Functional properties of multilayer vacuum-arc TiN/ZrN coatings

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Functional properties of multilayer vacuum-arc TiN/ZrN coatings

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Abstract.

Nanostructured multilayer Ti/ZrN coatings were synthesized by vacuum-arc deposition with a number of layers 134-533 and an average thickness 20-125nm of layers. A good planarity was revealed resulting in a range of nanometer layer from plasma streams in a reactive environment. Phase-structural changes mechanisms were established as a model of critical operating coatings' conditions of in the surface layers under the action of an aggressive oxygen atmosphere at high temperature (700 0C). The thickness parameter effect on its hardness of the multilayer system was shown. It was found that the maximum hardness of 42 GPa and the lowest abrasion of coating 1,3 ×10–5 mm3×H–1×mm–and counterbody 1,9 ×10–6 мм3×H–1×мм–1 inherent in TiN/ZrN system with the smallest layer thickness of 20 nm in the period. The results are explained by the influence of the size factor interphase boundaries magnified in a multilayer system with a nanometer thick layers.

1. Introduction

One of the ways to improve the functional properties of coatings based on refractory compounds nitrides is creating a multi-layer systems, in which the properties superior to the properties of each element individually can be attained by combining the various layers of nitrides. One of the most popular uses of such coatings is a cutting tool, and the friction units of machine parts [1].

Analysis of the literature indicates about perspectives of using for improving the mechanical properties of multilayer coatings in which the layers consisting of nitrides of refractory materials have a thickness of about 20 - 30 nm [2, 3]. Coatings consisting of two layers of hard refractory metals nitrides have high hardness because, tension created in layers prevents the movement of dislocations.

In this regard, unification of TiN and ZrN layers with high hardness in a multilayer coating allows greatly improve the strength of the material for the preservation of high hardness such a comprehensive cover by the formation of a large number of strongly phase boundaries.

2. Experimental details

Coatings were prepared by vacuum arc of the two evaporators. One of which contains titanium brand BT-1-00, the second - zirconium, obtained by electron-beam melting (EBM). Samples with size

(15×15×2,5 mm) from steel 12X18H9T (R_a = 0,09 m) were used as substrates for the deposition of coatings. Samples were obtained at PN = P_N= 3×10^{-3} Torr, and a constant bias potential U_b = -150 V.

During the experiment, three sets of coating samples were formed which differ in layers thickness in the period.

In the first series of samples, pair of TiN/ZrN layers had a thickness of about 40 nm λ at a total coating thickness of about 13 microns. In the 2nd series of samples, TiN/ZrN layers had a thickness of about λ ≈ 70 nm at a total coating thickness h ≈ 14 microns. The third series of samples' TiN/ZrN layers were formed with a thickness of λ ≈ 250 nm with a total coating thickness h ≈14 m.

A number of layers for the different series are: - for the 1st a number of layers 533, for the 2nd a number of layers 233, and for the third a number of layers 134.

Annealing of samples was carried out in a vacuum chamber previously evacuated to a pressure of 10^{-5} Torr in oxygen, self-inflicted to the pressure to 5×10^{-3} Torr.

The surface morphology, fractograph of fracture, friction track were studied by scanning electron microscope FEI Nova NanoSEM 450. Phase-structural condition research was carried out by diffractometer DRON-3M in the emission of Cu-K_α.

The tribological tests were performed in air on a "ball - drive". «Tribometer» was used as the friction machine, CSM Instruments. Coatings were deposited onto the polished surface of cylindrical samples (R_a = 0,088 microns), made of steel 45 (diameter 42 mm, height of 5 mm). A ball with 6.0 mm diameter was used as a counterface, made of sintered and certified material - Al_2O_3. The load was 6.0 N, sliding speed was 10 cm/s. The tests conform to international standards ASTM G99-959, DIN50324 and ISO 20808.

The hardness of the coatings was measured with a hardness tester Model DM 8 by micro-Vickers method at a load of 0.2 N on indenter.

3. Results and discussion

Fig. 1 shows a typical radiograph fragment of the multilayer coating sample. It is seen that layers containing TiN and ZrN phase with cubic (structural type NaCl) crystal lattice without expressly preferred orientation (texture) crystallites are formed after the precipitation on surface layers (informative layer depth of about 4 microns) are formed. TiN layers increases slightly with an increase in the specific contribution period λ, which is manifested in the intensity ratio change of TiN and ZrN phase peaks (see. Fig 1 a and b). The grating period of the nitride phase in the fibers changes with an increase in the duration of the deposition and, respectively, the thickness of layers and the total period of the multilayer system λ: the grating period decreases with increasing thickness of TiN from 0.4241502 nm at deposition time of 20 seconds (λ ≈ 70 nm) to 0.4238870 nm at the deposition time of 40 s (λ ≈ 250 nm). The decrease is less significant in ZrN from 0.4581055 nm at 20 seconds to 0.4581046 nm at 40 seconds.

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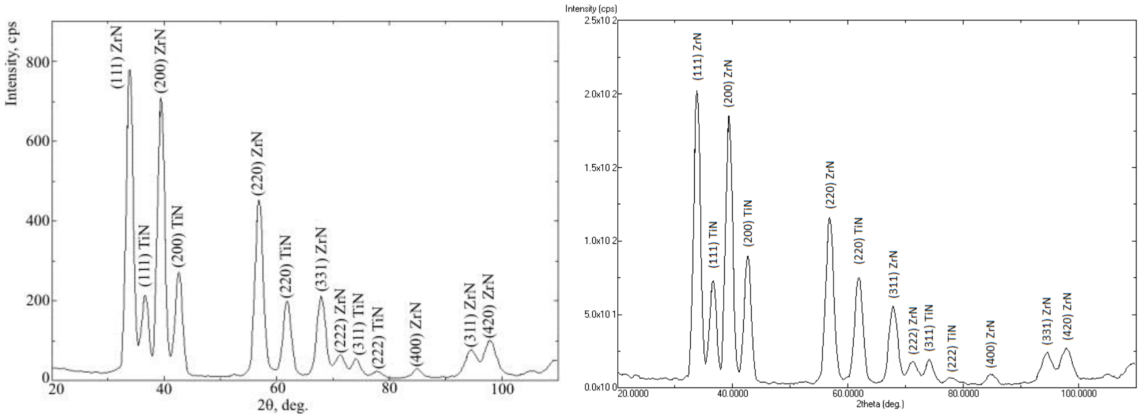
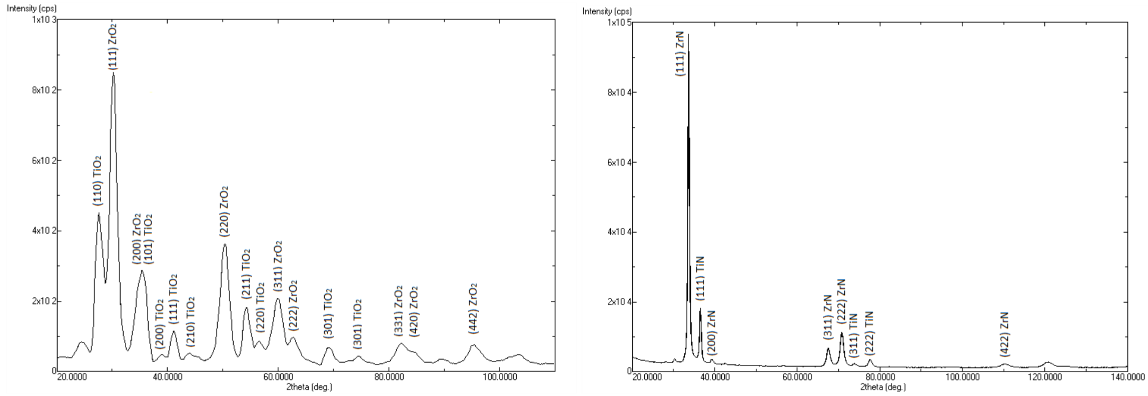


a) b)

Figure 1. Lands of coatings X-ray diffraction spectra with λ ≈ 70 nm (a) 2nd series and λ ≈ 250 nm (b) the 3[d] series

Annealing in atmosphere of oxygen leads to surface layers acidulation and the formation as the main phases in the dioxides fibers - TiO_2 with tetragonal type rutile (base, containing up to 95% in fibers based on Ti) and anatase (containing 5% and less.) Anatase (DB card number 5000223) is detected on the diffraction spectrum (Fig. 2a) by the most powerful first-line angle 2θ ≈25.36 deg. The whole diffraction spectrum (Fig. 2a) is shown for rutile (DB card number 9007531). Only one type of dioxide ZrO_2 (Arkel having a cubic system, DB card number 5000038) is formed in the layers of zirconium nitride by oxidation.



a) b)

Figure 2. The plot of X-ray diffraction spectra of TiN/ZrN coatings with λ ≈ 70 nm obtained after an hour annealing at 700 °C, a) – from the surface without grinding, b – after grinding with oxidized surface of 5 microns.

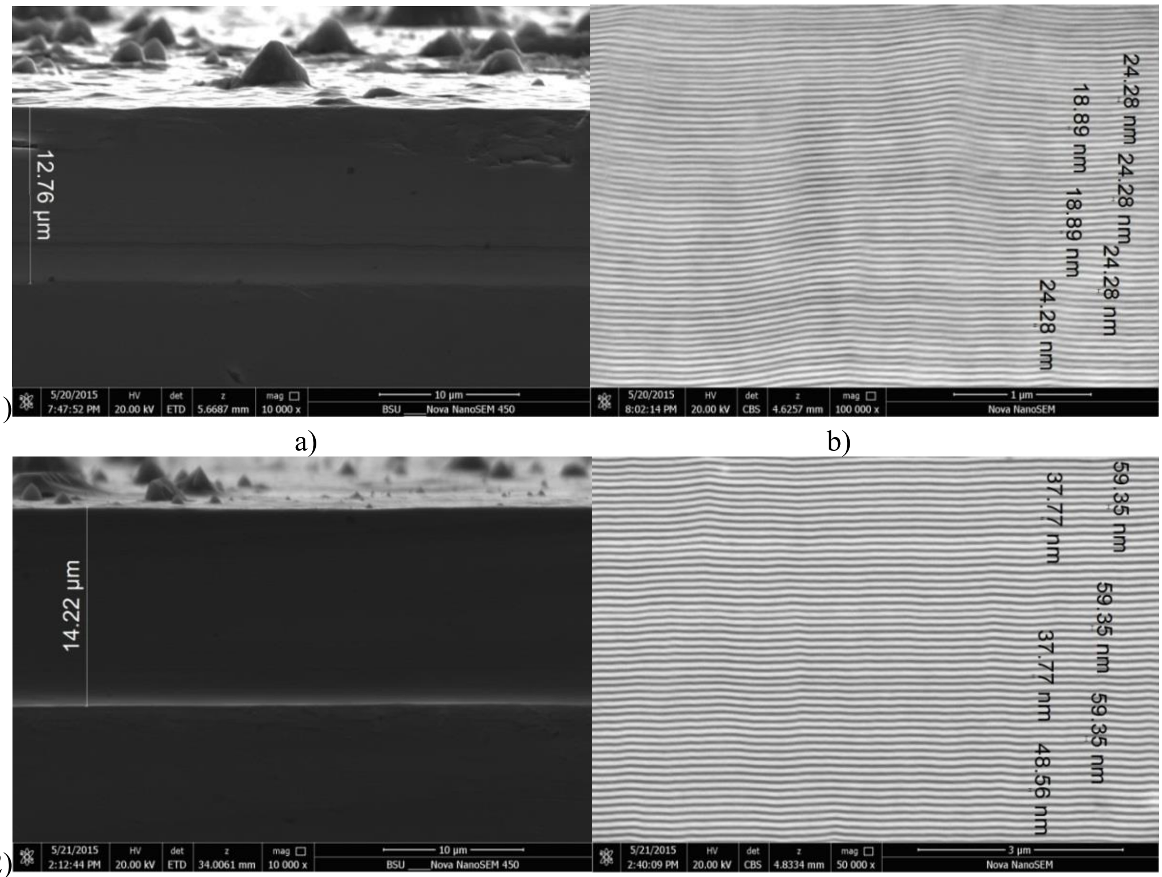
However, as fiberwise X-Ray analysis performed after grinding of a surface layer thickness of about 5 micrometers, the presence of oxides observed in the surface layer of the coating. Oxide formation is not observed in thicker layers after grinding (Fig. 2b), forming nitrides during the deposition have a preferred orientation of crystallites with [111] axis perpendicular to the plane of growth. From this it follows that the predominant orientation of TiN and ZrN crystallites with [111] axis is formed in the initial growth stage, which loses its priority and thus becomes non-oriented crystalline state in the process of increasing the total coating thickness and the relaxation of compressive stress growth.

In this connection, from the results of X-ray analysis it is shown in Figure 2, that oxygen from the atmosphere penetrates the subsurface layer of the coating during annealing, promoting the oxidation up to the formation of stable dioxide phase of metal due to disorientation of the crystallites in the surface layers and low compressive stress. Texture growth is developed in deeper layers under the influence of compressive stresses [111] [4.5], which reflects the initial growth stage, because of the high packing density (111) plane complicates the diffusion depth of such layers. Oxygen does not penetrate in an amount sufficient to form oxide phases.

A detailed analysis of the changes in the surface layers when oxidation allows for data transmission microscopy. Figure 3 shows the results of electron microscopic chips of samples for 3 sets at different magnifications.

It can be seen, that there is a good planarity of precipitation even for the greatest number of the thinnest layers of Series 1 (Figure 3, 1). Also the high denseness of the coating and the lack of it in the form of inhomogeneities in the droplet phase are characteristic and visible when deposited on the surface.

Energy dispersive spectrum is characteristic for all 3-series and shows the stoichiometry of the coating composition of the coating TiN/ZrN which is shown in Figure 4.



1) a) b)

2) a) b)

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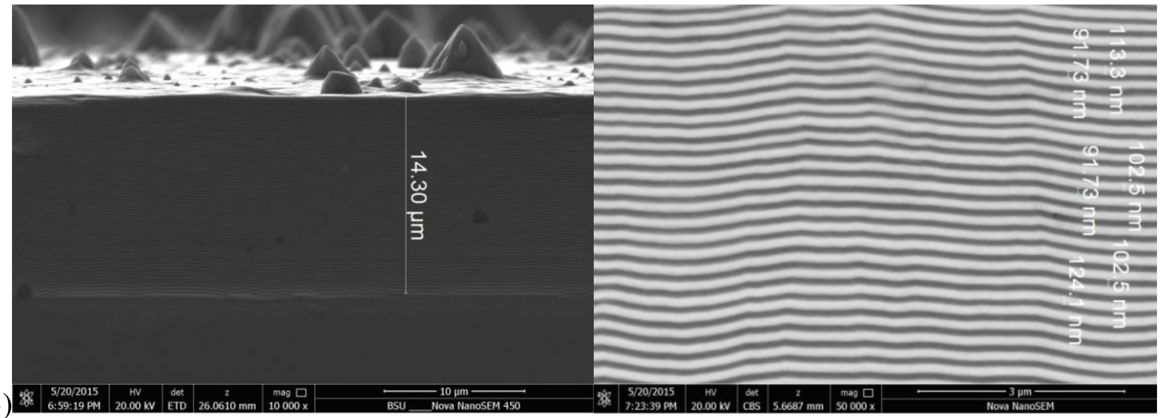
3)


a) b)

Figure 3. Electron micrographs of multilayer TiN/ZrN coatings cross-section: 1) for the first series with 533 the number of layers; 2) for the second series with 233 the number of layers; 3) for the third series with 134 the number of layers.
a) general view of the sample cleavage; b) an enlarged detail of the multilayer coating side surface.

4. Conclusion

The use of vacuum-arc method allows obtaining a two-phase multi-layer system TiN/ZrN with nanometer thickness range of good planarity. With increasing thickness of the composition TiN/ZrN, deposited under the action of U_s = -150 V, the transition occurs from the preferred orientation with [111] axis to the non-oriented state. The presence in the initial layers growth of coating with [111] texture prevents oxidation during high-temperature annealing at 700 ^{0}C in oxygen atmosphere.

References

[1] Cavaleiro, Albano, De Hosson, Jeff Th M, Springer 2006 *Nanostructured coatings*, pp. 648.
[2] Anishik B M, Uglov V V, Zlotskii S V, Emelyanov V A, Ponomar B N, Uhov V A 2003 Mnogosloinie nanostrukturirovannie pokritiya Ti/ZrN: struktura I mehanicheskie svoistva. Perspertivnie materiali. Vol. **4** pp. 75-78.
[3] Siao-Fan Chen, Yu-Chu Kuo, Chaur-Jeng Wang, Sung-Hsiu Huang, Jyh-Wei Lee, Yu-Chen Chan,Hsien-Wei Chen , Jenq-Gong Duh, Tsung-Eong Hsieh 2013 The effect of Cr/Zr chemical composition ratios on the mechanical properties of CrN/ZrN multilayered coatings deposited by cathodic arc deposition system. *Surface & Coatings Technology,* pp. 247–252.
[4] Sobol O V, Andreev A A, Gorban V F, Stolbovoi V A, Pinchuk N V, Meilehov A A 2015 Vliyanie potenciala smesheniya na phazavi sostav, strukturu, substrukturu I mehanicheskie harakteristiki mnogosloinoi systemi TiN/ZrN, poluchennoi vakuumno-dugovim ispareniem. *J. Nano I electronnoi phyziki.* Vol. **2** pp. 6.
[5] Sobol O V, Andreev A A, Gorban V F, Stolbovoi V A, Pinchuk N V, Meilehov A A 2015 *Vliyanie tolshini bisloev TiN/ZrN na strukturu I svoistva mnogosloinih pokritii, poluchennih vakuumno-dugovim ispareniem*. Vol. **2** pp. 124-129.