J. Nano- Electron. Phys.
3 (2011) No4, P. 73-80

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

STRUCTURE AND PHYSICAL-MECHANICAL PROPERTIES OF nc-TiN COATINGS OBTAINED BY VACUUM-ARC DEPOSITION AND DEPOSITION WITH HF DISCHARGE

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*Using the scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, adhesion strength, friction coefficient, and wear rate of the material we have studied properties of nc-*TiN *coatings. Depending on the bias potential applied to the substrate and the chamber pressure, the inclusion of HF discharge, it is shown that combination of different parameters recorded during scratching allows to distinguish the threshold values of the critical load which are linked to different types of cohesive and adhesive fracture of coatings in tribological tests. Sizes of nc-*TiN *nanograins, stoichiometry of coatings, as well as the phase and elemental composition and morphology of the coating surface were determined.*

Keywords: *nc-*TiN*, COATINGS, SEM, XRD, NANOHARDNESS, ELASTIC MODULUS, ADHESION, TRIBOLOGICAL AND DEFORMATION CHARACTERISTICS.*

(Received 12 September 2011, in final form 06 December 2011, online 30 December 2011)

1. INTRODUCTION

As known, TiN obtained by different deposition methods was one of the first coatings for wear protection for tool steel. It was shown that titanium nitride has sufficiently good physical and mechanical properties. However, nitrides of other metals (CrN, ZrN, AlN, SiN) and their combinations as well as alternation of thin layers of nitrides were used then. Recently it was discovered that with the decrease in the grain size and formation at least of two phases (which are different in sizes and disoriented with respect to each other), TiN coatings have very high hardness (more than ≥ 40 GPa) and good wear resistance [1-5]. It was found that with the decrease in the grain size to 10 and less nanometers, physical and mechanical properties, which, in turn, depend on the deposition conditions and methods, are sharply improved. Therefore, the problem was to investigate TiN as a standard, and then, changing the deposition conditions, to obtain nanostructural films with high physical and mechanical properties.

The aim of the given work consists in complex investigation of the phase composition, structure, surface morphology, physical and mechanical characteristics, and their comparison for nc-TiN coatings obtained in the conditions of continuous deposition and ion-plasma deposition with HF stimulation.

Distinctive feature of the system behavior (with HF stimulation) nc-TiN/steel substrate is the appearance of oscillations of functions and h (where μ is the friction coefficient; h is the indenter penetration depth) after reaching of the load $Lc_2 = 29N$. This is connected with the formation of local cleavages of the coating and extrusion of substrate material that leads to the decrease in the indenter penetration, increase in the friction coefficient, and slowing down of further galling of the coating till total or partial removal of the substrate material from the scratch bottom. For nc-TiN/substrate (deposited without HF stimulation) formation of first Lc_2 layers is observed at $17N$. Appearance of signal fluctuations of acoustic emission at small loads is not connected with coating damage, and, seemingly, is the result of the change in the shape, size, and number of pores (density over the coating thickness), and in the region of the coating/substrate transition. In this case at indenter penetration into coating/substrate, completely elastic contact up to $23N$ is realized, the value of the elastic recovery is almost 100%, and wearing-off is almost absent.

2. METHODS FOR OBTAINING COATINGS AND INVESTIGATION TECHNIQUES

Polished samples in the form of the five-kopeck coins with diameter of 20 mm and thickness of 3 mm were used as substrates. Stainless steel 12X18H10T was the substrate material. Substrates were cleaned in the vacuum chamber by ion bombarding before coating deposition. Titanium nitride coatings were obtained in the vacuum-arc plant "Bulat-3T". Description of the series plant is given in work [2]. Here, two coating deposition modes were used: continuous deposition mode and coating deposition mode with HF stimulation. During last mode, substrate is dipped into plasma [2] and negative pulse potential is given on it. Ion acceleration occurs in dynamic self-organizing border layer which is formed near the target surface under the negative pulse potential. Coating deposition was carried out in the conditions of simultaneous supply on the substrate of constant potential of 230 V and negative pulses of the amplitude of 2 kV with the pulse repetition frequency of 7 kHz and duration of 10 μs. Arc current was equal to 90 A. Nitrogen pressure during deposition was 10^{-2} Pa. Distance between evaporator and substrate was equal to 250 mm. Substrates were heated up to the temperature of 360 °C. During continuous coating deposition, the constant potential, arc current, nitrogen pressure in the chamber, distance between evaporator and substrate, and temperature of the substrates were those as mentioned above.

Thickness of the coatings, state of the boundary between base and coating were determined using the scanning electron microscope REM-106 by the fractographs of fracture at the accelerating voltage of 20 kV. Moreover, the surface morphology of the samples was studied using SEM.

X-ray diffraction investigations of the samples were performed using the X-ray diffractometer DRON-2 in CuK_α radiation.

Study of the mechanical characteristics of coating layers is carried out by the nanoindentation method on the plant "Nanoindenter G200" (MES System, USA) using Berkovich trihedral pyramid with blunting radius at the vertex of about 20 nm. Measurement accuracy of the hardness penetration depth was equal to ± 0,04 nm. In this case, indentations were placed at the distance of 15 μm from each other; measurements of the hardness were performed till the depth of 200 nm in order to decrease the influence of the substrate on the measured values of hardness.

To determine the adhesion/cohesive strength, scratching resistance and to study the fracture mechanism, we have used the "scratch-tester" REVETEST whose scheme is represented in [6]. Scratches at continuously increasing load were applied on the coating surface by the diamond spherical indenter with the radius of rounding of 200 μm. Simultaneously, acoustic emission power, friction coefficient, indenter penetration depth, as well as normal load were registered.

Obtained coatings and samples without coatings were tested for wear resistance on the friction machine SMTs-1 by the scheme "plane-cylinder" using technical petroleum jelly. During the whole test, sample was on the friction machine. Groove width and length in the wear region were realized using the Brinell microscope MPB-2 which provides the measurement precision of ± 0,025 mm.

3. INVESTIGATION RESULTS AND DISCUSSION

First of all, we have to note that all coatings, irrespective of the method of obtaining, were golden-yellow that is typical for stoichiometric titanium nitride.

Technique of the tribotechnical tests by the volume wear method allows to obtain the dependences of the fret size, volume wear, and wear resistance on the time, number of revolutions of the counterface, and path length. In Fig. 1 we represent the dependences of the change in the material volume, taken away by the counterface during the test, on the path length traveled by the counterface. Performed wear resistance tests have given the following results. Coating deposition considerably decreases the volume wear of samples. Carryover of the substrate material was catastrophic [8] (curve 3), whereas coatings of this stage did not achieve the test end. For base tests on 1000 revolutions no one coating was worn and discovered the substrate. Carryover of the coating material deposited in the ion-plasma deposition mode with HF stimulation is 1,5-2 times less than for coatings obtained during continuous deposition.

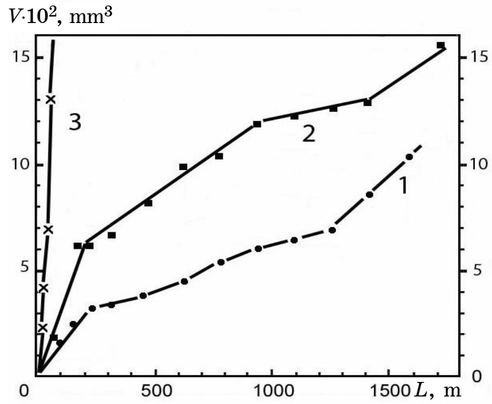


Fig. 1 *– Dependences of the change in the volume wear V on the path length L traveled by the counterface for the samples without coating (curve 3) and with* TiN *coatings obtained in the continuous deposition mode (curve 2) and in the mode with HF stimulation (curve 1)*

Tests for measurement of the sliding friction of coatings have also shown the advantages of the coatings obtained in the HF stimulation mode. Thus, coefficient of sliding friction of the second-type coating is 10-11% less than the corresponding coefficient of usual coating, respectively, at sliding on plastic and polished aluminum. X-ray diffraction investigations of the phase composition of coatings obtained during two modes have shown the presence of only one phase of titanium nitride with the fcc-lattice of NaCl B1Fm3m type [9]. Diffraction peaks (111), (200), (220), and (222) are present on all X-ray diffraction patterns. The values of peak intensity imply that this is the single-phase polycrystalline titanium nitride. Increase in the lattice parameter a (till to $0,42603 \pm 0,0141$ nm for the continuous deposition mode and $0,42599 \pm 0,0173$ nm for the mode with HF stimulation) in comparison with bulk titanium nitride (for which $a = 0,4244$ nm) was observed for both types of the samples [9]. Analysis of the intensities of diffraction maximums shows the presence of axial texture [111] for both modes. Estimation of crystallite sizes indicates that coatings obtained in the mode with HF stimulation have smaller grain sizes. Mean values of the crystallite sizes are equal to 9-10 nm, while during continuous deposition they are of 10,5-12 nm. Morphology of the coatings surface is the same: both drop fractions and pores are present on the coatings surface. The surface structure is shown in Fig. 2 and Fig. 3. However, coatings obtained at different modes have different quantitative characteristics of the surface (Table 1). From the data represented in Table 1 one can see that at pulse deposition mode mean values of the drop diameter, mean pore size, and pore concentration are less that those for the continuous deposition. And exactly this fact can explain the difference in the friction coefficients of the coatings. Fractures of the coatings are also studied by the SEM method. Analysis of fractures has shown that the obtained coatings have sufficiently good adhesion to substrate. It was established there are pores in the coatings irrespective of the deposition modes. These pores can be of two types: open pores situated on the coating surface and closed pores distributed inside the coatings. Through pores coming up to the substrate were not discovered. We have to note that directed growth of the coating particles is often observed in open surface pores. The abovementioned is well illustrated by the microphotographs in Fig. 2 and Fig. 3.

Table 1 – *Values of the experimental parameters for* TiN *coatings*

Parameter	Coating obtained at vacuum-arc deposition	Coating obtained with HF stimulation
Lattice parameter, a	$4,2603 \pm 0,0141$	$4,2599 \pm 0,0173$
$\Delta a/a$, %	0,38	0,24
Size of the coherent-scattering region, nm	10,5-12	9-10

Thus, nanocrystalline TiN coatings with the structure are obtained for the mentioned deposition modes. Deposition mode with HF stimulation provides more fine-crystalline structure; the average nanocrystallite size is equal to about 9-10 nm that, evidently, provides higher physical and mechanical characteristics.

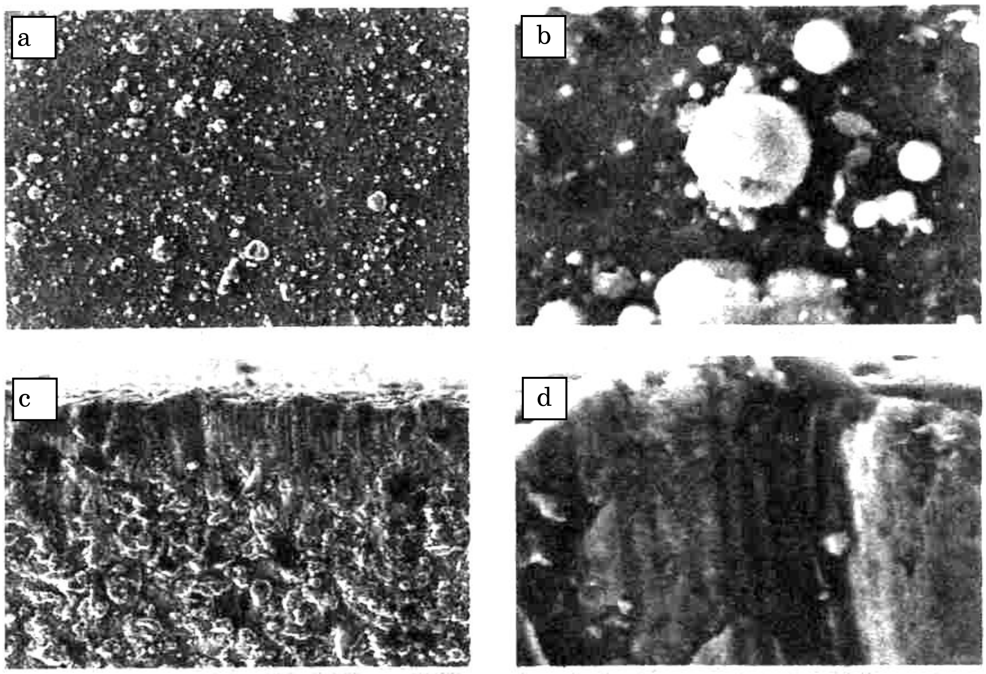


Fig. 2 *– Microphotographs of the surface and fracture of the* TiN *coating obtained at the continuous deposition mode*

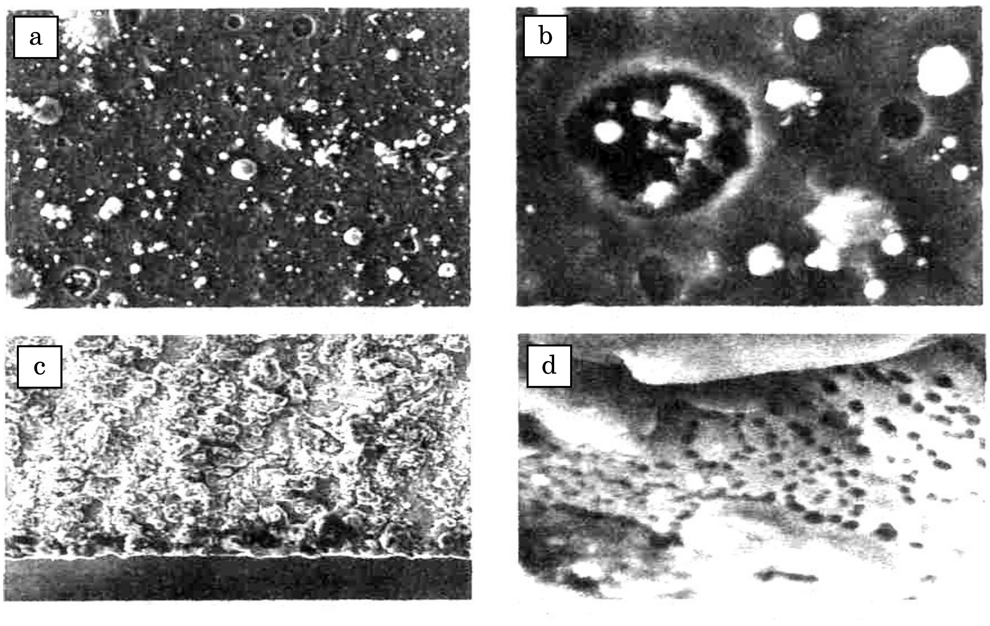


Fig. 3 *– Microphotographs of the surface (a, b) and fracture (c, d) of the* TiN *coating obtained at the ion-plasma implantation mode*

In Fig. 4 we show the profilogram of the initial steel (12X18H10T) sample after polish and before the nc-TiN deposition. As seen from the figure, there are nonuniformities with maximum value along the axis $x \approx 150$ nm. That is, one can state that surface of steel samples is of a sufficiently good quality. After deposition of nc-TiN film roughness appreciably decreases; in this case, maximum value of roughness is about 20 nm. Therefore, one can say that the whole surface consists of grains (drops) of the size in plane (150×200) nm and the height about (15×20) nm (see Fig. 5a, b).

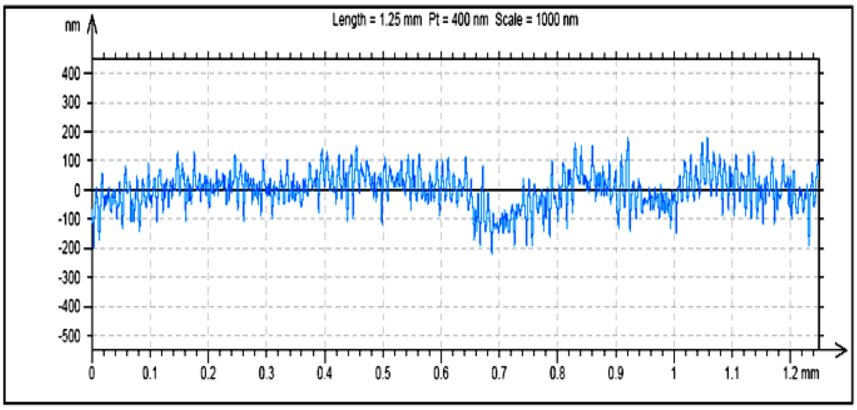
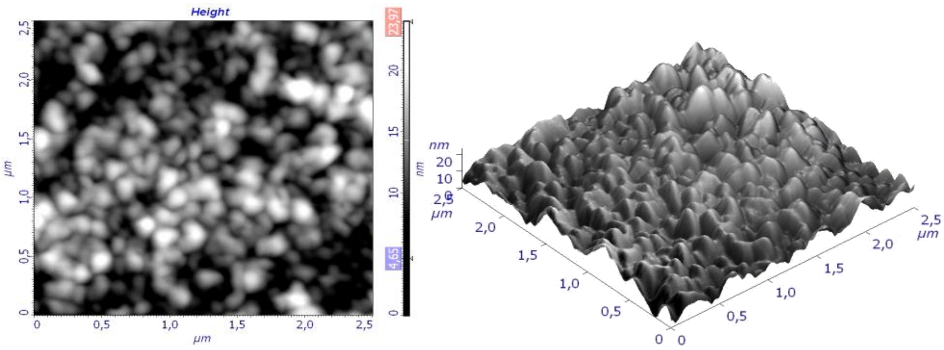


Fig. 4 – *Profilogram of the initial surface of steel (12X18H10T) samples*



a b

Fig. 5 – *Surface morphology of* TiN *coating obtained by the vacuum-arc deposition method: a – two-dimensional image obtained using AFM; b – three-dimensional image of the surface of nc-*TiN *coating obtained by AFM*

In Fig. 6 we show the dependences of the nanohardness on the indenter penetration depth for different coatings deposited on steel samples. One can see that the values of hardness for different deposition conditions in nc-TiN films are different: for deposition in HF discharge (the upper curve) the maximum value of nanohardness is about 32 GPa, while films obtained by the vacuum-arc deposition without HF stimulation have maximum 26 GPa (in this case minimum value is equal to 22 GPa) at the penetration depth for all coatings of 120 nm. Dots denote the measuring points.

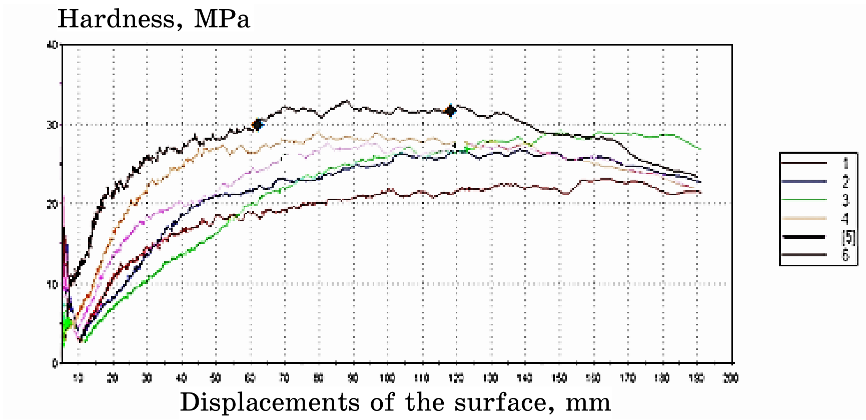


Fig. 6 *– Dependence of the hardness of* TiN *coatings deposited on a steel substrate on the indenter penetration depth*

In Fig. 7 we present the dependences of the elastic modulus on the indenter penetration depth for the samples with TiN coatings

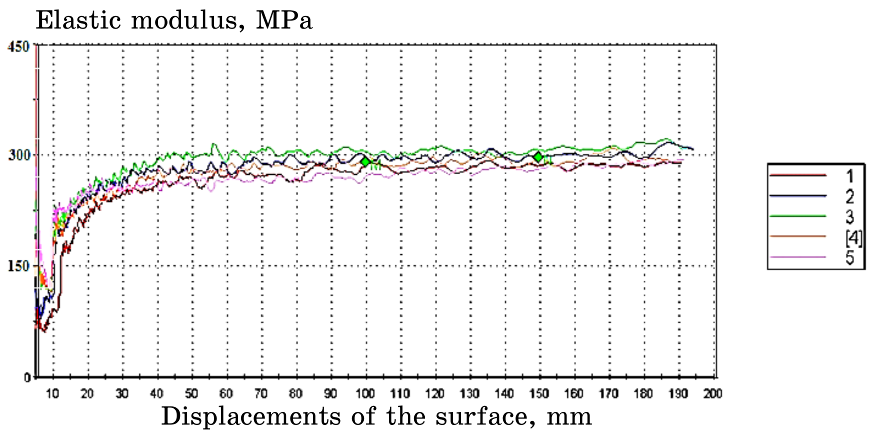


Fig. 7 *– Dependence of the elastic modulus of* TiN *coatings deposited on a steel substrate on the indenter penetration depth*

4. CONCLUSIONS

Thus, we have obtained and investigated the nc-TiN coatings which have the hardness to 32,6 GPa, elastic modulus of ≈ 300 GPa, not very high roughness (12,8-4,2 nm), possess a sufficiently high adhesion, with the nanograin size (coherent-scattering regions) of 9 and 10,3 nm depending on the deposition mode. During deposition by the vacuum-arc deposition method using the HF stimulation, nc-TiN films have smaller grain size in comparison with usual deposition technique.

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