Keywords: Vacuum-plasma deposition method, Nanocomposites, Nitrides of refractory metals, Tribological characteristics.

PACS numbers: 61.46. – w, 62.20.Qp, 62-65. – g

1. INTRODUCTION

The actual problem of modern industry is decreasing the wear rate of rubbing pairs of machine parts and cutting tools. Increase of wear resistance of friction pairs, as well as increase of efficiency of cutting tools, expand the areas of its application can be achieved by covering the working surface with coatings [1-3]. Various coatings based on multielement and composite systems with multiple functional structural components, which consist the coating are applied [4-6]. Many aspects of friction and wear processes of the coatings along with the use of solid and liquid lubricants are considered in most scientific publications [7, 8]. However these scientific publications often lack studying the tribotechnical characteristics during dry friction, thus the publications do not give a complete picture for behavior of such coatings during their operation. Therefore, in this paper we consider multi-element coatings based on Ti, Zr, Cr, Nb, Si nitrides, obtained by vacuum-arc deposition method. Parametric studies, establishing a relationship between the structural and phase composition and tribological properties of the coatings during friction in the atmosphere of air.

2. EXPERIMENTAL TECHNIQUES

The sputteded material of (Ti + Zr + Cr + Nb + Si) system was fabricated using vacuum-arc melting in a high purity atmosphere of argon Ar. In order to achieve uniformity of the alloy composition, the obtained ingots were melted repeatedly (4-5 times). The composition of the obtained cathode: Ti – 39.96 wt. %; Cr – 17.08 wt. %; Zr – 30.19 wt. %; Nb – 9.67 wt. %; Si – 3.1 wt. %. Formation of nitride coatings was carried out by mens of vacuum-arc deposition in the atmosphere of reaction gas – nitrogen on the "Bulat-6" installation. Two series of samples with the following deposition parameters have been obtained: 1 (No. 751) – bias potential on the substrate $U_b = -200$ V, the pressure of the working gas (nitrogen N_2) $P = 3.5 \times 10^{-3}$ Torr; 2 (No. 752) $U_b = -100$ V, the pressure of the working gas (nitrogen N_2) $P = 3.5 \times 10^{-3}$ Torr, arc current 100 A.

By means of scanning electron microscope Novascan 450 with energy dispersive analysis (SEM with EDS), the elemental composition of the obtained coatings has been investigated, and the images of the surfaces of the coatings, as well as their cross sections have been obtained. The studies of the structure and phase composition of nitride coatings of has been carried out using the method of XRD analysis in Cu-K_α radiation (ADVANCE, Bruker). Determination of residual macroscopic stresses in the coatings with cubic TiN (structural type NaCl) lattice were measured by means of X-ray tensometry method ($a - \sin^2\psi$ - method), and its modification in the case of strong texture of the axial type. In the latter case, the measurement of the interplanar distances was carried out from a variety of planes, under certain specified crystallographic tilt angles of a sample ψ. [9] The microhardness of the coatings was measured by means of microhardness measurer DM-8 by means of micro-Vickers method at a load of indenter 100 g.

The tribological tests were carried out on the friction machine, «Tribometer», CSM Instruments in the atmosphere of air by a scheme "ball-drive" at temperatures of 20 °C. A ball with diameter of 6.0 mm, manufactured from a sintered cpecified material Al_2O_3 was used as a counterbody. The discs, on which nanocomposite coatings were deposited, were made of steel 45 (HRC = 53), diameter $d = 45$ mm, and thickness $h = 3.5$ mm. The thickness of the coatings was 3.0 mcm. Test load at tests was was 6.0 N, and the sliding speed – 15 cm/s. The analysis of wear products, wear grooves, and the contact area on the counterbody have been carried out.

3. EXPERIMENTAL PART

The results of study using raster scanning microscopy (Figure 1) indicate the waviness on the surface and the droplet available component on the surface of the coating. The results of measuring of roughness of the surfaces of (TiNbCrZrSi)N indicate that the roughness value for 1 (No 752) series coatings was $R_a = 1.82$ m, and for 2 (No 751) series – $R_a = 1.02$ microns. This is due to the significant differrence between the bias voltage applied to the substrate in the first and second cases (No 751 – $U_b = -200$ V, No 752 – $U_b = -100$ V).

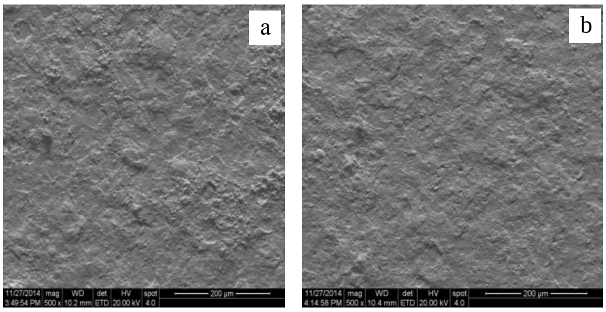

Fig. 1 – Morfology of the surface of the coating (TiZrCrNbSi)N: a) (No 751) – obtained at $P = 3.5 \times 10^{-3}$ Torr, $U_b = 200$ V; b) (No 752) – obtained at $P = 3.5 \times 10^{-3}$ Torr, $U_b = 100$ V

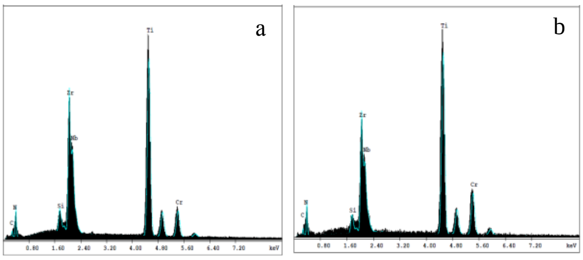

Fig. 2 – Energy dispersion spectra of the coatings based on (TiZrCrNbSi)N, obtained by means of vacuum-arc deposition method: a) (No 751) – obtained at $P = 3.5 \times 10^{-3}$ Torr, $U_b = 200$ V; b) (No 752) – obtained at $P = 3.5 \times 10^{-3}$ Torr, $U_b = 100$ V

Fig. 2 (a, b) and the Table 1 show the results of energy dispersion microanalysis of the surface of multicomponent coatings (TiNbCrZrSi)N.

Table 1 – Elemental composition of the coatings (TiNbCrZrSi)N

Coatings	Concentration, at. %						
	Ti	Cr	Zr	Nb	Si	C	N
No 1 (751) coatings	39.49	7.09	14.03	3.83	2.75	2.16	34.66
No 2 (752) coatings	35.34	11.00	11.58	7.36	2.12	2.15	35.34

Analysis of the coating (see Table 1) indicates that the elements, which are present in the coating composition, are present in the cathode. Presence of a minor amount of carbon can be explained by its diffusion from the surface layers of the substrate. Variation of the chemical composition of the elements affects distortion of the crystal lattice, and hence the physical and mechanical properties of the coatings.

From the obtained X-ray spectra (Fig. 3) it can be seen that, despite the large number of constituent metal elements and different inclinations of the constituent elements to nitride formation, a single-phase state on the basis of the fcc lattice is formed in the coatings, which in case the nitrides has a structure type NaCl. A characteristic feature of the obtained diffraction spectra is the presence of preferred orientation of crystallites, which manifests itself in the X-ray diffraction spectra as a relative change in the intensity of the diffraction peaks from different planes. The size of the crystallites, defined by means of Selyakov-Scherrer equation, also depends on the selected deposition mode. Thus, certain crystallite size in the coating of the first series averaged 11.5 nm in the direction of growth of crystallites with [111] axis, and 6.4 nm – in the direction of growth of crystallites with [100] axis. The conditions for obtaining in other series lead to smaller crystallite size. Thus, in series 2, the crystallite size in the direction of [111] axis was 9.7 nm, and in direction of crystallite growth axis [100] the size was 5.8 nm.

By means of $a - \sin^2\psi$ – macrodeformation method, compressive macrodeformation for the coatings of series 1 (752) with the texture [111] was determined, its value was – 1.65 %. The lattice period in the plane perpendicular to the direction of growth was 0.4332 nm, and the grating period of the second series was greater – 0.4337 nm

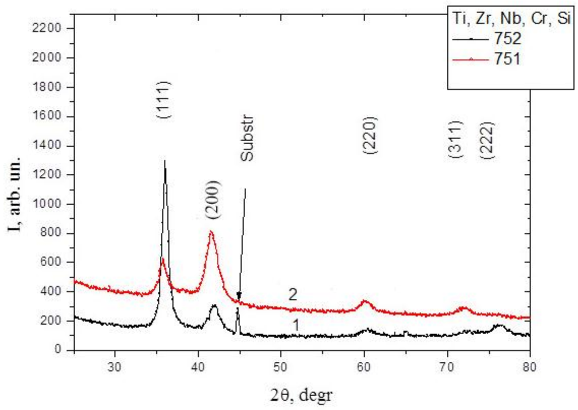

Fig. 3 – Difraction spectra areas of the coatings (TiNbCrZrSi)N, obtained at the following regimes: 1 – sample No 752; 2 – sample No 751

Thus, in case of Series 1 (No 752) we have the coatings with the preferred orientation of crystallites [111] and with their greater size in this direction (11.5 nm) under the action of higher macrodeformations compression in this coating. In the case of the coating Series 2 (No 751), a change of axis of preferred orientation [100] is observed, a significant reduction in the average size of the crystallites in this direction down to 5.1 nm, and the development of stretching macrodeformations in such coatings. In this case, the transition to the tensile strain can be associated with a significant decrease in crystallite size and the increase of the specific volume of the borders with disoriented structure, which have a lower bulk density. The hardness of the coatings according to the physical parameters of the deposition is in the range from 17 (at $U_b = -200$) to (at $U_b = -100$) 24 GPa.

Investigation of the thermal stability of the obtained coatings has been carried out at annealing of the coatings in vacuum in the atmosphere of nitrogen at $T = 700$ °C for 1 hour. Table 2 shows the results of the elemental composition of the coatings after annealing. The annealing did not change the phase composition of the coatings. The grating period of the first series of samples is reduced, which may be caused by the reduction of internal stresses and redistribution of the elements in the coating.

Table 2 – Elemental composition of the coatings (TiNbCrZrSi)N after annealing

Coatings	Concentration of the elements, at. %						Remarks
	Ti	Cr	Zr	Nb	Si	N	
No 1 (751) coatings	42.14	8.44	13.5	6.72	3.11	26.09	Annealing temperature 700 °C
No 1 (752) coatings	39.94	12.86	11.88	6.28	2.37	26.67	

The study of friction tracks is of considerable interest, as a result of which it is possible to characterize the mechanism of wear. The image of friction tracks, as well as the results of tribological tests are shown in Figure 4, Figure 5, and Table 3.

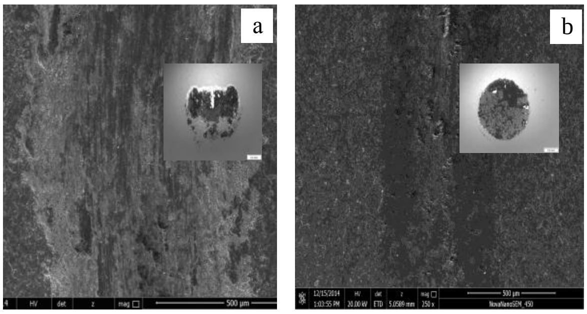

Fig. 4 – Image of the wear tracks, obtained by means of scanning electron miscoscope Novascan 450: a) (No 751) – $P = 3.5 \times 10^{-3}$ Torr, $U_b = 200$ V; b) (No 752) – $P = 3.5 \times 10^{-3}$ Torr, $U_b = 100$ V

The analysis of friction tracks according to [10, 11], see. Fig. 4, 5, shows that during the process of frictionm oxidation mechanical wear takes place. This is linked with the fact that wear occurs under conditions of exposure of the environment and dynamic interactions between the contacting materials. In the process of friction, the oxide films are formed on the surface, as evidenced by X-ray energy dispersive analysis of data for the tracks of friction, as well as for the wear products.

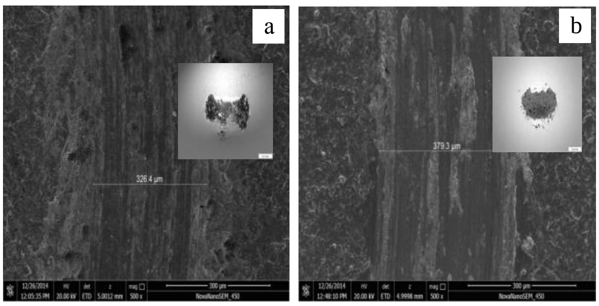

Fig. 5 – Images of wear tracks, obtained by means of scanning raster microscope Novascan 450 after annealing: a) (No 751\1) – $P = 3.5 \times 10^{-3}$ Torr, $U_b = -200$ V; b) (No 752/2) – $P = 3.5 \times 10^{-3}$ Torr, $U_b = -100$ V

Table 3 – Tribological characteristics of the coatings (TiNbCrZrSi)N before and after the annealing

No	Friction coefficient		Wear intensity, $mm^3 \times N^{-1} \times m^{-1}$		R_a, mcm	Remarks
	Initial	During the tests	Counter-body Al_2O_3	Coating		
751	0.512	0.934	1.47×10^{-5}	7.25×10^{-5}	1.02	Initial
752	0.273	0.867	1.91×10^{-5}	7.8×10^{-5}	1.82	Initial
751/1	0.82	0.95	1.01×10^{-5}	5.1×10^{-5}	0.97	After annealing
752/2	0.19	0.89	3.23×10^{-5}	1.03×10^{-5}	1.51	After annealing

All the samples coated with the coating have have coefficient of friction varied from 0.86 to 0.95 depending on the chenical contents. Such high values (Table 3) can be explained by the high riughness (Table 3), by the presence of the droplet fraction on the surface and in the coating (Figure 1), which are the result of continuous-flow vacuum-arc deposition process, however, the coatings show good results in wear resistance. During the test, there is no chipping, cracking or delamination of coatings, they have good adhesion. During abrasion the material of the coating is plastically deformed, and the observed pattern of wear is typical for soft metals. Abrasion tests have shown that the wear of the coatings after annealing compared with the initial coating is lower, and the depth of friction tracks is high, 3.6 mcm, and 2.1 mcm after annealing (see Figure 6).

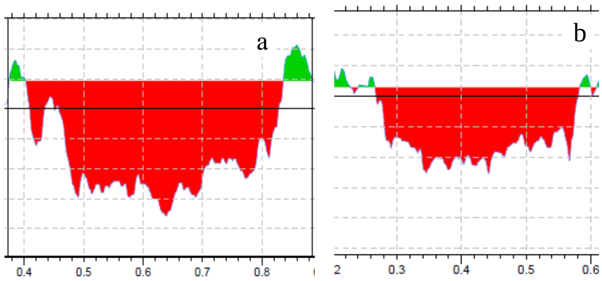

Fig. 6 – Wear depth profiles of the wear tracks of the coating (TiNbCrZrSi)N under the load 6.0 N: a) No 752 initial; b) No 752/2 after annealing

The images wear their products and their elemental composition after annealing are shown in Table 4 and Figure 6. Investigation of the element analysis of the wear products indicates the presence of alumina oxides, as well as the atoms of the elements, which compound the coating, namely: Ti, Cr, Zr, Nb, Si, and iron.

Table 4 – Elemental composition of wear products

Coating	Concentration of the elements, at. %								
	N	O	Al	Si	Zr	Nb	Ti	Cr	Fe
751		30.5	1.0	2.5	6.1	3.3	19.7	5.7	31.4
752	10.7	16.4	3.1	2.7	7.8	4.1	30.9	10.1	14.2

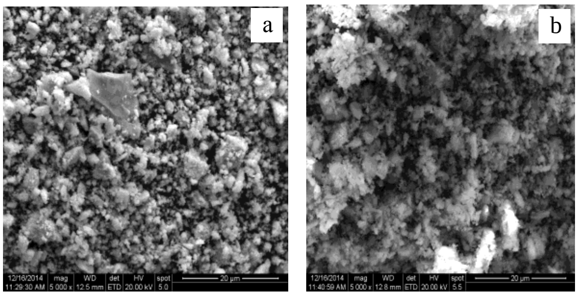

Fig. 7 – The image of the wear products of the coatings after the tests: a) No 751/1; b) No 752/2

This result indicates that, under these conditions, the friction is caused not only by transfer of the material, but also by the interaction of the surrounding atmosphere with the sliding surfaces, activited by the friction energy. The processes of tribomechanical oxidation are also important at sliding of dry surfaces of Al_2O_3 over the coatings in the atmosphere of air.

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4. SUMMARY

1. The coatings (TiZrCrNbSi)N were obtained by means of vacuum-arc sputtering of (TiZrCrNbSi) material in reaction medium.
2. It was shown, that nitride nanostructured coatings include only one phase of solid colution with fcc- lattice of NaCl structural type with preferred orientation (111).
3. The hardness of the coatings is in a range of 17 to 24 GP depending on physical deposition parameters.
4. Annealing of the coatings (TiZrCrNbSi)N at $T = 700$ °C hasn't changed phase composition of the coatings.
5. The tribological characteristics of the coatings obtained at bias potential $U_b = -100$ V and $U_b = -200$ V and partial presure of nitrogen $P = 3{,}5 \times 10^{-3}$ Torr before and after annealing have been studied.
6. It was detected that wear resistance (wear factor) of the coatings after annealing was $1{,}03 \times 10^{-5}$ mm$^3 \times$ $\times$ N$^{-1} \times$ m^{-1} has increased in regards with wear factor before annealing $7{,}8 \times 10^{-5}$ mm$^3 \times$ N$^{-1} \times$ m^{-1}.

Триботехнічні характеристики багатоелементних покриттів на основі нітридів Ti, Zr, Cr, Nb, Si, отриманих за допомогою вакуумно-дугових методів осадження

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В роботі були вивчені фрикційні властивості багатокомпонентних нанокомпозитних покриттів за допомогою трибометричного методу. Наноструктуровані нітридні покриття складаються з фази твердого розчину ГЦК-типу та фази типу NaCl з переважною (111) орієнтацією. Також був вивчений вплив температури відпалу на трибологічні характеристики. Зносостійкість після термообробки зменшується з 7.8×10^{-5} мм$^3 \times$ N$^{-1} \times$ м$^{-1}$ до 1.03×10^{-5} мм$^3 \times$ N$^{-1} \times$ м$^{-1}$.

Ключові слова: Метод вакуум-плазмового осадження, Нанокомпозити, Нітриди тугоплавких металів, Трибологічні характеристики.

Триботехнические характеристики многоэлементных покрытий на основе нитридов Ti, Zr, Cr, Nb, Si, полученных с помощью вакуумно-дуговых методов осаждения

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В работе были изучены фрикционные свойства многокомпонентных нанокомпозитных покрытий трибометрическим методом. Наноструктурированные нитридные покрытия состоят из фазы твердого раствора ГЦК-типа и фазы типа NaCl с подавляющей (111) ориентацией. Также было изучено влияние температуры отжига на трибологические характеристики. Износостойкость после термообработки уменьшается с 7.8×10^{-5} мм$^3 \times$ N$^{-1} \times$ м$^{-1}$ до 1.03×10^{-5} мм$^3 \times$ N$^{-1} \times$ м$^{-1}$.

Ключевые слова: Метод вакуум-плазменного осаждения, Нанокомпозиты, Нитриды тугоплавких металлов, Трибологические характеристики.

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