

Adhesion Strength of Multi-element Coatings of the System (TiNbCrZrSi)N

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The mechanical characteristics of the multi-element coatings (TiNbCrZrSi)N have been studied depending on the deposition process parameters, in particular the bias potential. X-ray diffraction spectra has shown, that the coating is formed on the basis of single-phase state of the fcc lattice, which in the case of nitrides has structural type NaCl. Hardness and elastic modulus of the coating (TiNbCrZrSi)N varies from $H = 24$ GPa and $E = 254$ GPa to $H = 28.9$ GPa and $E = 291$ GPa. Coatings' index of resistance to plastic deformation (H^3/E^2) has a value of 0.28.

Keywords: Multi-element nitride coatings, Adhesion strength, Hardness, Elastic modulus.

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1. INTRODUCTION

Functional characteristics of ion-plasma coatings, formed during the deposition process, depend on structure, phase composition and chemical composition, as well as on the adhesive and cohesive properties of the coatings. Literature data [1-3] show, that in order to obtain high adhesive strength of the coating to the substrate, it is necessary to provide a chemical reaction on the borderline of the two contacting surfaces "coating-substrate". This can be achieved by activation of the substrate surface by applying a negative bias potential on the substrate, which allows ion bombardment of the growing surface by the working gas ions and by the vaporized material ions [4, 5].

Currently, in order to improve the performance of cutting tools, friction joints and protect material against corrosion, multielement composite coatings, produced by various ion-plasma deposition techniques are used [6, 7]. Most studies are dedicated to the production of multielement coatings, as well as to the influence of physical and technological parameters of deposition on the structure, phase composition, hardness, and some of the studies are dedicated to the investigation of adhesion strength of multielement coatings.

In connection with this, the purpose of this study was to investigate the influence of physical and technological parameters of deposition on the adhesion strength of multielement coatings, obtained by vacuum-arc deposition method.

2. EXPERIMENT

Multielement coatings formed by vacuum-arc deposition method have been obtained on the "NNV 6.6 I-1" installation by spraying unit-cast cathodes obtained by vacuum-arc melting. Elemental composition of the cathode: Ti – 40 wt. %, Zr – 30 wt. %, Cr – 15 wt. %, Nb – 10 wt. %, Si – 5 wt. %.

Coatings were deposited on the polished surface of

the cylindrical steel samples X18H10T with the diameter of 32 mm and height of 5 mm. The influence of the bias potential on formation of the coatings has been studied. There were two series of samples of the coatings, obtained at $P = 3,5 \times 10^{-3}$ Torr: $U_b = -100$ V (Series 1); $U_b = -200$ V (Series 2). Before the deposition of the coatings, cyclic ion bombardment by metal ions of evaporated material at $P = 3 \times 10^{-5}$ Torr has been held, the potential, applied to the substrate was ~ 1100 V. The coating thickness was 6.2 mm.

In order to determine the adhesive/cohesive strength of the coatings and to determine the fracture mechanism, scratch tester Revetest (CSM Instruments) has been used. The moment of adhesive or cohesive failure was determined by means of sclerometry method (scratching), and was recorded after the test visually, using an optical microscope, equipped with a digital camera, as well as by the change the acoustic emission and the friction coefficient. As a result of testing, the minimum (critical) load L_c , which led to the failure, has been determined. To obtain reliable results, the test was carried out applying two scratches on each sample (see Fig. 1).

Microscopic studies of the coatings were conducted by means of electron-ion scanning microscope Quanta 200 3D. The phase composition of the coatings were analyzed by X-ray diffractometer DRON-4 in the radiation of $\text{CuK}\alpha$. The investigation of the hardness of the coatings was held by means of nanoindentation device Nanoindenter G200 (MES Systems, USA), using a triangular Berkovich diamond pyramid with a radius of curvature at the apex of about 20 nm. The study of the mechanical properties by means of nanoindentation was performed at a load of 10 mN with the depth of deformed layer of 110÷130 nm, which on one hand exceeds the surface layer more than one order of magnitude, enriched by the impurity atoms, and on the other hand has a value less than 0.1 times the thickness of the coating, when the influence of the substrate can be ignored.

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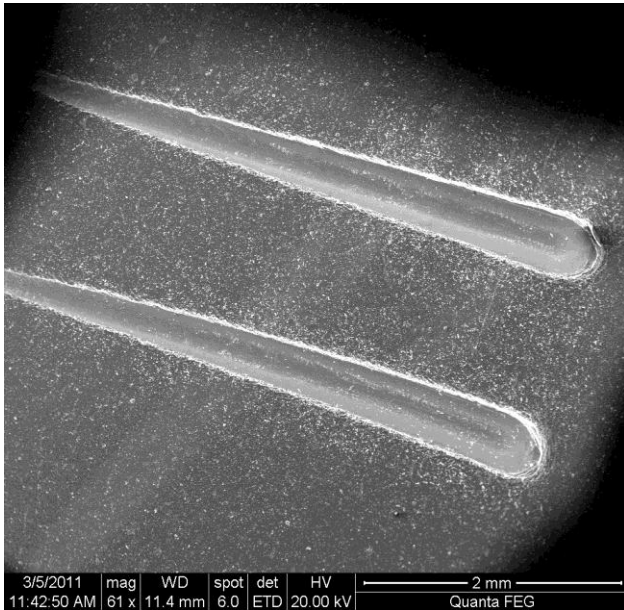


Fig. 1 – General view of the scratches on the surface of the coatings

3. RESULTS AND DISCUSSION

Results of the elemental analysis of the coatings (TiNbCrZrSi)N is shown in Table 1.

Coatings analysis shows, that the coating contains elements, which are a part of the cathode. The presence of uncontrolled impurity – carbon – is, obviously, linked with the residual gases in the working camera.

The results of X-ray analysis (Fig. 2) show, that despite the large number of components of metallic elements and different inclinations of the constituent elements to nitride formation, single-phase state is formed in the coatings on the basis of the fcc lattice, which in the case of nitrides has structural type NaCl. A characteristic feature of the obtained diffraction spectra is the presence of preferred orientation of crystallites, which is manifested in the X-ray diffraction spectra in the form of the relative change in the intensity of the diffraction peaks from different planes. Defined by Selyakov-Scherrer equation, the crystallite size also depends on the selected mode of deposition. The certain crystallite size in the coatings of Series 1 averaged of 11.5 nm in the direction of growth of crystallites with the [111] and 6.4 nm - in the direction of growth of the crystallites with [100] axis. Conditions for obtaining in other series lead to smaller crystallite size: in Series 2, the crystallite size in the direction of the [111] was 9.7 nm, and in the direction of crystallite growth with [100] axis it was 5.8 nm. The lattice parameter 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.

Thus, in Series 1 we obtained the coatings with the preferred crystallites orientation [111] with their size

Table 1 – Description of the special paragraph styles

Elements	Ti, % at.	Cr, % at.	Zr, % at.	Nb, % at.	Si, % at.	C, % at.	N, % at.
Series 1	34.5	10.7	12.0	3.3	2.1	2.1	35.3
Series 2	35.5	9.8	11.0	3.8	2.7	2.2	35.0

sufficiently large in this direction (11.5 nm) in the coating, under the action of high macrodeformation compression. In the case of Series 2, the change of the axis of preferred orientation to [100] is observed, a significant reduction in the average size of the crystallites in this direction to 5.1 nm and development of stretching macrodeformations. In this case, the transition to the tensile strain can be associated with a significant decrease in crystallite size and, thus, the increase in specific volume of the borders with disoriented structure, having a lower bulk density.

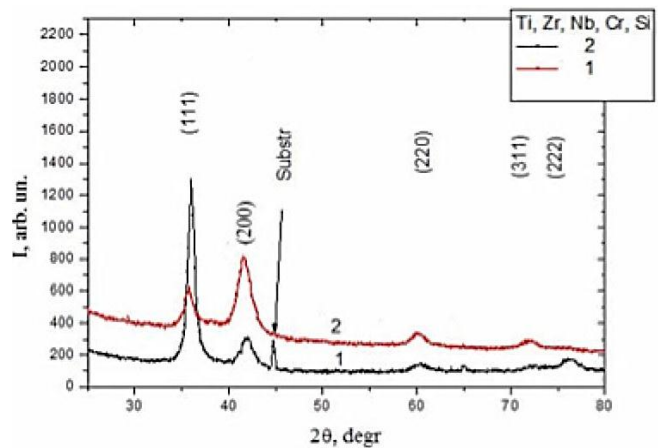


Fig. 2 – Areas of diffraction spectra of the coatings (TiNbCrZrSi)N, obtained under the following regimes: 1 – Series 1; 2 – Series 2

There are different ways to determine the critical load, at which the coating is destroyed. For example, in [8] Valli designated L_c as the normal load on the indenter, at which delamination of the coating takes place. Vercammen et al. [9] defined L_c as the normal load, at which the destruction of the primary coating takes place. However, for the interpretation of test results of the coatings, many researchers use the lower (L_{C1}) and upper (L_{C2}) critical loads, that characterize the adhesion strength. Lower critical load (L_{C1}) is the load, at which the primary coating destruction occurs, and the upper critical load (L_{C2}) is a load, at which the coating is completely peeled off from the substrate.

In this paper, we recorded the following major critical load curves to change the coefficient of friction and acoustic emission on the scribing load: L_{C1} is the moment of appearance of the first chevron cracks at the bottom of scratches; L_{C2} – the time of occurrence of chevron cracks at the bottom of scratches; L_{C3} – destruction has cohesively-adhesive character; L_{C4} – local flaking of the areas of the coating; L_{C5} – plastic abrasion of the coating to the substrate, loss of adhesion strength.

The dependence of change in the coefficient of friction, acoustic emission and load on the specimen, coated with (TiNbCrZrSi) N, for Series 1 and Series 2 are shown in Fig. 3.

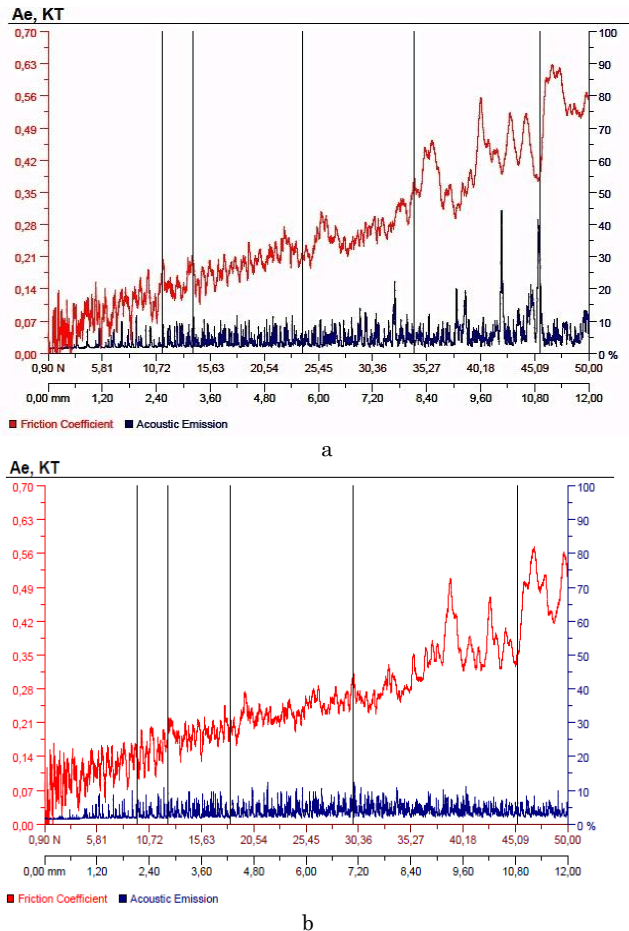


Fig. 3 – The dependence of the friction coefficient and acoustic emission on the load on the specimen, coated with (TiNbCrZrSi)N: a – Series 1, b – Series 2

Change of the acoustic emission signal at low loads is due to the presence of defects on the surface and in the surface region of the coatings, obtained by vacuum-arc deposition method.

When analyzing the surface of the coating of Series 1, it can be observed, that the load of 11 N (L_{C1}) corresponds to the appearance of the first cracks and chips (Fig. 4). This is confirmed by the beginning of the growth of the amplitude of the acoustic emission (Fig. 3). Initial abrasion of the coating occurs under load $L_{C3} = 24$ N (Fig. 4). Adhesive destruction and peeling of the coating is not observed until the load $L_{C5} = 46$ N (Fig. 4). When moving the indenter, squeezing of some volume of material occurs, which hinders its further movement, and this is the cause of growth of the friction coefficient to a maximum value of 0.63 (Fig. 3).

Topography of the scratches on the surface of the coating of the sample of Series 1 during the test on determination of the adhesive / cohesive strength is shown in Figure 4.

Similar results were obtained for the coating (TiNbCrZrSi)N of Series 2 (see Fig. 4b). Initial signal of the acoustic emission somewhat differs from the signal for coatings of Series 1, indicating minimal defects on the surface of the coating.

The appearance of the first chevron cracks is observed at load $L_{C2} = 9$ N (Fig. 4). With increasing load,

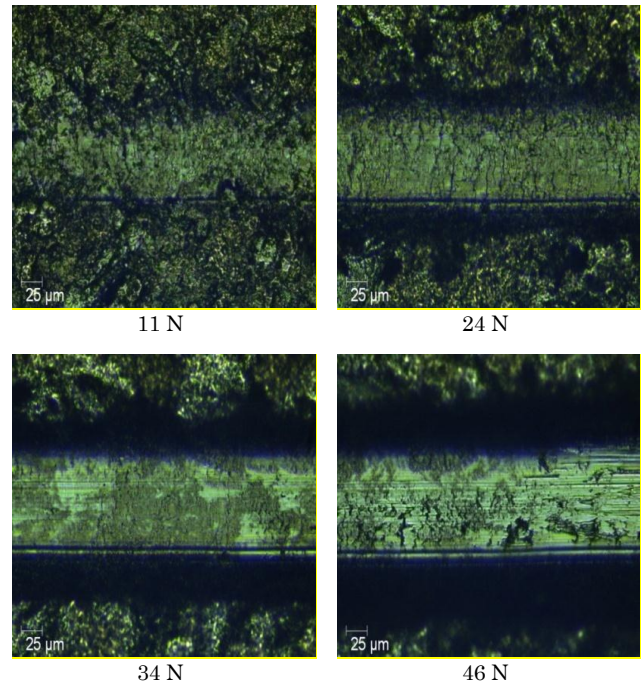


Fig. 4 – Photos of the scratches on the samples of coatings of Series 1 (TiNbCrZrSi) N under different loads on the indenter

the material of the coating starts to squeeze, new cracks appear, but chipping and flaking are not observed. With a load of 18 N, abrasion of the coating begins. Adhesion failure was not observed until the load of 45 N. As the plastic abrasion of the coating starts, friction increases, and at a load of 45 N, a sharp increase, accompanied by apparently rapid penetration of the indenter takes place, as well as the increase in the amplitude of the acoustic emission. This is due to the almost complete abrasion of the coating and reaching the substrate of the material, however, the study of the scratch indicates, that on the bottom of the scratch, the coated areas are observed. Adhesion failure is not observed up until the load of 45 N. The coefficient of friction reaches a value of 0.59.

For multicomponent coatings of Series 2, adhesion strength at different intervals of the experiment are significantly different from those of the samples of Series 1. With the increase of the load, noticeable cracks propagation on the surface of the coating does not occur. Based on the nature of the destruction, the main contribution seems to be by the shear stresses. Cohesive failure occurs through cracking in the plane, perpendicular to the direction of growth of the coating. The first signs of abrasion for the coating were recorded under a load of 18 N.

For comparison, test results for the adhesion strength of the coating of the system (TiNbCrZrSi)N with the coatings (TiHfSi)N and (TiZrSi)N, which were obtained by means of vacuum-arc deposition by cathode sputtering of unit-cast cathodes under the following physical and technological parameters: $P = 3.5 \times 10^{-3}$ Torr $U_b = -100$ V [10], are shown in Table 2. Comparative analysis demonstrates, that the coatings were worn during scratching, but did not peel off, i.e. the destruction occurs by cohesive mechanism, associated with the plastic deformation and formation of fatigue cracks in the material of the coating. [11]

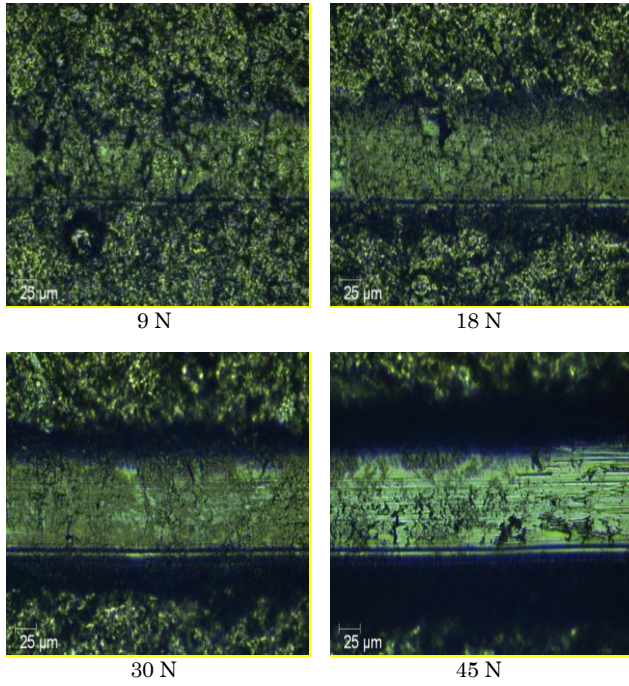


Fig. 5 – Photos of the areas of the scratches on the coated samples of Series 2 (TiNbCrZrSi)N under different loads on the indenter

Table 2 – Comparative results for the adhesive tests of the coatings

Critical loads	Coatings		
	(TiNbCrZrSi)N Series 1	(TiZrSi)N	(TiHfSi)N
L_{C1}	11	16	9
L_{C2}	14	21	12
L_{C3}	24	31	21
L_{C4}	34	40	30
L_{C5}	46	49	55

The difference in the adhesion strength of the coatings seems to be caused by the differences in their structure and mechanical properties.

The results of measurement of the hardness of the coatings, the elastic modulus, depending on the physical deposition parameters are shown in Table 3.

One of the parameters, that characterizes the structural state of the material is viscoplastic criterion [12], which for all the types of materials, studied in the bulk state, does not exceed 0.04 (for pure metallic materials). The results of the studies of the synthesized nitride coatings (Table 3) show, that the index of viscoplasticity H/E for all the investigated coatings is approximately 0.1, thus, approaching the maximum possible value of 0.14 – the amorphous state of the material.

Experiments have shown, that the resistance of the film to cracking increases with increasing the ratio

H^3/E^2 , which is proportional to the resistance to plastic deformation of the film [13].

Coatings (TiNbCrZrSi)N and (TiZrSi)N have smaller index of plastic deformation (H^3/E^2) – 0.28 and 0.31, compared with the coatings of the systems (TiHfSi)N (see Table 3) – 0.38.

Table 3 – Mechanical properties of the coatings, obtained by means of vacuum-arc deposition

Coatings	Hardness, N , GPa	Elastic Modulus E , GPa	H/E	H^3/E^2
(TiNbCrZrSi)N	28.9 ± 3.6	291 ± 34.7	~ 0.1	0.28
(TiZrSi)N	36.1 ± 1.2	391 ± 11	0.09	0.31
(TiHfSi)N	36.1 ± 1.2	383 ± 14	0.1	0.38

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4. SUMMARY

1. By means of vacuum-arc spraying method of the material (TiZrCrNbSi) in the reaction medium, the samples of the coatings (TiZrCrNbSi)N of two series have been obtained at $P = 3.5 \times 10^{-3}$ Torr: Series 1 at $U_b = -100$ V; Series 2 – at $U_b = -200$ V.

2. X-Ray spectra has shown, that the coating is formed on the basis of single-phase state of the fcc lattice, which in the case of nitrides has structural type NaCl. The lattice constant of the first series lies in the direction perpendicular to the plane of growth was 0.4332 nm, the value of macrodeformation compression – 1.69 %. The lattice constant of the second series was greater – 0.4337 nm

3. The effect of physical and technological parameters of deposition, in particular bias potential on nanohardness coatings has been studied. The hardness of the coatings of the system (TiNbCrZrSi)N, for the Series 1 was $H = 28.9$ GPa, $E = 291$ GPa; and for Series 2 $H = 24$ GPa, $E = 254$ GPa.

4. Adhesive strength of the coatings based on (TiNbCrZrSi)N, as compared with the coatings, based on system (TiZrSi)N and (TiHfSi)N was studied. Coatings (TiNbCrZrSi)N and (TiZrSi)N have lesser index of resistance to plastic deformation (H^3/E^2) – 0.28 and 0.31, compared with coatings of the systems (TiHfSi)N – 0.38.

Адгезионная прочность многоэлементных покрытий системы (TiNbCrZrSi)N

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Изучены механические характеристики многоэлементных покрытий (TiNbCrZrSi)N в зависимости от параметров процесса осаждения, в частности потенциала смещения. Спектры рентгеновской дифракции, показали, что покрытие формируется на основе однофазной ГЦК решетки, которое в случае нитридов имеет структуру типа NaCl. Твердость и модуль упругости покрытия (TiNbCrZrSi)N изменяется от $H = 24$ ГПа и $E = 254$ ГПа до $H = 28,9$ ГПа и $E = 291$ ГПа. Коэффициент сопротивления пластической деформации (H^3/E^2) имеет значение 0,28.

Ключевые слова: Многоэлементные нитридные покрытия, Адгезионная прочность, Твердость, Модуль упругости.

Адгезійна міцність багатоелементних покриттів системи (TiNbCrZrSi)N

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Вивчено механічні характеристики багатоелементних покриттів (TiNbCrZrSi)N у залежності від параметрів процесу осадження, зокрема потенціалу зсуву. Спектри рентгеновської дифракції, показали, що покриття формується на основі однофазної ГЦК решітки, яке у разі нитридів має структуру типу NaCl. Твердість і модуль пружності покриття (TiNbCrZrSi)N змінюється від $H = 24$ ГПа і $E = 254$ ГПа до $H = 28,9$ ГПа і $E = 291$ ГПа. Коefіцієнт опору пластичної деформації (H^3/E^2) становить 0,28.

Ключові слова: Багатоелементні нитридні покриття, Адгезійна міцність, Твердість, Модуль пружності.

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