

Multilayer Nanostructured Wear-Resistant Coatings with Increased Thermal Stability, Adapted to Varying Friction Conditions

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The work covers studying of influence of indexes of an ion-plasma vacuum-arc deposition method to the structure, composition and properties of Ti-Al-N/Zr-Nb-N/Cr-N multilayer nanostructured coatings (MNC). The average crystallites size within the layers is about 5-10 nm. Received coatings are featured by absence of any change in the composition and properties after heating up to 1000 °C, the coatings hardness is up to 36,6GPa, Young's modulus of elasticity is up to 580 GPa, plastic work of deformation is up to 64 %, adhesive strength is about 100 N and coefficient of friction is 0,45.

Keywords: Wear-resistant, Nanostructured multilayer coatings, Arc-PVD coatings, Hardness, Nanoindentation, Tribological properties, Adhesion.

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1. INTRODUCTION

Formation of wear-resistant arc-PVD coatings as a multilayered structures with nanoscale layers size being shaped based on the nitrides of elements, entered into evaporated cathodes structure is a new stage on the path of efficient control of its properties. Meanwhile the share of interphase and intergranular interfaces being an obstacle on the way of movement of dislocations and propagation of cracks increases in the structure of the coatings material. It predetermines, as our studies shown, even more increase in the hardness of such coatings jointly with its viscosity [1-3].

Influence of indexes of an ionic-plasma vacuum-arc method of deposition to structure, the composition and properties of multilayered Ti-Al-N/Zr-Nb-N/Cr-N nanostructured coatings (MNC) is studied in the work.

2. EXPERIMENTAL

Coatings were deposited using a Bulat-NNV 6.6-11 vacuum-arc installation for ion-plasma deposition. We used a three-cathode sputtering system with Ti-Al (VT5 alloy), Zr-Nb (composed by the zirconium host with a niobium insertion at the area ratio Zr : Nb = 3 : 1), and Cr cathodes. The coatings were deposited using nitrogen as a reaction gas. The varied parameters of the process were the rate of the samples coated relative to sputtered cathodes (n), current (I_{ZrNb}) of the sputtering arc on the zirconium-niobium cathode, and negative electrical bias (U_b) supplied to the substrate, varied from 1 to 3 rpm, from 135 to 170 A, and from - 80 to - 160 V, respectively. The deposition time of the coatings was approximately 60 min. Replaceable polyhedral

hard-alloy plates of VK6 VK 6HCT, VRK 15, TT10K8B and TT10K8B grades were used as substrates.

The phase composition and the substructure of developed coatings were investigated by the X-ray diffraction method using a DRON-4 diffractometer.

The chemical composition and the bond energy of coating phases were studied by X-ray photoelectron spectrometry (XPS) using a PHI 5500 spectrometer (Physical Electronics, United States). The element structure, as well morphology of the coatings were additionally defined using the JSM-6700F scanning electronic microscope (JEOL, Japan) equipped by JED-2300F accessory for energy dispersive spectroscopy (JEOL, Japan).

The structure of coatings was studied using Quanta FEG 3D high-resolution multifunctional scanning electron microscope (SEM) (FEI, The Netherlands) and by transmission electron microscopy (TEM) using a JEM-2100 device (JEOL, Japan).

Hardness (H), Young's modulus (E), and work of plastic deformation (W_p) of coatings were determined by the method of measuring indentation under small loads according to the Oliver and Farr technique, carried out using the Micro-Hardness Tester microindenter (CSM Instruments, Switzerland).

The adhesion/cohesion strength in the coating-substrate system was evaluated using the scratching method by the results of the destruction of the samples at a definite load. The Studies were performed using a Revetest device (CSM Instruments, Switzerland). We've found the critical loads L_{c1} , which defines the instant of the first crack appearance, and L_{c3} , which corresponds to the complete abrasion of the coating to its substrate.

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Comparative studies of the tribological properties (wear resistance and coefficient of sliding friction) of the Ti–Al–N/Zr–Nb–N/Cr–N multilayered nanostructured coatings were performed in air under the rod–disc scheme at a normal load of 10 N, linear speed of 20 cm/s, and a wear groove radius of 4 mm) using a Tribometer device (CSM Instruments, Switzerland).

3. RESULTS AND DISCUSSION

Elemental composition of the deposited MNC has shown the content of 24 - 26 atomic. % Cr, 15 - 17 % atomic. Ti, 7 - 12 atomic. % Zr, 43 - 47 atomic. % N, 1 - 2 atomic. % Al and 2 - 4 atomic. % Nb depending on the deposition parameters.

An increase in the current of the sputtering arc on the zirconium–niobium cathode from 135 to 170 A resulted in a rise in niobium and zirconium contents in the MNC from 2, 7% to 4, 12%, respectively; whereas a

corresponding decrease in concentrations of the other elements was observed. A rise in the bias potential on the substrate from –80 to –160 V, caused an increase in energy of the sputtered ions, resulted in a decrease in nitrogen content in the MNC from 47 to 43 atomic % due to the preferential sputtering of this element as a lightest one within the MNC, by heavy metal ions.

The presence of the ZrN, TiN, and Cr₂N phases within the MNP structure was established by X-ray diffraction. It can be assumed that the absence of the aluminum and niobium phases within the MNP is caused by dissolution of these elements in ZrN and TiN nitrides, yielding the according solid solutions. Additional data related to the phase composition of the MNP was obtained out of analysis of the high-resolution XPS spectra of Cr2p, Zr3d, Ti2p electrons as shown in Fig 1.

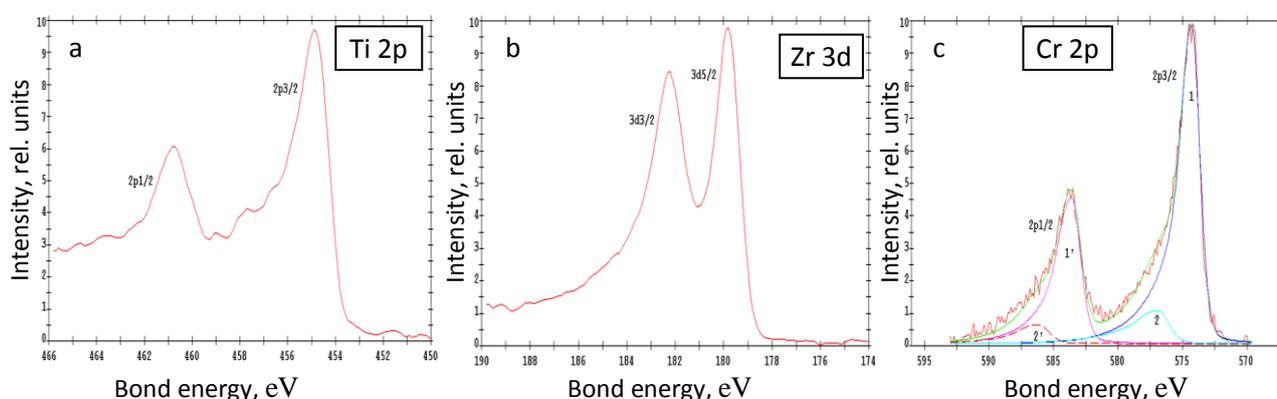


Fig. 1 – High-resolution XPS spectra of Cr 2p (a), Zr 3d (b), Ti 2p (c), Nb 3d (d) MNC

Localization of the maxima of the Ti2p_{3/2} (Fig. 1 a) and Zr3d_{5/2} (Fig. 1b) peaks at the bond energies of 455.0 and 179.9 eV, respectively, is typical for Ti bond in TiN and Zr bond in ZrN in non-stoichiometric zirconium nitride ZrN_{0.68}. The maximum of the Cr2p_{3/2} peak, 574.3 eV (Fig. 1c), corresponds either to metallic chromium or to its bond with nitrogen in the Cr₂N composition. The presence of a second doublet of the Cr2p_{3/2} peak also gives the grounds to assume existence of CrN phase.

It was found that the micro deformation values and the lattice periods of nitrides change non-monotonically with increasing of the bias potential.

An increase in the bias potential supplied to the substrate from –80 to –120 V results to rise in micro deformation values 1,3 to 1.5% and 2 to 2,7% accordingly for titanium nitrides and zinc and the simultaneous rise in lattice periods of nitrides 4,24 to 4,27 Å and 4,43 to 4,44 Å. This is caused by the fact that the energy of the ions bombarding the MNC surface increases with the bias potential and the increased probability of formation of anti-Schottky defects and Frenkel pairs induced by the ion peening effect. The subsequent increase in the bias potential from –120 to –160 V results in a decrease in the micro deformation values and the lattice periods of nitrides, which is associated with the washing-out of the borders between specific nanolayers and formation of solid solutions (Ti, Cr)N and (Zr, Cr)N

[the metal dissolution in TiN and ZrN nitrides causes a decrease in their lattice periods].

The rate of the substrate, which determines the duration of formation and thickness of each nanolayer, affects substantially the performances of structure of the MNC -forming phases. The physical broadening (β) of line (111) for ZrN and TiN was shown to increase with the rate (Fig. 4). This is caused by both decrease in crystallite size (D) and increase in the level of micro deformations of the crystal lattice. Thus, the rise in the rotation speed of the substrate from 1 to 2 rpm leads to the changes in crystallite size from 11 ± 2 to 6 ± 2 nm. and further increase in the rotation speed to 3 rpm causes no changes. The constancy of the crystallite size can presumably be attributed to a decrease in time of nucleation and growth of the nuclear phase based on the components of each cathode. This takes place due to a decrease of the residence time of the substrate in the region of preferential condensation of the components of one of the sputtered cathodes as the substrate intersects the plasma flows generated by corresponding cathode.

The nanolayer thickness in MNC was determined using the XPS method using layer-by-layer etching of MNC surface by argon ions. The etching rate was approximately 2 nm/min at the used energy of argon ions. The elements were found to be non-uniformly distributed in the MNC (Fig. 2).

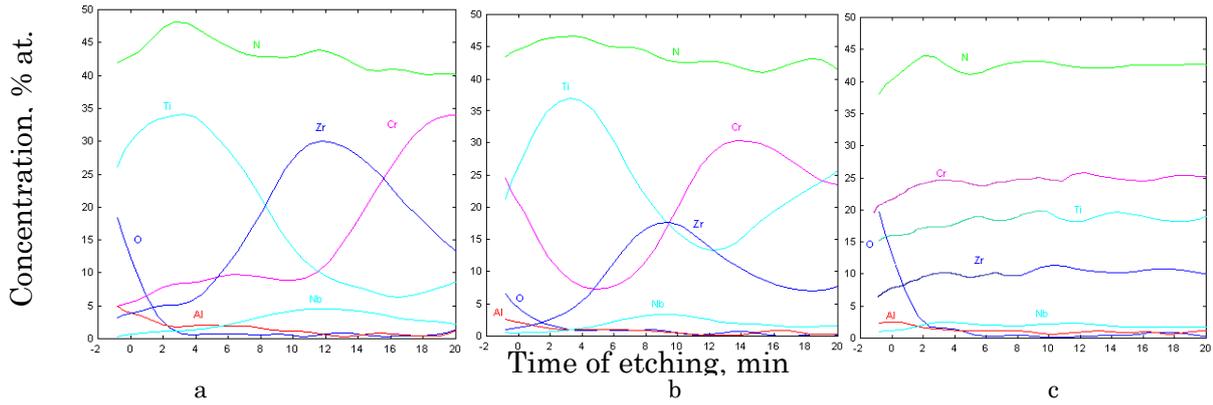


Fig. 2 – The element concentration profile in the multilayer coating obtained at $U_b = -120$ V and different rates of the substrate [(a) 1, (b) 2, and (c) 3 rpm]

It is clear that an increase in the rate of the samples in relation to sputtered cathodes from $n = 1$ rpm to $n = 2$ rpm results in reduction in layer thickness (e.g., for TiN, from ~ 16 to ~ 12 nm) (Figs. 2a and 2b). The homogenization of the coating composition (absence of the multilayer structure) was observed at $n = 3$ (Fig. 5c); i.e., the structure degradation took place.

Similar results were obtained by investigating the MNP structure via high-resolution SEM imaging in an end section (Fig. 3); it can be seen that the coating has a layered structure.

The average crystallite size within the layers, which was estimated using the high-resolution microimages of the MNP structure (Fig. 8), is approximately 5–10 nm, which meets the data obtained by approximation using the physical broadening of X-ray diffraction lines ($D = 6 \pm 2$ nm).

To evaluate thermal stability the MNC were annealed under $\sim 10^{-3}$ Pa vacuum at 800, 900, and 1000 °C for 1 h.

Subsequent analysis of concentration profiles of the basic metal elements (Ti, Zr and Cr) through thickness of MNC, obtained at different annealing temperatures has shown that no noticeable changes in MNC composition or structure occur at temperatures up to 1000 °C. Significant diffusion mixing of layers is observed at 1000 °C, which is attested by a decrease in the intensity of the concentration peaks of Cr and Ti. Which evident the drop in MNC hardness from 32.3 to 28.1 GPa.

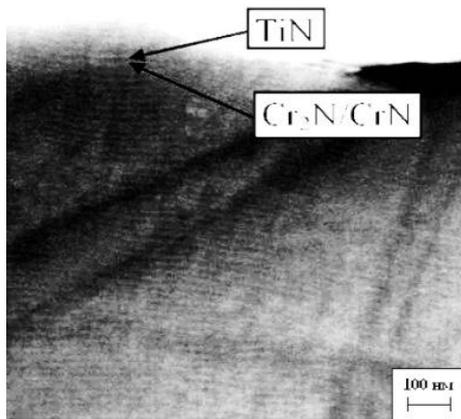


Fig. 6 – Nanolayered multilayer NMC, received at $U_b = 80$ V and $n = 1$ r/min

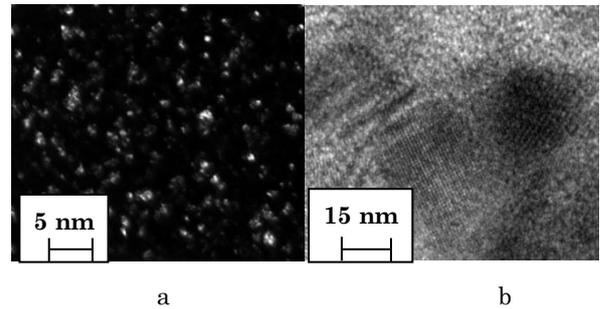


Fig. 7 – Electron microscopy images of the MNC received at $U_b = -80$ V and $n = 1$ rpm: (a) dark field image, (b) high-resolution image

Experimental study of affection of MNC reception indexes to its physicomechanical properties allowed to define correlation between change in physicomechanical properties of MNC and its structure depending on the bias potential and the rotation speed of the substrate during vacuum arc ion-plasma sputtering. It was shown that measurements of hardness and the Young’s modulus are subjected to the same regularities as the structure parameters (micro deformations and crystallite size). Maximum level H (36,6GPa) and E (580GPa) means thinning of layers decrease of crystallite size and the maximum level of micro deformations. Meanwhile no viscosity loss happens (W_p , plastic work of deformation value is appr. 56 %).

Increase in rate of the substrate above 2 rpm, leading to the degeneracy of the MNC, affects insignificantly its hardness, which is mainly determined by crystallite size.

the study of cohesion and adhesion strength of the MNC by scratch test it was shown, that increase in potential of displacement (-80V to-160V), leads to degeneration of multilayer structure, and MNC cohesion strength decreases, that is revealed as reduction of the load at first crack: $L_{c1} = 49,7$ H, $L_{c1} = 47,8$ H and $L_{c1} = 28,4$ H accordingly.

As the load rises, the intense cohesion destruction of MNC occurs which is revealed in the formation of many diagonal cracks on the scratch bottom, but no exfoliation of the coating from the substrate is observed. Meanwhile the friction coefficient increases and it abruptly increases at $L_{c3} > 98.3$ N ($U_b = -80$ V), $L_{c3} > 100$ N ($U_b = -120$ V), and $L_{c3} = 89.5$ N ($U_b = -$

160 V), accordingly which is related to the full destruction of MNC and reaching of the substrate material by the indenter.

The coatings that are more resistant to plastic deformation demonstrate the highest values of Lc3 index. Thus, parameter H3/E2, based on which we can estimate the material resistance to plastic deformation, is equal to 0.09, 0.11, and 0.14 GPa for the coatings formed at $U_b = -160, -80, \text{ and } -120$ V, respectively.

Analysis of received data set allows to conclude about cohesion mechanism of destruction of MNC formed over the entire range of used deposition parameters.

The friction coefficients of developed coatings were compared to ones of MNC of other compositions and multicomponent single-layer coating (AlCrTaTiZr)N (0.6), created by the magnetron sputtering.

These results show that the Ti-Al-N/Zr-Nb-N/Cr-N MNC have more less friction coefficient compared to one for the known Ti-Al-N/Zr-N, Ti-Al-N/Cr-N MNC, which may be related to the more tribological adaptability of these coatings, revealing through the development of the tribofilm consisting of aluminum, zirconium, and chromium oxides during friction accompanied by heating which protects MNC surface and improves

its lubricating ability during friction. However, less friction coefficients of these MNC compared to the Ti-Al-N/Zr-N coating indicate substantial influence of chromium oxides on its tribological properties.

4. SUMMARY

Influence of ion-plasma vacuum-arc method of deposition (rate of rotation of deposited samples in relation to sprayed cathodes (n) is investigated; current of the sputtering arc on the zirconium-niobium cathode (I_{ZrNb}) and negative electric bias potential (U_b), supplied to the substrate) to the structure, composition and properties of Ti-Al-N/Zr-Nb-N/Cr-N multilayer nanostructured coatings (MNC) was studied. The average crystallites size within the layers is about 5-10 nm. The coatings are featured by absence of any change in the composition and properties in case of heating up to 1000 °C. The coatings hardness is up to 36,6GPa, Young's modulus of elasticity is up to 580 GPa, plastic work of deformation is up to 64 %, adhesive strength is about 100 N and coefficient of friction is 0,45. Those properties define the prospects of developed coatings application as wear-resistant, and able to be operated under alternate loads and high temperatures condition.

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