



Influence of Thermal Treatment on the Structure, Physical and Mechanical Properties of Nanostructured Coatings (Ti, Hf, Nb, Si)N Deposited by C-PVD Method

A.A. Demianenko*, V.M. Rogoz†

Sumy State University, 2, Rymsky Korsakov Str., 40007 Sumy, Ukraine

(Received 05 July 2013; published online 03 September 2013)

The paper describes the nanostructured coatings produced by C-PVD method at various deposition conditions. Samples with thickness of 2, 3 mm and diameter 10, 42 mm were constructed of steel 0.55 % Fe, 0.45 % C with polished surface. The samples were tested by XRD (small angle X-Ray diffraction), SEM with EDX, AFM, scratch – tester REVETEST, tests of wear resistance and acoustic emission, nanoindenter before annealing. It was discovered that the size of nanograins varied from 3,3 nm to 8 nm by annealing at 500°, 800° and 1000°C. By dint of μ -PIXE were discovered the segregation process of impurities at the junctions of interfaces and at nanograin boundaries. Moreover as a result of the thermal annealing hardness of coatings increased on 18- 20 %.

Keywords: Nanostructured Coatings, Thermal Treatment, C- PVD, μ - PIXE, Nanocrystallites, X-Ray Diffraction, (Ti, Hf, Nb, Si) N.

PACS numbers: 61.05.cm, 61.46.Hk,
62.20.Qp.68.37.Hk, 81.15.-z

1. INTRODUCTION

Multicomponent and nanostructured coatings are being nowadays one of the most promising protective materials because of their high hardness, high abrasion, corrosion and fatigue resistance as well as high temperature of oxidation, etc. [1-10]. It is well known that binary - TiN, CrN, MoN, triple - TiAl, TiCrN, and quaternary - Ti-Zr-Si-N, Ti-Hf-Si-N [2-4] compounds are commonly used for wear protection, corrosion protection, and possess high thermal stability even up to (900 ÷ 1000)°C.

Recently published works [2-5] have shown that nanostructured (nanocomposite) (Ti-Hf-Si-N) coatings, obtained by C-PVD method may have two-phases: (Ti, Hf)N - solid solution phase and α -Si₃N₄ - amorphous phase at the same time these coatings exhibit high hardness up to 48 GPa (superhardness), along with low friction coefficient of 0.12 to 0.45 and thermal stability up to 900 °C. Therefore, it is of particular interest to add to such system Nb, which has (as Hf) a high enthalpy of mixing, for improving the resistance to high temperature oxidation and possibly to improve other physical and mechanical properties of coatings such as abrasion resistance and elastic modulus.

For providing of studies multielement coatings (Ti, Hf, Nb, Si)N were selected. According to the proposed and experimentally proven concept of high entropy multicomponent alloys such coatings significantly improve thermal stability of the material [1]. Therefore, the creation of new types of nanocomposite (nanostructured) coatings on the basis of (Ti, Hf, Nb, Si) N by means of cathode vacuum arc evaporation (CAVD) and subsequent study of their physical and mechanical properties is an important task of modern materials science.

2. EXPERIMENTAL AND DETAILS

A Cathodic - Arc - Vapor - Deposition "Bulat - 3T" with HF generator [3, 5] was applied. Potential bias was applied to the substrate from the HF generator of pulsed damped oscillations with a frequency of < 1 MHz. The duration of each pulse of 60 us, with a repetition rate of ~ 10 kHz. The amount of negative self-bias potential of the substrate caused by HF diode effect was 2 + 3 kV.

Cathodes of the multicomponent alloys (Ti, Hf, Nb, Si) N were prepared by vacuum-arc melting in an atmosphere of high purity argon.

The bonding state's were determined using photoelectron spectroscopy (XPS, Kratos Axis Ultra) with a nanochromatic Al_{K α} (1486,71 eV, X-ray emission/radiation 15 kV/10 mA).

The elemental composition, was studied with scanning electron microscope (SEM) with EDX - microanalysis JEOL - 7000F (Japan). To perform the element analysis over a sample depth, we employed the Rutherford backscattering (RBS) method with He⁺ ions of 1.7 MeV (the scattering angle was $\theta = 170^\circ$) with a normal fall of probing ions to the surface of coated samples. The energy resolution of detector was 13 keV. A dose of helium ions was 5 μ Ci. To interpret the RBS spectra and to obtain the element profiles over the coatings depth, we employed standard software.

The phase composition and structural studies were performed on the X-ray diffractometer DRON-3M and Rigaku RINT-2500 - MDG Japan, in the filtered radiation of Cu-K α using in the secondary beam graphite monochromator. The diffraction spectra were surveyed in the point-by-point scanning mode with a step $2\theta = 0.05 - 0.1^\circ$. We also employed the diffraction of X - rays using a grazing incidence beam, in Cr

* artem.demyanenko@gmail.com

† v.rogoz@yandex.ru

emission, at angle 3°. In order to study the stress-strain state of the coatings, we employed the method of X-ray strain measurements (« $\alpha - \sin^2 \varphi$ » - method) and its modifications, which are commonly applied to the coatings with strong axial texture [10 - 14].

The distribution of elements in nanostructured coatings has been studied by micro-proton beam induced X-ray emission (μ -PIXE) measurements at an initial particle energy of 1,4 MeV – these measurements were performed using an IAPC (Sumy) electrostatic accelerator with a beam diameter of 0,4 μ m the raster was 50 \times 50 at a step of 0,5 μ m and a change of 3×10^{-10} C/pixel.

To determine the adhesive/cohesive strength, scratch resistance, and also to study the fracture mechanism the scratch tester REVETEST see (CSM Instruments) [6] was used (Fig. 1). The scratches were applied to the coating surface at continuously increasing load by diamond spherical indenter "Rockwell C" with a radius of curvature of 200 μ m. Simultaneously the power of acoustic emission, friction coefficient and the penetration depth of the indenter and the value of the normal load (F_N) were recorded. Three scratches were applied to each sample.

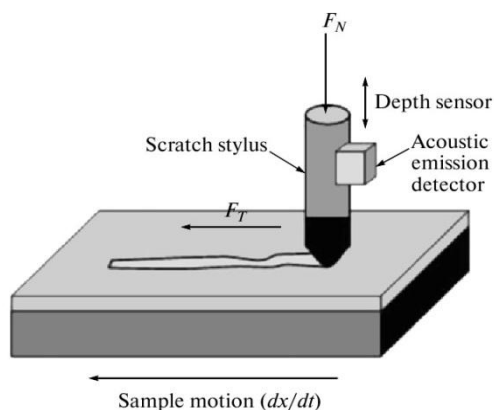


Fig. 1 – Experimental setup for the determination of the adhesive/cohesive strength.

Tests were carried out under the following conditions: the load on the indenter increased from 0.9 to 70 N, speed of the indenter movement was 1 mm/min, scratch length – 10 mm, the loading rate - 6.91 N / min, the frequency of a digital signal – 60 Hz, acoustic emission – 9 Db. Tests determined the minimum (critical) load LC_1 , which corresponds to the beginning of the indenter penetration into the coating; LC_2 - top when the first cracks appear; LC_3 - the peel of some parts of coating; LC_4 - plastic abrasion of the coating to the substrate. Registration, during a test, (a relatively large number of different physical parameters) improves the reliability and accuracy of the method the critical load determination. The deformation of the coating by the diamond indenter was investigated further using the integrated optical microscope and electron-ion scanning microscope Quanta 200 3D, equipped with an integrated system of Pegasus 2000 for microanalysis.

3. RESULTS AND DISCUSSION

Coatings deposition was performed by vacuum-arc method on set up Bulat-6. A constant negative potential $U_s = (-40 - 200)$ V was applied to the substrate, the residual gas pressure was 0.0066 Pa and arc current did not exceed 85 A. Figure 2 shows image of a coating (Ti, Hf, Nb, Si) N in the initial state.

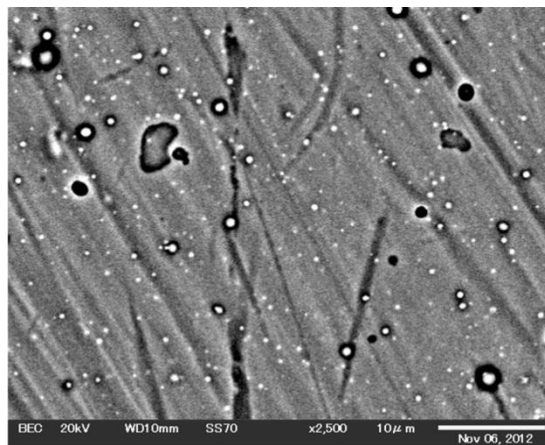


Fig. 2 - The image of surface of nanocomposite combined coatings obtained by scanning electron microscopy.

Before turning to the analysis of X-ray data, it should be noted that, for understanding of the sequence of processes occurring in the surface region during the deposition, it is necessary to compare the heat of formation of possible nitrides.

Table 1 – Crystallite size and the lattice period at different temperatures of annealing

No	Annealing temperature °C	a, nm	Crystallite size, nm
1	-	0,4344	5,0
2	1000	0,42752	7,7
3	500	0,44398	5,9
4	800	0,4352	6,4

Table 2 - The enthalpies of formation (ΔH) of the five binary nitrides

	TiN	HfN	NbN	Si ₃ N ₄
ΔH , KJ/mole	-	-	-	-
	337,7	373	234,7	738.1

In accordance with [7] the enthalpies of formation (ΔH) of the four binary nitrides are shown in Table 2. It means that the heat of formation of all systems is a relatively large and negative, indicating that there is a high probability of the formation of such systems through the transfer of material from the target to the substrate. In this case, the proximity of the values of the heat of formation of TiN and HfN creates conditions for the formation of sufficiently homogeneous solid solution (Ti, Hf, Nb) N.

Figure 3 and Table 2 shown study the X-ray diffraction. The first annealing (Fig. 3 curve 2) leads to an abrupt relaxation of compressive stresses, which is accompanied by a decrease of lattice period in direction perpendicular to the plane of growth. This annealing leads to a considerable recrystallization processes.

Then, annealing up to 800°C (Fig. 3 curve 4) has practically no effect on the stress state, leaving period of lattice the same. A significant relaxation processes were detected after annealing up to 1000°C, which leads to the sharp decrease of the lattice period in the direction perpendicular to the plane of growth. At the same time the average size of the crystallites are exposed to the increase throughout the all temperature range of annealing and reaches maximum size of 7.7 nm at 1000°C, i.e. increases for more than 60 % compared to the initial state.

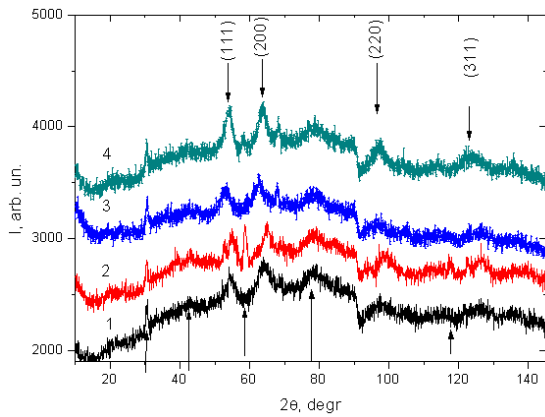


Fig. 3 - Diffraction spectra of coatings obtained by GXR: 1 - as deposited 2 - annealed at 1000°C, 3 - annealed at 500°C, 4 - annealed at 800°C.

The following figure 4 shows the energy spectra of backscattered ⁴He⁺, obtained from samples coated with (Ti, Hf, Nb, Si) N on a steel substrate.

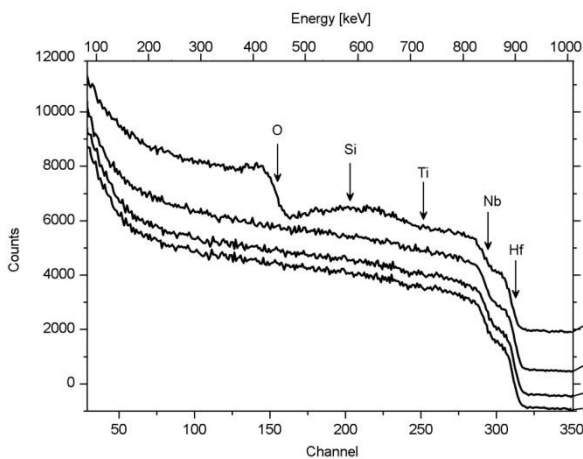


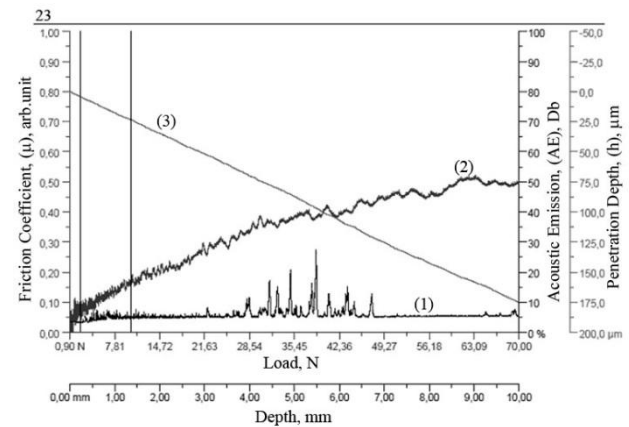
Fig. 4 - Energy RBS spectra obtained for coatings (Ti, Hf, Nb, Si) N, at the initial state and after annealing at T = 500°C, 800°C, 1000°C for 30 min. in air

As it is seen from the figure, the concentration of Ti, Hf, Nb, Si elements after annealing at T = 500°C and 800°C is comparable to concentration of these elements before annealing, which indicates the uniformity of distribution of elements through the thickness of the coating. Annealing of samples up to 1000°C for 30 min. led to formation of oxide film on the surface of coating and to redistribution of the elements in the form of films.

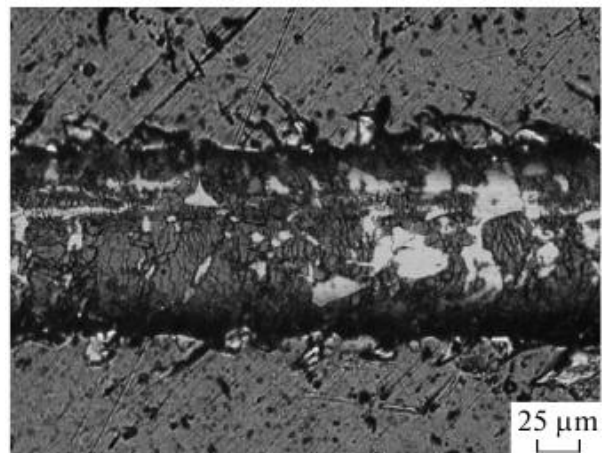
Preliminary results obtained by μ-PIXE microbeam

in depth and on the surface of nanostructured coatings showed that the annealing to 800°C leads to the segregation of impurities (for example, the elements Hf and Nb) in nanograins. A siliconitride layer which is formed as a result of the thermal diffusion of Si along nano-grain boundaries leads to the formation of SiN_x - amorphous phase. It is also reflected in the results of XPS (peak in radon 101.9 KeV) wherein Si concentration in this compound estimated as (4.9 ~ 5.2) at %.

Figure 5 a shows the results of tests performed on the scratch tester REVETEST of sample Ti- Hf- Nb- Si) N at the minimum (critical) load L_{C1} = 2,46 H and at the load at which the first cracks appear L_{C2} = 10,25 N.



a



b

Fig. 5 - Results of adhesion of tests system coatings (Ti, Hf, Nb, Si) N steel substrate: a - dependence AE (1), μ (2), and the depth of penetration (3); b - structure of the coating in the fracture zone at loads in the range 0.9 - 90.0 N

It should be noted that when the load increases, the curve describing the dependence of friction coefficient on the load gets an oscillatory character. The increase of the friction coefficient is accompanied by a surge of acoustic emission. The above described behavior of all recorded parameters in these experiments (coefficient of friction, hardness) shows that the hard coating with thickness of ≤ 1μm deposited on a surface of softer material (steel) shows a substantial resistance to diamond indenter to almost its full abrasion under high loads. [15-16].

When testing coatings it can be clearly distinguished different threshold values of critical load which lead to different types of destruction. What is more only a minimum (critical) LC_1 load and a load at which the first crack appears LC_2 can be associated with the adhesive destruction of coatings.

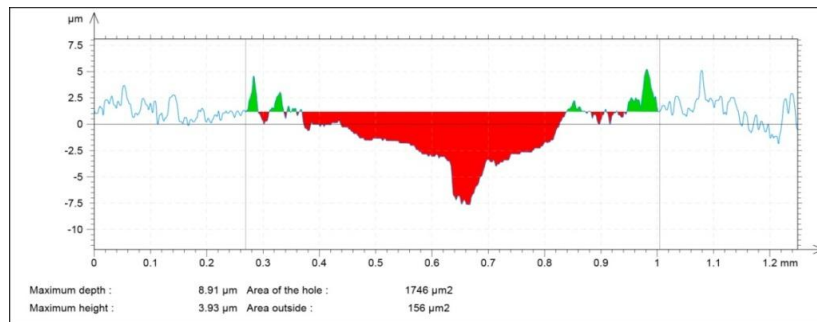
Destruction of the coating begins with the appearance of chevron cracks at the bottom of wear groove, which causes the increase of local stresses and friction. This leads to the subsequent rapid abrasion of coating (Fig. 5b).

According to the results of adhesion tests, cohesive destruction of the coatings (as-deposited) (Ti-Hf-Nb-Si)N appears at the minimal (critical) load $LC_1 = 2.38$ H and adhesion destruction occurs at a load when the first crack appears $LC_2 = 9.81$ N. Figure 6 (a, b, c) shows the results of scratch tests of samples after annealing at 500, 800 and 1000°C. according to obtained results it can be argued that the greatest resistance to wear is demonstrated by coatings after high-temperature annealing up to 1000°C (lowest takeout

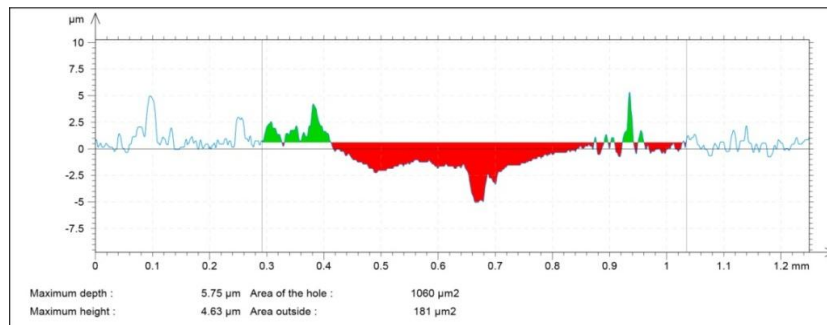
of coating material (c)). Accordingly, the degree of wear resistance decreases with decreasing stresses, and perhaps this is also associated with an increase of friction coefficient (although as can be seen from the results of EDX analysis there is an oxide film with thickness of 60 – 75 nm).

4. CONCLUSIONS

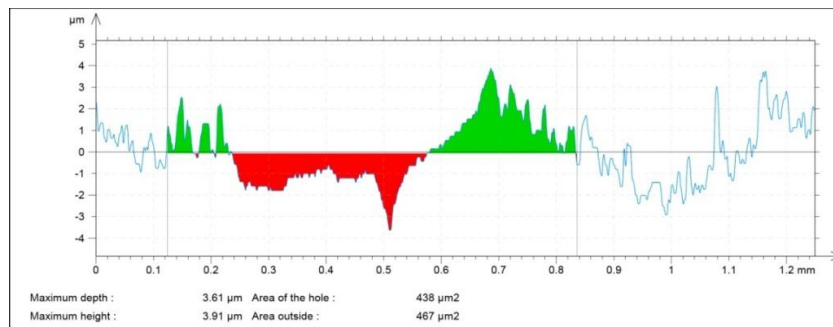
It is shown that high temperature annealing leads to an increase of the nanocrystallites size of the solid solution from 3 nm to 7.7 nm and to different recrystallization processes. High macro- and microdeformation occurring in the coating seems to be related to an “atomic peening” effect resulting to non-ordered distribution of titanium atoms implanted to the film during its growth. In the course of annealing, the macro- and micro-deformation relaxed. The relaxation was accompanied by formation of deformation packing defects in a metallic sublattice of (Ti, Hf)N, (Ti, Nb)N solid solution.



a



b



c

Fig 6 - The results of wear resistance tests obtained by scratch tester REVETEST of samples (Ti, Hf, Nb, Si)N: a – after annealing 500°C, b – after annealing 800°C, c – after annealing 1000°C

ACKNOWLEDGMENTS

Ministry of Education and Science of Ukraine (state program, order №. 411), and in collaboration with NIMS (Tsukuba, Japan) and Martin-Luther University (Dresden, Germany). The work was supported by Ministry of Education and Science of Ukraine (project № 0112U005920) and Ministry of Education and Science of Russia (grant № 12-08-31060).

Authors are grateful to the staff of the Joint Reserch Center “Diagnostics of Structure and Properties of Nanomaterials” (Belgorod State University, Russia) for their assistance with instrumental analysis. And authors acknowledge Dr. Sc. F.F.Komarov (Belarusian State University, Minsk, Belarus) for their help in performance of these experiments.

REFERENCES

1. A.D. Pogrebnjak, A.G. Ponomarev, A.P. Shpak, Yu.A. Kunitskii, *Physics-Uspekhi* **55** No3, 270(2012).
2. A.D. Pogrebnjak, A.P. Shpak, N.A. Azarenkov, V.M. Beresnev, *Physics-Uspekhi* **52** No1, 29 (2009).
3. A.D. Pogrebnjak, E.A. Bazyl, *Vacuum* **64** No1, 1 (2001).
4. A.D. Pogrebnjak, V.M. Beresnev, D.A. Kolesnikov, M.V. Kaverin, A.P. Shpylenko, K. Oyoshi, Y. Takeda, R. Krause-Rehberg, A.G. Ponomarev, *Technical Physics Letters* **39** No3, 280 (2013).
5. A.D. Pogrebnjak, O.V. Sobol, V. M. Beresnev, P.V. Turbin, G.V. Kirik, N.A. Makhmudov, M.V. Il'yashenko, A.P. Shpylenko, M.V. Kaverin, M.Yu. Tashmetov, A.V. Pshyk *Ceramic Engineering and Science Proceedings*, **31**, 127 (2010).
6. O.V. Sobol, A.D. Pogrebnjak, V.M. Beresnev, *The Physics of Metals and Metallography*, **112** No2, 199 (2011).
7. J. Musil, P. Zeman, *Advances in Applied Ceramics* **107** No3, 148 (2008).
8. A.D. Korotaev, V.D. Borisov, V.Y. Moshkov, S.V. Ovchinnikov, J.P. Pinzhin, A.N. Tyumentsev, “Elastic stress state in superhard multielement coatings”, *Physical Mesomechanics* **12** No5-6, 269 (2009).
9. A.D. Pogrebnjak, V.M. Beresnev, D.A. Kolesnikov, M.V. Kaverin, A.P. Shpylenko, K. Oyoshi, Y. Takeda, R. Krause-Rehberg, A.G. Ponomarev, *Technical Physics Letters* **39** No3, 280 (2013).
10. O.V. Sobol', A.A. Andreev, V.F. Gorban, N. Krapivka, V.A. Pole, I.V. Serdyuk, V.E. Filchikov, *Technical Physics Letters* **38** No7, 616 (2012).
11. I.V. Blinkov, S.A. Volkhonsky, V.N. Anikin, M.I. Petrzhik, D.E. Derevtsova, *Physics and Chemistry of Materials Processing* **4**, 37 (2010) (in Russian).
12. Shao-Yi Lin, Shou-Yi Chang, Yi-Chung Huang, Fuh-Sheng Shieu, Jien-Wei Yeh, *Surface and Coatings Technology*, **206** No24, 5096 (2012).
13. J. Musil, *Surface and Coatings Technology* **207**, 50 (2012).
14. A.D. Pogrebnjak, A.P. Shpak, V.M. Beresnev, D.A. Kolesnikov, Yu.A. Kunitsky, O.V. Sobol, V.V. Uglov, F.F. Komarov, A.P. Shpylenko, A.A. Demyanenko, V.S. Baidak, V.V. Grudnitskii, *Journal of Nanoscience and Nanotechnology* **12**, 9213 (2012).
15. S.V. Rempel, A. Gusev, *JETP Letters* **88** No7, 508 (2008).
16. *Nanomaterials, nanostructures and nanotechnology* (Ed. A.I. Gusev) (Moscow: Fizmatlit:2005).