PHYSICAL AND MECHANICAL PROPERTIES RESEARCH OF HIGH ENTROPY (TI-ZR-NB)N COATINGS OBTAINED BY VACCUM-ARC DEPOSITION METHOD]

D.K. Yeskermessov[1]S.V. Plotnikov[1], A.D. Pogrebnjak[2], Yerokhina L.N.[1], , N.K. Yerdybaeva[1]

[1] D. Serikbayev East Kazakhstan State Technical University, Kazakhstan;

[2] Sumy State University, Ukraine.

Abstract

Purpose – the purpose of the work is studying of ion-plasma coatings formation particularities by multiple system sputtering based on Ti+Zr+Nb, and carrying out the analysis of obtained physical and mechanical coatings properties.

Methodology – the coatings were formed by vacuum arc deposition. Unit cast target (cathodes) was used on the basis of 30 atm. % Ti, 35 at. % Zr and 35 atm. % Nb as the vaporized materials. Molecular nitrogen was used as the working gas. The thickness of the coatings in the experiments was 4.0 microns. The surface morphology fractograph fracture, track friction were investigated in a scanning electron microscope JSM-6390 LV.

Originality/Value – the use of multicoatings based on carbides is very promising to ensure the high performance properties of the complex, nitrides and silicides of transition metals.

Findings – nanostructured coating of (Ti-Zr-Nb) N was obtained by vacuum arc evaporation cathode-cast in a nitrogen gas reaction medium. Multicomponent films have a pronounced columnar structure. Elemental composition was obtained by the vacuum arc deposition of coatings (Ti-Zr-Nb) N, depending on the physical parameters of the deposition process, in particular the pressure of the reaction gas nitrogen.

Keywords: superhard coatings, structure, wear, adhesion, nanostructure

1. INTRODUCTION

During the process of work the surface layer of machine elements and mechanisms are subjected to strong mechanical, heat and chemical influence. The loss of working functionality in most cases is the result of surface wear, erosion, corrosion, etc. Significant resource to increase the working operating capacity may be referred to material of which the details having been made. Due to this reason modern machine building pays great attention to tribotechnical material technology. To apply for this reason volumetric alloyed steel is often uneconomic and sometimes technologically non-profitable. However, the necessary results may be received by many functional coatings on working surfaces. They may simultaneously unite high hardness, wear resistance and heat endurance. For ensuring the complex of high working service property the usage of multielements coatings on the bases of carbides, borids, nitrides and silicides of transitional metals is rather perspective [1 – 4]. Stability and structure of composition, also high running quality of multicomponental elements of nitride systems make possible development of surface physic-mechanical characteristics and their application in the form of safety films protecting from ingress of contamination into subsurface of items layers [5, 6].

At present the most widely used are ion-plasmous techniques by film deposition coatings, in particular vacuum-arc and magnetron sputtering [7, 8].

We investigate the peculiarities of ion-plasma coatings by multielements system sputtering on the basis of Ti+Zr+Nb and we also perform analysis of physic-mechanical properties of the received coatings.

2. EXPERIMENTAL METHODOLOGY

The coatings have been made by vacuum-arc depositions. For vaporizing materials we use solid accumulation electrode (cathode) on the basis of system: 30 at. % Ti, 35 at. % Zr and 35 at. % Nb. For active gas we apply molecular nitrogen. The thickness of all coatings in our experiments was 4.0 μm. Deposition parameters are given in Table 1.

Table 1 Physic-technological deposition parameters of coatings on the basis of (Ti-Zr-Nb)N

# series	Vaporized material	I_∂, A	U_{sm}, B	P_N, Torr
1a	Ti+Zr+Nb	95	100	3×10^{-4}
1b	Ti+Zr+Nb	95	100	7×10^{-4}
1c	Ti+Zr+Nb	95	100	4×10^{-3}

Surface morphology of fractography break, friction tracks were under research on scanning electron microscope JSM-6390LV. The research of elements composition of coatings was conducted by methods of X-ray characteristic spectrum analysis generated by electron beam in scanning electron microscope. Time-resolved spectrum was read with the help of X-ray system energodispersion spectrometer PEGASUS firm EDAX, installed in microscope. X-ray structure research of samples with coatings were conducted on diffractometer DRON-4 in Cu-k_α radiation. The coatings hardness was determined with the help of hardness testing machine mode DM 8 according to micro-Vickers method with load on indenter 0.05 H. Adhesion-cohesion solidity, firmness to tracking and mechanism of coatings damages were under research in the air with the usage of scratch-tester Revetest (CSM Instruments). Tribological tests were conducted in the air according to scheme «ball-disk». As for friction machine we use «Tribometer», CSM Instruments. For this coatings were deposited on the surface of polished cylindrical samples (R_a = 0.088 μm), made of steel 45 (HRC = 55) diameter 42 mm, hight 5 mm. The coatings thickness comprised ~ 3.5 – 4.0 μm. For rider we use a ball 6.0 mm in diameter, made of sintered certified body - Al_2O_3. The load was 3.0 H, slide rate 10 sm/s. Tests correspond to international standards ASTM G99-959, DIN50324 and ISO 20808. The coatings wear groove structure and wear spots on balls were under research after tests using light optical inverted – stage microscope Olympus GX 51 and scanning ionic-electron microscope Quanta 200 3D. The quantitative evaluation of samples wear resistance and rider were conducted according to wear-out factor *W* [9], methodology of calculation was given in work [10].

3. RESULTS OF DISCUSSION

Image of surface coatings and also fractography break are shown on Fig.1

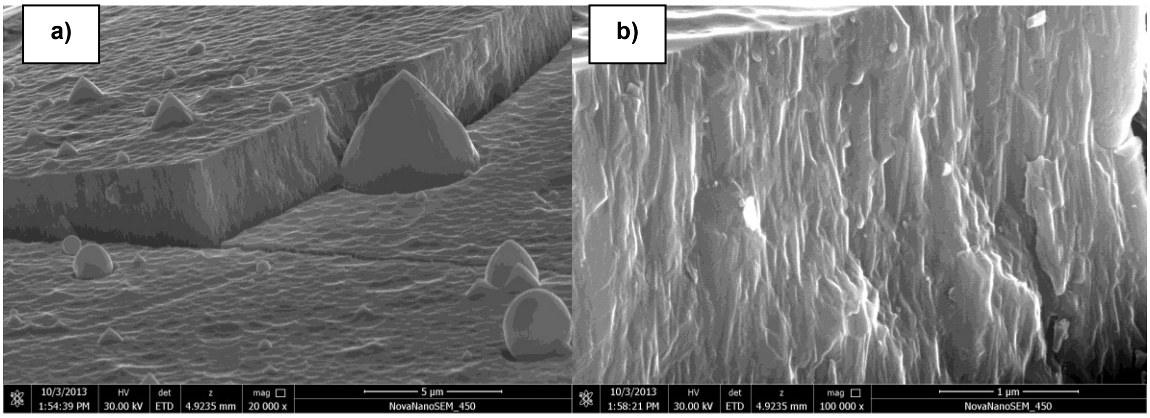

Fig. 1 Image of coatings fractography break (Ti-Zr-Nb)N, received at nitrogen partial pressure: a – P = 4×10^{-3} Torr.; b – magnified image of coating part

P = 4×10^{-3} Torr

The research of surface morphology points that the pressure increase by nitric agent reaction leads to lessening of macroparticles quality and diameter.

That is particularly significant in active gases vacuum chamber forming with evaporated material refractory compounds [11]. We also observe the coating roughness lowering.

Coating element composition received by vacuum-arc deposition method was analyzed by energy dispersed method. (Table 2).

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

# series	Composition of elements, at. %			
	N	Ti	Zr	Nb
a	38.72	20.91	20.38	19.99
b	40.00	22.57	18.04	19.39
c	40.86	20.52	19.36	19.26

If to compare elements composition of coatings series *b* and *c*, we can see that the first series samples the number of nitrogen atoms practically is equal. For samples *c* series, received at more higher pressure of N_2 atmosphere, the significant increase of zirconium atoms is noticeable, also several decrease of titanium atoms part. While this the niobium atoms for both series samples is actually the same. The increase of titanium atoms content in condensate of *b* series is possibly explained by more effective interaction of titanium atoms with nitrogen in subsurface layers.

The research of surface coatings fractography break (Fig. 1), received at different nitrogen partial pressure, testifies the formation of columnar structure (Fig. 1b), characteristic for coatings received by vacuum-arch precipitation method.

X-ray diffractometrical spectrum analysis presented on Fig.2 shows that the determining phase composition is phase with face-centered cubic alloy with crystal lattice. Low-intensity peak in section 2θ = 38° testifies the minor inclusion presence with BCC lattice characteristic while vacuum-arch method for drip-feed stage [12].

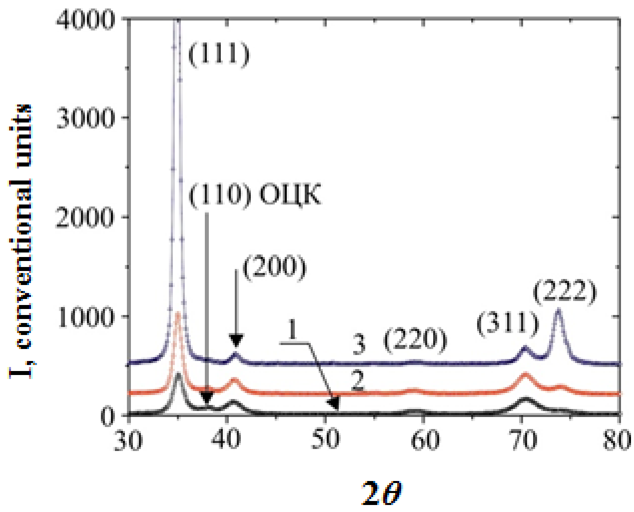

Fig. 2 Sections of X-ray diffraction spectrums coatings received at different nitrogen partial pressures: curve 1 – P = $3 \cdot 10^{-4}$ Torr; 2 – P = $7 \cdot 10^{-4}$ Torr; 3 – P = $4 \cdot 10^{-3}$ Torr; indicated planes of GCC lattice

It should be marked that with pressure increase the peak intensity becomes lower (ibid. spectrum 1 and 3 on Fig. 2), it may be determined by significant decrease of drip-feed phase in coating and correlate with results of surface research. The set of planes {111} increase is a characteristic feature that is determined by perfection increase of preferred crystal growth orientation with axis [111] perpendicular to surface flatness.

The crystal size determined by approximation method with increase of pressure grows from 10 nm at lowest pressure $3 \cdot 10^{-4}$ Torr up to 63 nm at highest nitrogen work pressure $4 \cdot 10^{-3}$ Torr.

Adhesive-corrosion solidity research, endurance to coating tracking are given on Figures 3 – 4. Based on friction coefficient modification graph and acoustics emission from scribing load we determine the following critical loads: L_{C1} – the appearance of first chevron crack on the bottom and diagonal on the sides of tracking; L_{C2} –chevron cracks lots formation at the bottom of scratch and local chalking of coating, formation of chevron cracks at the bottom of scratch; L_{C3} – cohesive adhesive coating demolishing; L_{C4} – plastic abrasion of coating.

For criteria of adhesive firmness we adopt the critical load L_{C4}, leading to coating abrasion. Fig. 3 presents the dependence of friction coefficient and acoustic emission signal from applied load while *c* test samples scratch testing .

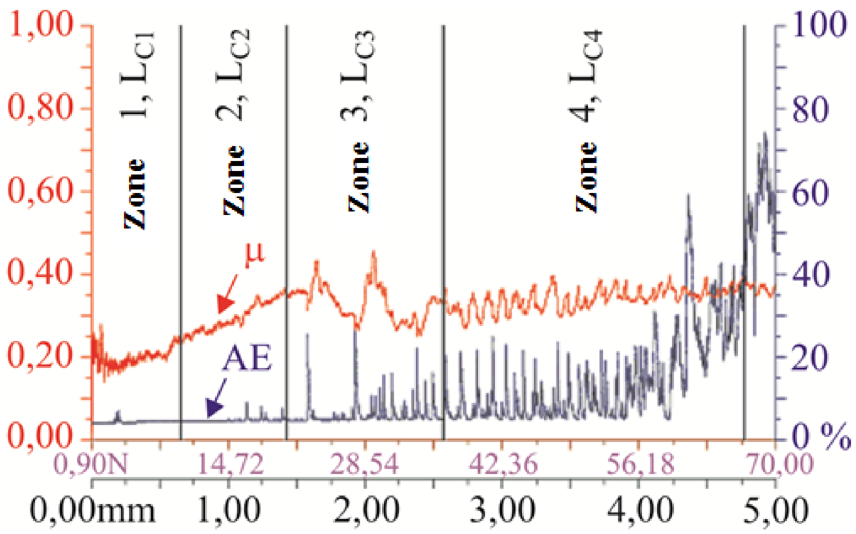

Fig. 3 Dependence of friction coefficient from applied load while coating (Ti-Zr-Nb)N scratch testing received at P = 4×10^{-3} Torr

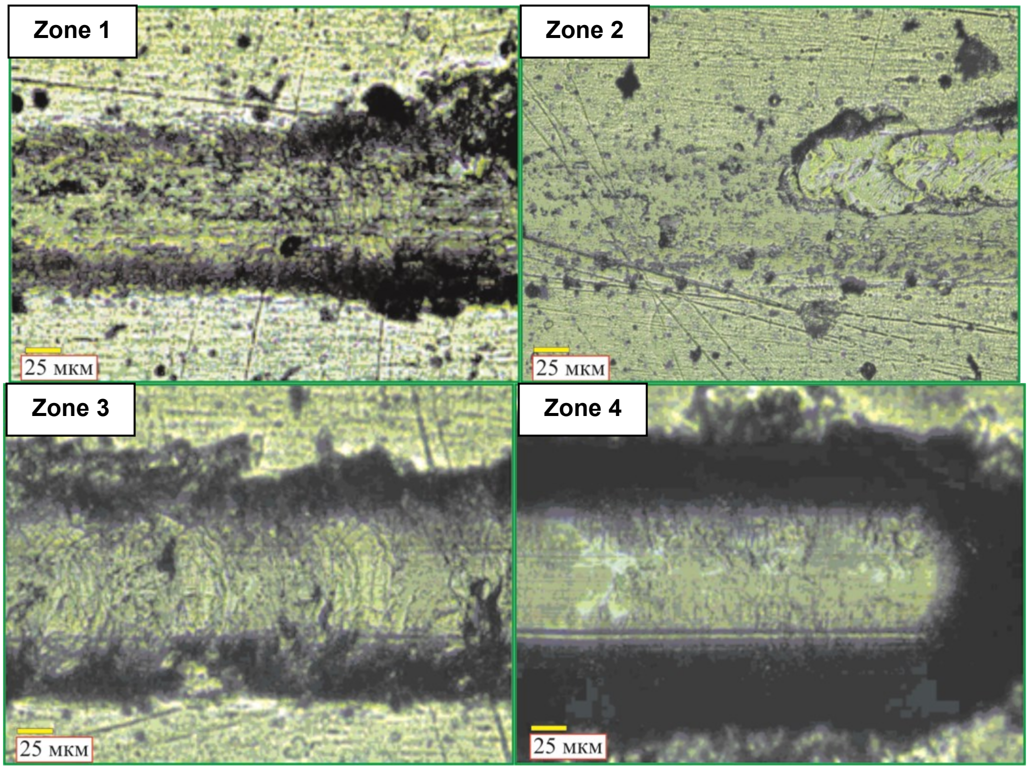

Fig. 4 Diamond indenter contact zones with (Ti-Zr-Nb)N coating

Conventionally the process of coating demolishing while indenter tracking may be divided into four stages. In the load range from *F* = 0,9 H up to *F* = 9.89 H indenter monotonous penetration comes into coating: friction coefficient slightly increases, acoustic emission signal preserved without changes At load *F* = 15.81 H indenter fully submerges into coating.. The sliding of diamond indenter along the coating has friction coefficient 0.35.

According to load increase (*F* = (20.6 – 36.4) H) runs out of stuff occurs in front of the indenter in the form of knob and increases the depth of indenter penetration.

Table 3 shows the samples test results with coatings (Zr-Ti-Nb)N comparing with coatings (Ti-Zr-Si)N and TiN received by us [13].

Table 3 Comparative results of adhesive coatings tests in systems (Zr-Ti-Nb)N and(Ti-Zr-Si)N, TiN

Crytical loads	Coatings				
	(Zr-Ti-Nb)N Series, a	(Zr-Ti-Nb)N Series, *b*	(Zr-Ti-Nb)N Series, c	(Ti-Zr-Si)N [12]	TiN [12]
L_{C1}	2.91	0.9	9.89	3.91	21.31
L_{C2}	29.04	15.82	20.62	18.15	30.91
L_{C3}	43.18	42.37	36.43	24.29	40.28
L_{C4}	59.26	66.24	66.77	43.15	48.84

According to research [14] while testing for adhesive solidity depending upon different meanings of critical loadings several physic-chemical processes are being carried out simultaneously while abrasion, however only L_C is directly connected with adhesive demolishing.

The most important problem in the field of protective overlayer is the increase of their physic-mechanical characteristics, in particular hardness, wear resistance, and that allows to increase the operating characteristics of different items. The results of mechanical characteristics measurements, in particular hardness, received for coatings (Zr-Ti-Nb)N are given in Table 4.

Table 4 Average values of coatings hardness on the system (Zr-Ti-Nb)N base

#series	hardness $HV_{0,05}$ GPa	Endnote
a	37.21	Forward flow
b	40.21	Forward flow
c	44.57	Forward flow

The way it may be seen from Table 4 maximum meaning of hardness H = 44.57 GPa was received at pressure of reactionary gas $P = 4\times10^{-3}$ Torr may be referred according classification [15], to superhard coatings with hardness $HV_{0.05} \geq 40$ GPa. Before the wearing tests profile record of steel disks surfaces on which coverings were overcoated were taken off.

Overcoatings of (Zr-Ti-Nb)N system on steel disk polished surface leads to roughness increase at the account of drip-feed component of plasma flow.

The average meaning of friction coefficient (μ) in system «covering – Al_2O_3» while tests comprises 1.1.

As it follows from Table 6, coverings of system (Zr-Ti-Nb)N, received at reaction gas pressure $P = 4\times10^{-3}$ Torr, possess hard constituency. On Figures 5 – 7 the pictures of friction track on coatings surface (Zr-Ti-Nb)N are given, and also the data of their energy dispersive analysis.

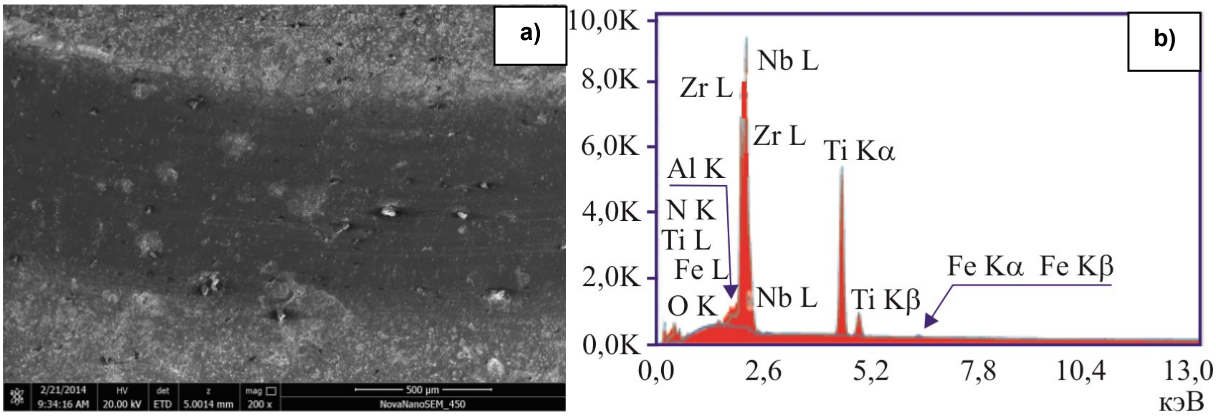

Fig. 5 Image of sample surface series *a* covering system (Zr-Ti-Nb)N, after tests: a – surface coating general view with friction track, b – chemical composition of friction track

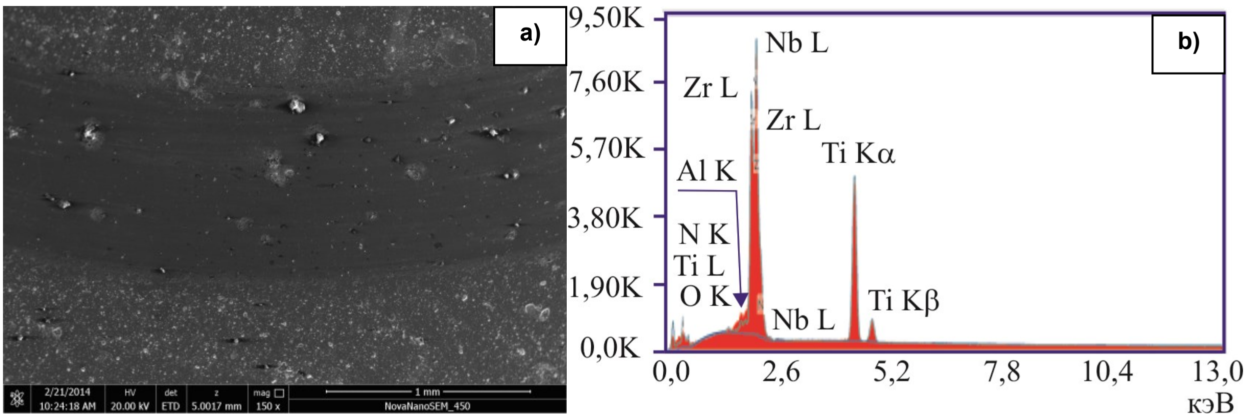

Fig. 6 – Image of sample surface series *b* covering system (Zr-Ti-Nb)N, after testing: a – surface general view with friction track, b– chemical composition of friction track

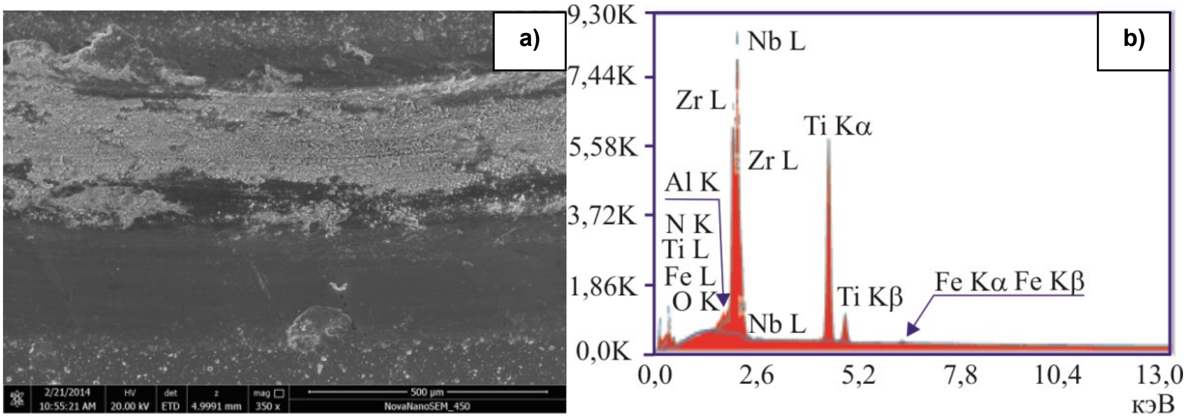

Fig. 7 – Image of sample surface series *c* covering system (Zr-Ti-Nb)N, after testing: a – surface general view with friction track, b– chemical composition of friction track

Tribological tests of samples with coatings are given in Table 5. Under the friction conditions being held in our experiments, sample with covering is in more heavy conditions of loading comparing with rider. Rider's surface – ball is under constant loading and constantly undergoes cyclic loading connected only with elastic joining, breaking of adhesion tires in the limits of separate micro areas of real contact one and the same area

Table 5 Tribological characteristics of covering system «covering (Zr-Ti-Nb)N – Al_2O_3»

#series	Friction coefficient, μ		Wear factor, $mm^3 \times H^{-1} \times m^{-1}$	
	Initial	During tests	Rider ($\times 10^{-5}$)	Sample ($\times 10^{-5}$)
a	0.61	1.95	0.391	9.69
b	0.45	1.19	2.84	3.1
c	0.491	1.05	3.21	2.4

Along disk circumference with coating an elastic wave may appear from interaction with rider- ball (every point on disk surface with covering with every rotation will rise and fall) while this processing into the process significantly grater volume of sample stuff matter with coating. Failure of covering occurs on wearing abrasive mechanism [16, 17].

The results of friction tracks elements' analysis are given in Table 6.

Table 6 Friction tracks of elements composition

#series of samples	elements, at. %							
	N	O	Al	Zr	Nb	Ti	Fe	Mn
a	41.5	11.58	0.28	11.86	12.57	22.54	-	-
b	43.66	11.79	0.32	11.12	11.42	21.24	0.34	-
c	-	41.98	0.64	1.7	1.73	3.32	50.37	0.27

It is well known that while forecasting the working characteristic of different wares connected with friction it is necessary to treat friction characteristics of tribosystem (body - rider) not for separately taken element but in general because structural-phase coating condition and its physic-mechanical characteristics plays decisive role in the process of tribosystem operation.

CONCLUSION

1. We received nanostructural coating systems (Ti-Zr-Nb)N by method of solid cathode vacuum-arc evaporation in the medium of reacting gas nitrogen Multicomponent films have clearly expressed columnar structure.

2. Elements composition being got by method of vacuum-arc deposition of covering systems (Ti-Zr-Nb)N, depends upon physic-technological parameters of deposition, in particular of reacting gas nitrogen pressure.

3. X-ray analysis displays that the basic phase is the phase with face-centered cubic crystal lattice. Nanocrystals dimentions increase under pressure up to 10 nm from minor pressure of 3×10^{-4} Torr up to до 63 nm while the major pressure of running nitrogen atmosphere is 4×10^{-3} Torr. While pressure increase of reacting gas we observe set of peaks reinforcement {111}, that may be determined via the perfection of crystal growth increase with primary axial orientation [111] perpendicular to plane of growth.

4. Physic-technological parameters on solid coverings deposition were explored. Covering system (Ti-Zr-Nb)N hardness received at partial pressure P == 4×10^{-3} Torr forms $H_{0.05}$ = 44.57 GPa, and at pressure P = 3×10^{-3} Torr hardness makes $H_{0.05}$ = 37.21 GPa.

5. For covering series 1*c* on the system basis (Ti-Zr-Nb)N, overlayed on steel X18H10T substrate material, the starting point of cracks L_{C2} appearance occurs at load F = 20.62 GPa, adhesive destruction at load F = 66.77 GPa. In case 1*c* series L_{C2} occurs at F = 29.14 GPa, and destruction appears at F =59.26 GPa, that is 15 % higher.

6. Adhesion solidity of coverings on the basis (Ti-Zr-Nb)N is evidently higher comparing with coverings on the basis (Ti-Zr-Si)N and TiN, and adhesion destruction is observed at load F = 66.77 GPa for covering (Ti-Zr-Nb)N for covering on the basis (Ti-Zr-Si)N F = 48.84 GPa; and for TIN – F = 55.2 GPa.

7. Coverings wear resistance on the system basis (Zr-Ti-Nb)N series 1*c* is higher than wearing resistance of covering on basis (Zr-Ti-Nb)N series 1*a*. Significance of friction coefficient for coating (Zr-Ti-Nb)N while system testing «covering – Al_2O_3» makes μ ~1.1.

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