

STRUCTURE AND PHYSICAL AND MECHANICAL PROPERTIES OF NANOCOMPOSITE COATINGS OF THE SYSTEM (Zr-Ti-Cr-Nb)N, OBTAINED BY VACUUM-ARC EVAPORATION METHOD

*I.N. Toryanik¹, V.M. Beresnev^{1,5}, I.V. Serduyk³, A.D. Pogrebnyak²,
O.V. Sobol⁴, O.A. Druchinina⁶, M.G. Kovalyova⁶, P.V. Turbin^{1,5},
U.S. Nyemchenko¹, D.A. Kolesnikov⁶, A.E. Dmytrenko³*

¹*Karazin Kharkiv National University, Kharkiv, Ukraine;*

²*Sumy National University, Sumy, Ukraine;*

³*National Scientific Centre «Kharkov Institute of Physics and Technology»,
Kharkov, Ukraine;*

⁴*National Technical University «Kharkov Polytechnical Institute», Kharkov, Ukraine;*

⁵*Scientific Center of Physical Technologies, Kharkov, Ukraine,*

E-mail: turbin-scpt@yandex.ru;

⁶*Belgorod State National University, Belgorod, Russia*

Nanocomposite coatings of the system (Zr-Ti-Cr-Nb)N were obtained by vacuum-arc evaporation of a unit-cast cathode with the use of pulse stimulation. The structure of the coatings is characterized by the size of crystallites of 5 - 10 nm. Increased bias potential leads to more intense nitride formation thus increasing the relative content of Cr and Ti atoms and improving the hardness up to 4500 HV_{0.1} GPa. Sclerometry studies showed high adhesive strength, which in combination with high hardness makes them promising for use as protective coatings for cutting tool.

INTRODUCTION

Protective coatings are an effective means of increasing the productivity and durability of functional materials. Due to the high mechanical properties and thermal stability, the protective layer can maintain the functionality of tools in severe operating conditions for a long time. Protective coatings were designed for providing high hardness of material on its surface, low friction coefficient, oxidation resistance and wear resistance. [1-3].

One of the most called-for materials among those which are widely used for the formation of protective coatings, are nitrides of transition metals which perform one of the best complex of their properties. Among the binary systems of the nitrides, titanium nitride (TiN) is the most widely used material due to its high mechanical properties and corrosion resistance [4].

In the last decade the titanium-aluminum nitride (Ti_{1-x}Al_xN) has got the wide application. It increases hardness and durability of the cutting tool in high-speed machining. Besides, the addition of aluminum in the coating composition leads to the increased oxidation resistance in the temperature interval of 500 °C to 800 °C, due to formation of resistant layer of aluminum oxide on the surface [5]. Adding such elements as chromium or zirconium in order to form a ternary systems, leads to the positive effects in improving the functional properties of the coatings [6, 7]. Thus, the transition from the two-element coatings to the more complex ones by means of doping by the elements of the transition metals is the effective way to significantly change the functional properties of the coating.

The next step in the universalization of properties of the obtained nitride materials is the use of four- and five-component coating systems in which there are 3 and 4 transition metal components respectively, and the nitro-

gen as a component of the filling, stimulating strong covalent bonds [8]. The most frequently used vacuum-plasma methods, used for obtaining the mentioned systems of coatings are the following: vacuum-arc deposition, magnetron sputtering [8, 9].

The aim of this paper is to study the regularities of the structure formation of multi-component coating of the system (Zr-Ti-Cr-Nb)N and the investigation of their physical and mechanical characteristics.

EQUIPMENT AND METHODES OF INVESTIGATION

As a method of obtaining coatings of (Zr-Ti-Cr-Nb)N system, the vacuum-arc evaporation method was used. The unit-cast cathode Zr+Ti+Cr+Nb with the composition: Ti – 12.32 at.%, Zr – 27.99 at. %, Cr – 37.39 at.%, Nb – 22.30 at.%, was used as a vaporized material. The cathode was made by electron-beam melting method. Coatings were deposited in the installation “BULAT-6” in the atmosphere of molecular nitrogen on the polished surface of the steel 45 substrate as well as on the surface of the silicon substrate.

Table 1 shows the physical and technological parameters of obtaining the coatings based on (Zr-Ti-Cr-Nb)N system.

The thickness of the coatings, the state of the boundaries between the substrate and the coating and the surface morphology were investigated by means of scanning electron microscope FEI Quanta 600 FEG. The X-ray diffraction studies of the coated samples were held using DRON-4 diffractometer in Cu- k_{α} radiation. The analysis of the surface topography of the coatings was performed additionally by means of atomic force microscope NT-MDT, Russia, in the atmosphere of air. Si-cantilevers NSG10/W2C with a solid current-conductive W₂C coating with a thickness of 30 nm were

used. The thickness of the coatings was ~ 7.0 microns. Study mechanical characteristics (hardness) of the layers of the coatings was carried out on DM-8 hardness tester.

Table 1
Physical and technological parameters obtaining the coatings based on (Zr-Ti-Cr-Nb)N system

Evaporated material	Coatings	I_a , A	P_N , Pa	U_{cm} , V	Series No
Zr+Ti+Cr+Nb	(ZrTiCrNb)N	110	0.3	-100	1
Zr+Ti+Cr+Nb	(ZrTiCrNb)N	110	0.7	-100	2
Zr+Ti+Cr+Nb	(ZrTiCrNb)N	110	0.3	-200	3
Zr+Ti+Cr+Nb	(ZrTiCrNb)N	110	0.7	-200	4
Zr+Ti+Cr+Nb	(ZrTiCrNb)N	110	0.7	-200	5*

*Pulse stimulation was used

EXPERIMENTAL RESULTS AND DISCUSSION

The results of research of elemental composition of the coatings based on the system (Zr-Ti-Cr-Nb)N as a function of the physical and technological deposition parameters are given in Table 2.

Table 2
The results of energy dispersion analysis for the coatings based on the system (Zr-Ti-Cr-Nb)N

Series No	Elemental composition of the coatings, at.%			
	Zr	Ti	Cr	Nb
	27.99	12.32	37.39	22.30
1	27.87	13.47	14.89	43.77
2	23.55	12.07	14.82	49.56
3	18.54	25.73	36.95	18.78
4	20.74	28.15	31.27	19.84

Fig. 1 shows the XRD spectra of the coatings. The lattice is cubic, structure type NaCl. The results of the structural conditions of the obtained coatings are shown in Table 3.

As can be seen from the Table 3, with increasing the values of the bias potential applied to the substrate, the size of the crystallites (L) increases.

The analysis held on the basis of the data from the Table 2 indicates a significant dependence of the composition of the coatings on the bias potential applied to the substrate, i.e. due to the bias potential the energy of the sputtered particles increases, which leads to higher radiation component while the formation of structure of the coatings. Thus, the increase of the bias potential to -200 V leads to an increase of the strong nitrides forming components of Ti and Cr, as well to an increase of content of the nitrogen atoms.

The direct studies of the structure of the obtained coatings based on (Zr-Ti-Cr-Nb)N system were carried out by using an electron microscope Jeol Jem-2100. Fig. 2 shows an electron microscopic image of the coatings based on (Zr-Ti-Cr-Nb)N system. It can be seen that the formed crystal structure is very finely dispersed, which corresponds to the results presented in Table 3.

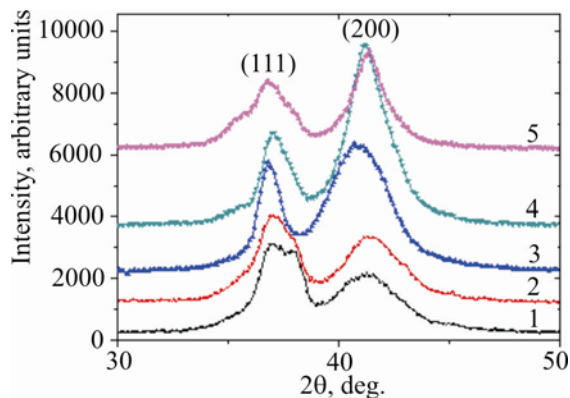


Fig. 1. Parts of diffraction spectra of the condensate (Zr-Ti-Cr-Nb)N, deposited by vacuum-arc method:

1 – $P = 0.3$ Pa, $U_b = -100$ V;

2 – $P = 0.7$ Pa, $U_b = -100$ V;

3 – $P = 0.3$ Pa, $U_b = -200$ V;

4 – $P = 0.7$ Pa, $U_b = -200$ V;

5 – $P = 0.7$ Pa, $U_b = -200$ V (pulse stimulation)

Table 3
The crystallite size (L) and the lattice constant (a) of the coatings based on the system (Zr-Ti-Cr-Nb)N

Parameters	Series No.				
	1	2	3	4	5
L , nm	4.5	5.2	5.1	6.9	7.3
a , nm	0.4359	0.4365	0.441	0.4381	0.4371

Hardness, as the most revealing mechanical characteristic of the coatings based on (Zr-Ti-Cr-Nb)N system is given in Table 4. The imprints were made at the distance of 1.0 mm between each other, 10 measurements were held for each sample. In order to reduce the impact of droplet component and in order to measure the hardness of the coatings more accurately, part of the coatings had been polished after deposition.

The adhesive properties of the coatings were determined by the scratch tester REVETEST (CSM Instruments). For this the scratches were made on the surface of the coated samples at continuously increasing load by means of the diamond spherical indenter "Rockwell C" type with a radius of curvature of 200 μ m and the following physical parameters were registered: acoustic emission, coefficient of friction and the depth of penetration of the indenter. To obtain the reliable results, two scratches on the surface of the coating were made. The substrates for the deposition of the coatings were steel 18Cr10NiTi cylinders with the diameter of 30.0 mm, and the height of 5.0 mm. The coatings of (Zr-Ti-Cr-Nb)N system were deposited on their polished surface. The thickness of the coatings was 6.2 μ m.

The following critical loads changing the coefficient of friction and acoustic emission curves from the scribing load: L_{C1} – characterizes the time of occurrence of the first chevron crack; L_{C2} – the moment of the appearance of chevron cracks; L_{C3} – the destruction has cohesive and adhesive nature; L_{C4} – local flaking of the areas of the coating; L_{C5} – plastic abrasion of the coating to the substrate.

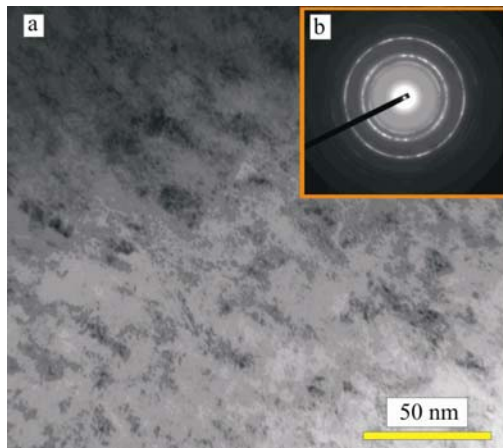


Fig. 2. Electron microscopy image of the coatings of the system (Zr-Ti-Cr-Nb)N: a – bright field image of the microstructure of the coating; b – microdiffraction image

Table 4
The results of hardness measuring for the coatings based on the system (Zr-Ti-Cr-Nb)N

Series No	Hardness, HV _{0.1} GPa	Note
1	3093	Coatings were not polished
1	3652	Coatings were polished
2	3478	Coatings were not polished
3	3886	Coatings were not polished
3	3996	Coatings were polished
4	4393	Coatings were polished
5	4457	Coatings were polished

Table 5 shows the results of adhesion tests of the coated samples, obtained at different technological deposition parameters. After the deposition of the coatings in order to reduce the influence of the droplet constituents, the coatings were polished. For comparison, the samples coated by TiN, obtained by the vacuum-arc deposition method with the hardness of $H = 28.0$ GPa were taken.

Fig. 3 shows the curve of the change of the coefficient of friction (μ) when moving the diamond indenter on the surface of the coating of the (Zr-Ti-Cr-Nb)N system (sample 4), and the curve of change of the acoustic emission (AE).

As seen from the results shown in Fig. 3, the process of destruction of the coating when scratched by the diamond indenter can be conventionally divided into several stages. In the beginning the monotonous penetration of the indenter into the coating takes place, and the first cracks appear (load up to 15.21 N), the coefficient of friction (μ) is increasing, but the acoustic emission signal remains unchanged.

Subsequently, with the increased load, the appearance of chevron and diagonal cracks takes place [11, 12], which leads to increase of coefficient of friction to a value of 0.3. At a load of up to 14 N, the amplitude of the of the acoustic emission signal dramatically increases, and its value remains at the same level until the end of the test. After this, with the increase of the load reaching 62 N, there is a local abrasion of the coating down to the substrate material (Fig. 4).

Table 5
Comparative results of adhesion testing for the coatings based on the system (Zr-Ti-Cr-Nb)N and on the system TiN

Critical load	Series No					
	1	2	3	4	5	TiN
L_{C1}	10.9	11.8	10.3	15.2	9.4	21.3
L_{C2}	18.6	20.9	18.4	24.2	30.3	30.9
L_{C3}	26.9	30.3	23.1	33.4	34.3	40.2
L_{C4}	39.1	45.9	45.1	40.9	40.4	48.8
L_{C5}	49.0	56.1	61.0	62.0	58.2	-

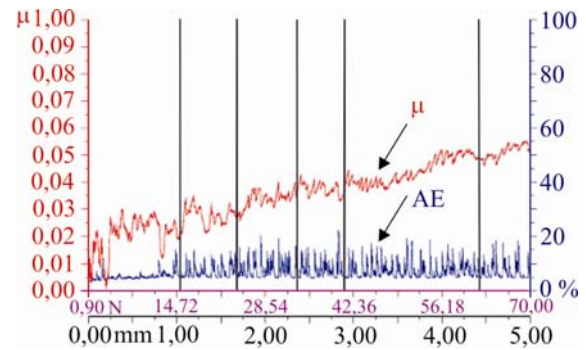


Fig. 3. The results of measurement of the friction coefficient and acoustic emission (sample 4), the length of the scribing path is represented in in millimeters

Comparative analysis shows that the coatings wear away when scratched, but no chalking takes place, i.e. they are destroyed following the cohesive mechanism which is associated with the plastic deformation and the formation of fatigue cracks in the coating material.

The work was performed by the authors in the framework of complex state-funded research works 0112U006974 and 0113U001079, funded by the Ministry of Education and Science of Ukraine. Part of the work is performed using the diagnostic equipment of the Center for collective use of scientific equipment of Belgorod State National Research University “Diagnostics of the structure and the properties of nanomaterials” of the Ministry of Education and Science of the Russian Federation.

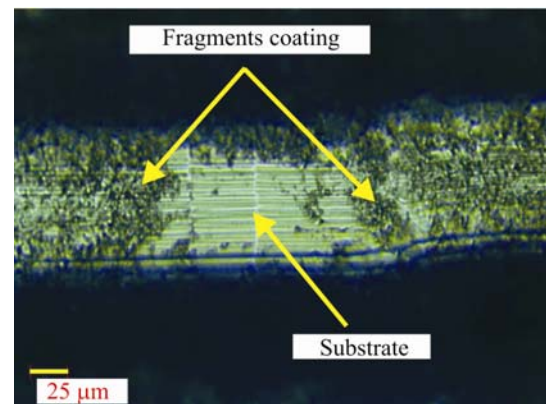


Fig. 4. Image of the remaining fragments of the coating on the bottom of the scratch after the influence of the diamond indenter

The authors are grateful to the collaborators from the National Science Center “Kharkov institute of physics

and technology”: to professor A.A. Andreyev and to senior researcher V.A. Stolbovoy for the assistance in preparing and carrying out the experiments and informative discussion of the results obtained.

SUMMARY

1. The coatings of the system (Zr-Ti-Cr-Nb)N were obtained by means of evaporation of the unit-cast cathode in the nitrogen medium using the vacuum-arc method.

2. Crystallites of the coatings based on (Zr-Ti-Cr-Nb)N system are characterized by an average size of 5...10 nm, depending on the deposition parameters.

3. The hardness of the obtained coatings reaches the value of 4457 HV_{0,1} GPa.

4. The coatings exhibit high adhesion strength and are characterized by cohesion mechanism of destruction during the testing.

5. By physical and mechanical properties, the obtained coatings of the system (Zr-Ti-Cr-Nb)N have shown themselves as promising for using them as protective coatings for cutting tools.

REFERENCES

1. *Nanostructured coatings* // Edited by A. Kavaleiro and D. de Hossona. M.: «Technosphere», 2011, 792 p.

2. E.V. Berlin, L.A. Seydman. *Ion-plasma processes in thin film technology*. M.: «Technosphere», 2010, 528 p.

3. N.A. Azarenkov, O.V. Sobol, A.D. Pogrebnyak, S.V. Lytovchenko, O.N. Ivanov. *Material Science of nonequilibrium state of the modified surface*. Sumy: «Sumy State University», 2012, 683 p.

4. G.V. Samsonov, I.M. Vinnitskiy. *Refractory compounds*. M.: «Metallurgy», 1976, 530 p.

5. T. Ikeda, H. Satoh. Phase formation and characterization of hard coatings in the Ti-Al-N system prepared by the cathodic arc ion plating method // *Thin Solid Films*. 1991, v. 195, p. 99-110.

6. M.V. Goltsev, S.V. Gusakova. Ion-plasma coatings based on triple nitrides of refractory compounds // *Newsletter BelGU*. 2008, v. 1, N 2, p. 15-18.

7. 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 multicomponent nitrides // *Metal physics and modern technologies*. 2013, v. 35, N 8, p. 1001-1024.

8. I.I. Aksenov, A.A. Andreyev, V.A. Bilous, V.E. Strelnitsky, V.M. Khoroshikh. *Vacuum arc: plasma sources, coatings deposition, surface modification*. Kyiv: «Scientific thought», 2012, 727 p.

9. N.A. Azarenkov, O.V. Sobol, A.D. Pogrebnyak, V.M. Beresnev. *Vacuum-plasma coatings engineering*. Kharkiv: Karazin Kharkiv National University, 2011, 344 p.

10. D.V. Shtansky, A.N. Sheveiko, M.I. Petrzhik, F.V. Kiryukhantsev-Korneev, E.A. Levashov, A. Leyland, A.L. Yerokhin, A. Matthews. Hard tribological Ti-B-N, Ti-Cr-B-N, Ti-Si-B-N and Ti-Al-Si-B-N coatings // *Surface and Coatings Technology*. 2005, v. 200, p. 208-212.

11. D.V. Shtansky, M.I. Petrzhik, I.A. Bashkova, F.V. Kiryukhantsev-Korneev, A.N. Sheveyko, E.A. Levashov. Adhesion, friction and deformation characteristics of the coatings Ti-(Ca, Zr)-(C, N, O, P) for orthopedic and teeth implants // *Solid State Physics*. 2006, v. 46, issue 7, p. 1231-1238.

Article received 25.09.2013

СТРУКТУРА И ФИЗИКО-МЕХАНИЧЕСКИЕ СВОЙСТВА НАНОКОМПОЗИТНЫХ ПОКРЫТИЙ СИСТЕМЫ (Zr-Ti-Cr-Nb)N, ПОЛУЧЕННЫХ МЕТОДОМ ВАКУУМНО-ДУГОВОГО ИСПАРЕНИЯ И.Н. Торьяник, В.М. Береснев, И.В. Сердюк, А.Д. Погребняк, О.В. Соболев, О.А. Дручинина, М.Г. Ковалева, П.В. Турбин, У.С. Немченко, Д.А. Колесников, А.Е. Дмитренко

Методом вакуумно-дугового испарения цельнолитого катода с применением импульсной стимуляции получены нанокomпозитные покрытия системы (Zr-Ti-Cr-Nb)N. Структура покрытий характеризуется размером кристаллитов 5...10 нм. Увеличение потенциала смещения приводит к более интенсивному нитридообразованию, увеличивая относительное содержание атомов Ti и Cr и повышая твердость до 4500 HV_{0,1} ГПа. Склерометрические исследования показали высокую адгезионную прочность, что в комплексе с высокой твердостью обуславливает перспективное применение покрытий в качестве защитных для режущего инструмента.

СТРУКТУРА І ФІЗИКО-МЕХАНІЧНІ ВЛАСТИВОСТІ НАНОКОМПОЗИТНИХ ПОКРИТТІВ СИСТЕМИ (Zr-Ti-Cr-Nb)N, ОТРИМАНИХ МЕТОДОМ ВАКУУМНО-ДУГОВОГО ВИПАРОВУВАННЯ

І.М. Торьяник, В.М. Береснев, І.В. Сердюк, О.Д. Погребняк, О.В. Соболев, О.О. Дручиніна, М.Г. Ковальова, П.В. Турбін, У.С. Немченко, Д.О. Колесніков, О.Є. Дмитренко

Методом вакуумно-дугового випаровування суцільнолитого катода із застосуванням імпульсної стимуляції отримані нанокomпозитні покриття системи (Zr-Ti-Cr-Nb)N. Структура покриттів характеризується розміром кристалітів 5...10 нм. Підвищення потенціалу зсуву призводить до більш інтенсивного нітридоутворення, при цьому збільшуючи відносний вміст атомів Ti та Cr і підвищуючи твердість до 4500 HV_{0,1} ГПа. Склерометричні дослідження показали високу адгезійну міцність, що у комплексі з високою твердістю обусловлює перспективне застосування покриттів у якості захисних для різального інструменту.