Alexander POGREBNJAK[1,2], Olga MAKSAKOVA[1], Czeslaw KOZAK[2], Tomasz N. KOLTUNOWICZ[2], Sergey GRANKIN[3], Oleksandr BONDAR[1], Didar ESKERMESOV[1,4], Aleksey DROZDENKO[1], Sergey PETROV[1], Nazgul ERDYBAEVA[4]

Sumy State University (1), Lublin University of Technology (2), Kharkiv National University of Karazin (3), East-Kazakhstan State Technical University (4)

doi:10.15199/48.2016.08.49

Physical and mechanical properties of nanostructured (Ti-Zr-Nb)N coatings obtained by vacuum-arc deposition method

Abstract. *By vacuum-arc evaporation of multielement Ti+Zr+Nb cathode in nitrogen atmosphere, (Ti-Zr-Nb)N coatings have been deposited on steel substrates. The coatings are characterized by a columnar structure with nanosized (10-63 nm) crystallites of the main FCC nitride phase (Ti-Zr-Nb)N. Such coatings seem to having prospects as protective ones for couples of friction and cutting tools.*

Streszczenie. *Metodą próżniowo-łukowego osadzania z katod systemu Ti+Zr+Nb w atmosferze azotu otrzymano powłoki na podłożach (Ti-Zr-Nb)N. Powłoki charakteryzują się słupową strukturą z nanowymiarowymi (10-63 nm) kryształami w podstawie których jest FCC faza azotku Ti-Zr-Nb)N.* ***(Fizyko-mechaniczne właściwości powłok (Ti-Zr-Nb)N otrzymanych metodą próżniowo-łukową)****.*

Keywords: vacuum-arc evaporation, hardness, wear, adhesion strength.
Słowa kluczowe: próżniowo-łukowe osadzanie, twardość, zużycie, przyczepność.

Introduction

During the exploitation the surface layer of machine parts and mechanisms subjected to heavy mechanical, thermal and chemical resistance. The loss of efficiency in most cases occurs from the surface as a result of wear, erosion, corrosion, and so on. A significant resource increase of capacity lies in the material of which made parts.

To provide complex high performance properties very promising can be the use of multi coatings based on carbides, borides, nitrides and silicides of transition metals [1–5]. The stability of the structure and composition, as well as high performance multi-element nitride systems provide improvement of physical and mechanical characteristics of the surface and use of them as a protective film prevents the penetration of harmful impurities in the surface layers of articles [6-8]. Currently, the most widely used are methods of ion-plasma deposition of coatings, in particular vacuum-arc and magnetron sputtering [9-13].

In this work features of formation of ion-plasma coatings by spraying a multi-element systems based on *Ti+Zr+Nb* were investigated and an analysis of the physical and mechanical properties of the coatings was made.

Experimental details

The coatings were formed by vacuum arc deposition. As the evaporating materials used solid target (cathodes) based on system: 30 at.% *Ti,* 35 at.% *Zr* and 35 at.% *Nb*. Coating deposition at a pressure of the working gas (molecular nitrogen) 3×10^{-4}, 7×10^{-4}, 4×10^{-3} Torr (coating series A, B and C, respectively).The thickness of all coatings in the experiments was 4.0 microns.

As a substrate for the deposition of coatings were chosen samples measuring 15×15×2,5 mm from steel 12×18H9T roughness of the original surface R_a = 0.09 microns. Deposition parameters and roughness surface after deposition of the coating are given in Table 1.

The surface morphology fraktogramm fracture, friction track studied scanning electron microscope FEI Nova NanoSEM 450.

Investigation of the elemental composition of coatings was conducted by analysing the spectra of the characteristic X-rays generated by an electron beam in raster electron microscope. The spectra were recorded using a X-ray energy dispersive spectrometer system PEGASUS company EDAX, installed in the microscope. X-ray diffraction studies of the samples with coating was carried out on diffractometer DRON-4 in Cu-Kα radiation in the pointwise mode scanning step 2θ = 0.05 .

The microhardness measurements were carried out by using an automatic system for analysis of DM-8 microhardness with a load on the indenter 0.05 H by the micro-Vickers method.

Table 1. Technological parameters of deposition and surface roughness surface (*Ti-Zr-Nb*)*N* coatings

Series	Arc current I_d, A	Bias voltage U_{sm}, B	Nitrogen pressure P_N, Torr	Roughness R_a, mcm
A	95	100	3×10^{-4}	1.17
B	95	100	7×10^{-4}	0.54
C	95	100	4×10^{-4}	0.42

Adhesion-cohesive strength, scratch resistance and failure mechanism of coatings was performed on the air using the scratch tester Revetest (CSM Instruments).

The tribological tests were carried out in air in a "ball-ROM" drive friction "Tribometer" (CSM Instruments). To this coating with thickness 4.0 microns was deposited on the polished surface (R_a = 0.088 mm) of the samples in the form of discs made of steel 45 (HRC = 55) with a diameter 42 and a height of 5 mm. As counterbody the ball with diameter 6.0 mm was used, it is made of sintered material certified - Al_2O_3. The load was 3.0 H, the sliding speed of 10 cm/s. Test conditions meet international standards ASTM G99-959, DIN50324 and ISO 20808.

The roughness and the amount of coating material removed was determined by the cross section of track wear on the surface of a sample with an automated precision contact profilometer model Surtronic 25. The structure of the groove wear coating and wear and tear on the spot beads investigated optical inverted microscope Olympus GX 51 and the scanning ion-electron microscope Quanta 200 3D. As a result of the wear tests evaluated factor [14] the coated sample and statistical partner (ball) as described in [15].

Results and discussion

Image surface of the coatings as well as fractogramm fracture showned on Figs. 1 and 2.

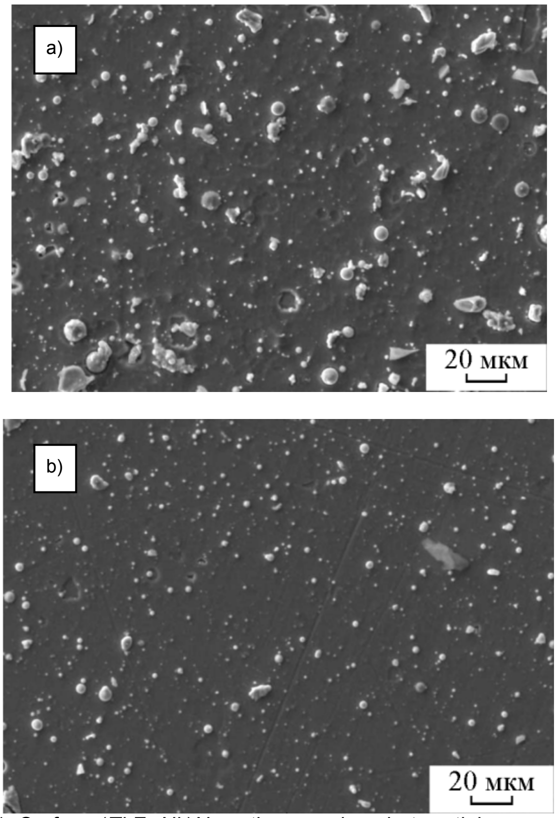

Fig.1. Surface (*Ti-Zr-Nb*)*N* coatings produced at partial pressure of nitrogen: pressure of nitrogen during deposition P = 3×10^{-4} Torr, the surface roughness R_a = 1.17 microns (a); P = 4×10^{-3} Torr, R_a = 0.42 microns.

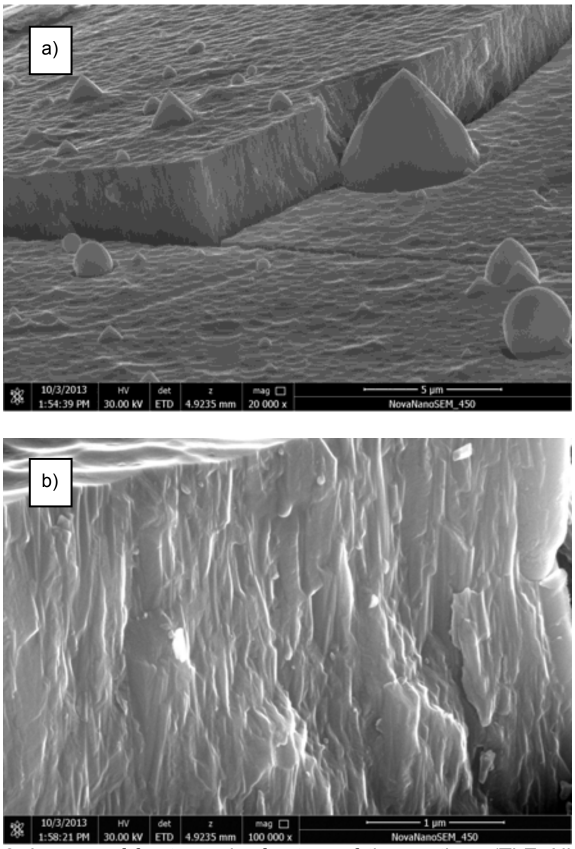

Fig.2. Images of fractographs fracture of the coatings (Ti-Zr-Nb)N, obtained at a partial pressure of nitrogen: P = 4×10^{-3} Torr

The investigation of the surface morphology indicates that increasing of pressure of the reaction nitrogen environment reduces the amount and size of macroparts.

This is particularly important at presence in the vacuum chamber of reactive gases, forming with vaporizable material refractory compound. Also, it is observed a decrease in the roughness of the coating.

The elemental composition of coatings produced by vacuum arc deposition was analyzed by energy dispersive method (Table 2).

If you compare the elemental composition of the coatings used in the series, it can be seen that the samples of the first series of the number of nitrogen atoms is almost identical. For a series of samples obtained at a higher pressure N_2 atmosphere, characterized by a significant increase in the proportion of zirconium atoms and a decrease in the proportion of titanium atoms.

The content of niobium atoms samples of both series remains virtually unchanged. Increasing the content of titanium atoms in the condensates B series is explained, it seems to be more effective interaction with the nitrogen atom of titanium in the surface region.

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

Series	Elemental composition, 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

Investigation of fraktogramm fracture surfaces (Fig.2) obtained at different partial pressures of nitrogen, indicating the formation of the columnar structure (Fig.2b), the characteristic of coating produced by vacuum-arc deposition.

The analysis X-ray diffractometer spectra on Fig.3 shows that as the determining phase composition is the phase with a face-centered cubic lattice. Low-intensity peak at 2θ = 38° indicates the presence of small inclusions with BCC lattice, typical for vacuum-arc method for dropping phase [16].

It should be noted that with increasing of pressure the intensity of this peak decreases (see the spectra 1 and 3 on Fig.3), which determined by a significant decrease of content in the droplet phase in the coating and correlates with the results of surface examination.

A characteristic feature with increasing pressure of the reaction gas is strengthening the peaks of the family of planes {111}, which is determined by the increase of perfection preferred orientation of growth of crystallites with [111] axis perpendicular to the plane of the surface. Specific method of approximating the size of the crystallites with an increase in pressure increases from 10 nm at the lowest pressure of 3×10^{-4} Torr to 63 nm at the maximum working pressure nitrogen atmosphere 4×10^{-3} Torr.

The study results of the adhesive-cohesive strength, scratch resistance of coatings shown on Fig.4 and Fig.5. On the basis of the graphs the change of the friction coefficient and acoustic emission from the load of scribing determined the following main critical loads: L_{C1} – *the emergence of the first chevron cracks on the bottom and diagonal around the edges of crack;* L_{C2} – *the formation of a plurality of chevron cracks on the bottom of the crack and local peeling of coating, appearing of chevron cracks on the bottom of the crack;* L_{C3} – *cohesively-adhesion failure of the coating;* L_{C4} – *plastic abrasion of the coating.*

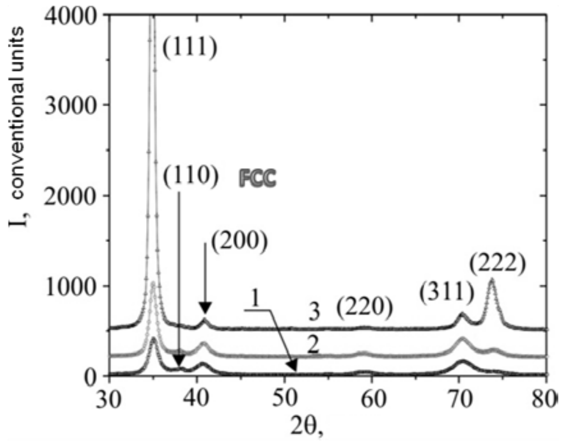

Fig.3. Areas of the diffraction spectra of coatings obtained at different partial pressure of nitrogen: curve 1 – $P = 3×10^{-4}$ Torr; 2 – $P = 7×10^{-4}$ Torr; 3 – $P = 4×10^{-3}$ Torr; identified planes of FCC lattice

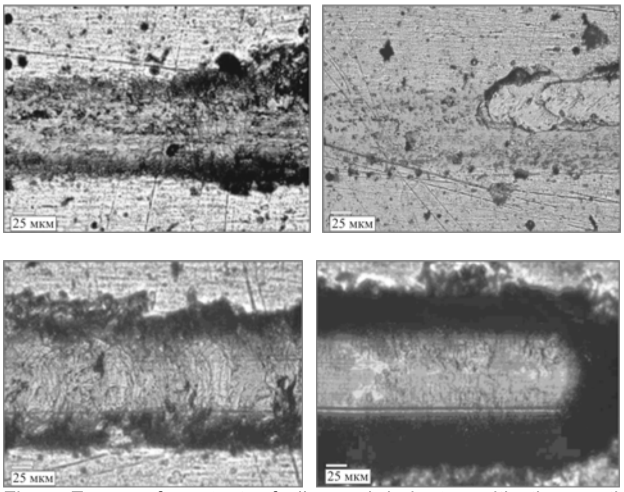

Fig.5. Zones of contact of diamond indentor with the coating (*Ti-Zr-Nb*)*N*

As criteria of the adhesion strength was accepted critical load L_{C4}, leading to abrasion of the coatings. Fig. 4 shows the dependence of the friction coefficient and acoustic emission signal from the applied load at scratch test samples of series B.

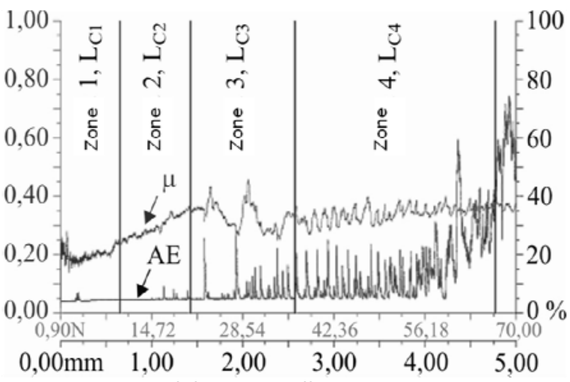

Fig.4. Dependence of friction coefficient on the applied load at a scratch test of the coating (*Ti-Zr-Nb*)*N*, obtained at $P = 4×10^{-3}$ Torr

Conventionally, the process of destruction of the coating in scratching with the indenter can be divided into four stages. At the load range of F = 0.9 H to F = 9.89 H appears the monotonically penetration of the indenter into the coating: the friction coefficient slightly increases the acoustic emission signal remains unchanged. When the load F = 15.81 H indenter is completely immersed in the coating. Slipping diamond indenter for cover run with friction coefficient 0.35.

Important parameter governing performance coatings are also its tribological properties (coefficient of friction and wear factor). The friction coefficient μ defines a traction friction material and the factor of wear - wear resistance (less than a factor wear, the better the durability).

As the load increases (F = (20.6 – 36.4) H) occurs the extrusion of the material before the indenter as hillocks and increased the penetration depth of the indenter.

Table. 3 shows the results of tests of samples with coatings (*Zr-Ti-Nb*)*N* coatings in comparison with the (*Ti-Zr-Si*)*N* and *TiN* obtained by us [17].

Table 3. Comparative results of the adhesion tests of coatings (*Zr-Ti-Nb*)*N*, (*Ti-Zr-Si*)*N* and *TiN*

Critical loads	Coatings				
	(Zr-Ti-Nb)N seria *a*	(Zr-Ti-Nb)N seria *b*	(Zr-Ti-Nb)N seria c	(Ti-Zr-Si)N	TiN
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

All coated samples (series A, B, C), the friction coefficient was higher than 1.0. Such high values may be explained by the high roughness (Fig.1), associated with the presence at the surface and in the coating of the droplet fraction formed by vacuum-arc deposition. The appearance of a solid component of dropping and formation of degradation during the coating of wear in the form of particles consisting of hard nitrides, leads to abrasion of the coating.

Reducing the surface roughness decreases with a coefficient of friction of 1.95 to 1.05. With the increase in the hardness of the coating wear factor W coating decreases and counterbody – increased. With the increasing of pressure and the appearance of preferential orientation of crystallite growth with the axis [111] (Fig.2) observes a decrease in the setting and wear material, which correlates with the previously established increase in hardness with increasing pressure of nitrogen during deposition of the coating. These results can be explained by an increase in the packing density of the atoms (111) plane of the FCC lattice [18], which increases the hardness cover, as the introduction of the indenter in the axis of the texture in the coating [111] is perpendicular to these planes. Increased resistance wear in this case is determined by the wear that in the process of wear occurs removal of a solid layer-planes (111) of a material that minimizes destruction.

Conclusions

1. With method of vacuum arc evaporation solid cathode in the medium of reaction gas nitrogen obtained nanostructured coating of (*Ti-Zr-Nb*)*N*. Multicomponents films have a pronounced columnar structure.
2. Elemental composition of obtained with vacuum-arc deposition coatings (*Ti-Zr-Nb*)*N*, depends on the physico-technological parameters, by precipitation, particularly on the pressure of the reaction gas nitrogen.

3. From X-ray analysis follows that the main phase is a face-centered cubic lattice. With the increasing of the pressure dimensions of nanocrystals increases from 10 nm at the lowest pressure of 3×10^{-4} Torr to 63 nm at the maximum working pressure nitrogen atmosphere 4×10^{-3} Torr.
4. Investigation of the effect of physical and technological parameters of deposition on the hardness of coatings. The hardness of the coatings of (*Ti-Zr-Nb*)*N* system, obtained at a partial pressure of $P = 4\times10^{-3}$ Torr is $H_{0,05}$ = 44.57 GPa, and at a pressure $P = 3\times10^{-3}$ Torr hardness is $H_{0,05}$ = 37.21 GPa.
5. The adhesion strength of coatings based on (*Ti-Zr-Nb*)*N* markedly higher compared to coatings based on (Ti-Zr-Si)N and TiN, and the adhesion failure is observed at the load F = 66.77 GPa for coating (Ti-Zr-Nb)N for coating based on (Ti-Zr-Si)N F = 48.84 GPa; and for TiN F = 55.2 GPa.

This work was done under the aegis of scientific-technical collaboration program between Sumy State University (Sumy, Ukraine) and University of Poitiers (Institut P', University of Poitiers, Poitiers, France), and Ukrainian complex state budget programs "Creation of basis of superhard nanostructure coatings fabrication with high physical and mechanical properties" (registration number 0112U001382) and "Physical principles of plasma technologies for complex treatment of multicomponent materials and coatings" (registration number 0113U000137c).

The authors are thankful to Prof. O.V. Sobol, Prof. V.M. Beresnev, U.S. Nemchenko, D.A. Kolesnikov.

Authors: *prof. Alexander Pogrebnjak, Sumy State University, 2, R.-Korsakova Str. 40007, Sumy, Ukraine, E-mail: alexp@i.ua; Olga Maksakova, Sumy State University, 2, R.-Korsakova Str., 40007, Sumy, Ukraine, E-mail: maksakova.tereshenko@gmail.com; Dr. Czeslaw Kozak, Lublin University of Technology, 38d, Nadbystrzycka Str., 20-618 Lublin, Poland, E-mail: c.kozak@pollub.pl; Dr. Tomasz N. Kołtunowicz, Lublin University of Technology, 38d, Nadbystrzycka Str., 20-618 Lublin, Poland, E-mail: t.koltunowicz@pollub.pl; dr. Oleksandr Bondar, Sumy State University, 2, R.-Korsakova Str., 40007, Sumy, Ukraine, E-mail: oleksandr.v.bondar@gmail.com; dr. Aleksey Drozdenko, Sumy State University, 2, R.-Korsakova Str., 40007, Sumy, Ukraine, E-mail: aleksey.drozdenko@gmail.com; dr. Sergey Petrov, Sumy State University, 2, R.-Korsakova Str., 40007, Sumy, Ukraine, E-mail: sergpet@gmail.com; prof. Nazgul Erdybaeva, East-Kazakhstan Technical University, 69, Protozanov Str., 070004, Ust-Kamenogorsk, Kazakhstan, E-mail: nerdybaeva@mail.ru; Didar Eskermesov, East-Kazakhstan Technical University, 69, Protozanov Str., 070004, Ust-Kamenogorsk, Kazakhstan, E-mail: didar.eskermesov@mail.ru; Sergey. Grankin, Karazin Kharkiv National University, 4, Svobody Sq., 61022,, Kharkiv, Ukraine*

REFERENCES

[1] Pogrebnjak A.D., Ruzimov Sh.M, Increased microhardness and positron annihilation in Al exposed to a high-power ion beam, Phys.Lett., 120 (1987), n.5, 259-261.
[2] Pogrebnjak A.D., Structure and Properties of Nanostructured (Ti-Hf-Zr-V-Nb)N Coatings, *J. of Nanomaterials*, 780125 (2013), 12.
[3] Pogrebnjak A.D., Beresnev V.M., Demianenko A.A., Baidak V.S., Komarov F.F., Kaverin M.V., Makhmudov N.A., Kolesnikov D.A., Adhesive strength, superhardness, and the phase and elemental compositions of nanostructured coatings based on Ti-Hf-Si-N, *Physics of the Solid State*, 54 (2012), 1882-1890.
[4] Pogrebnjak A.D., Bagdasaryan A.A., Yakushchenko I.V., Beresnev V.M., The structure and properties of high-entropy alloys and nitride coatings based on them, *Russ Chem Rev*, 83, (2014), 1027-1061.
[5] Pogrebnjak A.D., Eyidi D., Abadias G., Bondar O.V., Beresnev V.M., Sobol O.V., Structure and properties of arc evaporated nanoscale TiN/MoN multilayered systems, *International Journal of Refractory Metals and Hard Materials*, 48, (2015), 222-228.
[6] Pogrebnjak A.D., Ladysev V.S , Pogrebnjak N.A., Michaliov A.D., Shablya V.T., Valyaev A.N., Valyaev A.A , Loboda V.B , A comparison of radiation damage and mechanical and tribological properties of α-Fe exposed to intense pulsed electron and ion beams, *Vacuum,* 58 (2014), n.1, 45-52.
[7] Pogrebnyak A.D., Proskurovskii D.I., Use of Low-energy High-current Electron Beams for Surface Treatment of Materials, *Physica Status Solidi (A) Applied Research*, 145 (2015), n.1, 137-145.
[8] Pogrebnjak A., Lebed A., Ivanov Y., Modification of Single Crystal Stainless Steel Structure (Fe-Cr-Ni-Mn) by High-Power Ion Beam, *Vacuum*, 63 (2001), n.4, 483-486.
[9] Veprek S, Veprek-Hejiman M.G.L., Karvankova P., Prohazka, Different approaches to superhard coatings and nanocomposites, *J., Thin Solid Films*, 476 (2005), n.1, 1-29.
[10] Pogrebnjak A.D., Beresnev V.M., Nanocoatings, Nanosystems, Nanotechnologies, *Bentham Sci.Publ.*, (2012),155 p.
[11] Larkin A.V., Fedotov A.K., Fedotova J.A., Koltunowicz T.N., Zhukowski P.: Temperature and frequency dependences of impedance real part in the FeCoZr-doped PZT nanogranular composites, *Materials Science-Poland* 30 (2012), n.2, 75-81.
[12] Kołtunowicz T.N., Zhukowski P., Fedotov A.K., Larkin A.V., Patryn A., Andriyevskyy B., Saad A., Fedotova J.A., Fedotova V.V.: Influence of matrix type on negative capacitance effect in nanogranular composite films FeCoZr-Insulator, *Elektronika ir Elektrotechnika (Electronics and Electrical Engineering)* 19 (2013), n.4, 37-40.
[13] Koltunowicz T.N.: Dielectric properties of $(CoFeZr)_x(PZT)_{(100-x)}$ nanocomposites produced with a beam of argon and oxygen ions, *Acta Physica Polonica A* 125 (2014), n.6, 1412-1414.
[14] Musil J., Baroch P., Zeman P., *Plasma Surface Engineering Research And Its Practical Applications,* Kerala Research Signpost Publ., (2008), 1-34.
[15] Overview of mechanical testing standards. Ed. N.Randall. CSM Instruments Applications *Bulletin*, (2002), n.18, 3; http://www.csm-instruments.com/en/tests-Standards.
[16] Azarenkov N.A., Sobol' O.V., Beresnev V.M., Pogrebnjak A.D., Litovchenko S.V., Ivanov O.N. Materialsscience Nonequilibrium State of Modified Coating, *Sumy*, (2013), 683 p.
[17] Pogrebnjak A.D., Yakushchenko I.V., Bagdasaryan A.A, Bondar O.V., Krause-Rehberg R., Abadias G., Chartier P., Oyoshi K., Takeda Y. , Beresnev V.M., Sobol O.V., Physical and Chemical Properties of nanostructured (Ti-Hf-Zr-V-Nb)N coatings under different deposition conditions, *Materials Chemistry and Physics,* 147, (2014), 1079-1081.
[18] Pogrebnjak A.D., Bratushka S. Boyko V.I. et.al. A review of mixing processes in Ta/Fe and Mo/Fe systems treated by high current electron beams, *Nucl.Instrum .and Meth.*145 (1998), n.3, 373-390.