

# THE USE OF STRUCTURAL ENGINEERING FOR OBTAINING SUPERHARD COATINGS BASED OF NITRIDES TRANSITION METALS

## ИСПОЛЬЗОВАНИЕ СТРУКТУРНОЙ ИНЖЕНЕРИИ ДЛЯ ПОЛУЧЕНИЯ СВЕРХТВЕРДЫХ ПОКРЫТИЙ НА ОСНОВЕ НИТРИДОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ

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**Abstract:** System analysis of impact negative bias potential on structure, substructure and mechanical characteristics of single-layer ZrN and multilayer ZrN/TiN coatings that been obtained by vacuum arc evaporation done at article with the aim of development of direction «Structural Engineering of Nitride coatings».

Obtained results have allowed to identify three levels of impact:

- macro- level (phase composition, macrostructure, macrostresses state);

- micro- level (preferred orientation of crystallites – texture);

- nano- level (size of areas of coherent scattering (crystallites), microdeformation).

Superhard state with the magnitude micro-hardness of 44.8 GPa been reached in ZrN/TiN coatings as a result of using Structural Engineering.

**KEYWORDS:** NEW MATERIALS, COATINGS, VACUUM ARC, NITRIDES, STRUCTURAL ENGINEERING, MACROSTRUCTURE, MICRODEFORMATION, SUPERHARD COATINGS

### 1. Introduction

In recent years is observed heightened interest in new class of materials with unique functional properties – nanostructured materials. For today one of most prospective are nanostructured materials that created in non-equilibrium conditions ion-plasma condensation. The non-equilibrium of conditions of obtaining (typical for these processes) leads to impossibility of accurate modeling of mechanisms of formation and materials properties. Use of structural approach to managing of properties (structural engineering) is proposed in the article to resolve this problem.

In recent years zirconium nitride (ZrN) attracts increased interest due to unique combination of good corrosion resistance, low electrical resistivity, high melting point (about 2990°C), sufficiently high mechanical properties and high chemical stability [1; 2]. Latest makes it demanded as coatings on blade tool that operating at high cutting speed.

Structure and properties of coatings is largely determined by negative potential of bias that supplied to substrate at deposition ( $U_b$ ) with a high degree of ionization as in the case vacuum arc method of receiving [3].

The aim of article is explore possibilities of using  $U_b$  for structural engineering of single- and multi-layer coatings based on ZrN.

### 2. Material and methods

Vacuum arc with feeding of negative bias potential (in constant or impulse form) onto a substrate (CIB (condensation - ion bombardment) method) has been used as a main method of getting. Basic installation for deposition – modernized «Bulat-6». ZrN coatings were obtained at a pressure of nitrogen atmosphere  $P_N = 4.7 \cdot 10^{-3}$  Torr, the value of the negative DC bias potential of the substrate supplied to the  $U_b = (-27 \dots -300)V$ . The duration of the deposition process is 1 to 2 hours. Stainless steel plate 12X18H10T 18x18x2 mm sizes and copper foil used as the substrates.

Multilayered two-phase nanostructured coatings TiN/ZrN were precipitated by evaporation of the two types of cathodes: titanium Ties 1-0; low-alloy zirconium; active gas – nitrogen (99,95 %). Procedure of deposition of multilayer coatings is included following operations. Vacuum chamber was evacuated to a

pressure of  $10^{-5}$  Torr. Then to swivel apparatus with substrate holder were fed negative potential of 1 kV, were included evaporator and were produced purification of surface of first of the two substrates by bombardment of ions of chromium during 3 ... 5 min. Thereafter substrate holder was rotated 180° and was carried out same purification of second substrate. Further concurrently were included are both evaporators, was fed nitrogen into the chamber and were precipitated first layer from one side ZrN, and from the opposite – TiN.

Process of deposition was performed at the following technological conditions. After deposition of first layer are both evaporators were turned off, were turning substrate holder for 180° and again concurrently have included both evaporators. Arc current during the deposition was 100 A, nitrogen pressure ( $P_N$ ) in the chamber  $4.8 \cdot 10^{-3}$  Torr, distance from the evaporator to the substrate – 250 mm, substrate temperature ( $T_s$ ) was in the interval 250 ... 350 °C. Were obtained coatings of thickness about 10 microns. At the time of deposition on a substrate was fed constant negative potential  $U_b = -70 \dots -200V$ .

Micrographs of coatings obtained by raster electron microscope JEOL JSM 840. For the electron microscopy studies of the coating deposited on the copper substrate thickness of 0.2 mm.

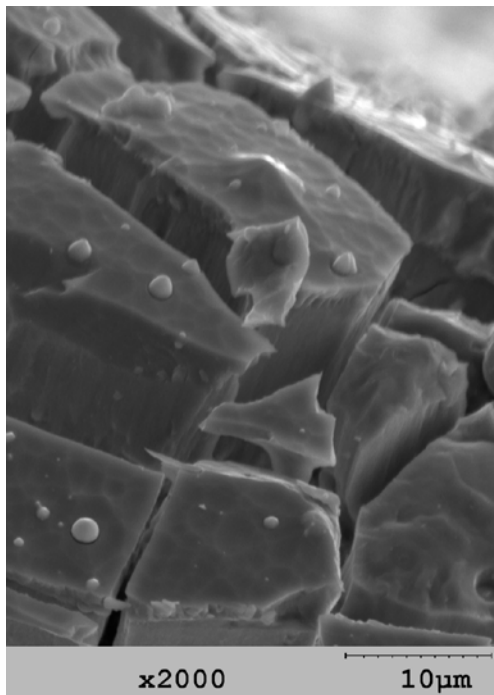
Phase composition, structure and substructural characteristics have been studied by method X-ray diffractometry (DRONE-4) with use Cu- $K_\alpha$ -radiation. For monochromatisation of registered radiation was used graphite monochromator, which was installed in a secondary beam (ahead of the detector). Study of phase composition, structure (texture, substructure) were produced by means traditional methods of ray diffractometry through the analysis of position, intensities and forms of profiles of the diffraction reflexes. For decryption of diffractograms were used tables of International Centre for Diffraction Data Powder Diffraction File. Substructure characteristics were determined by method approximation.

The hardness of the samples was determined by using installing "Micron-gamma" equipped pyramid Berkovich at room temperature (up to a maximum load of 0.5H).

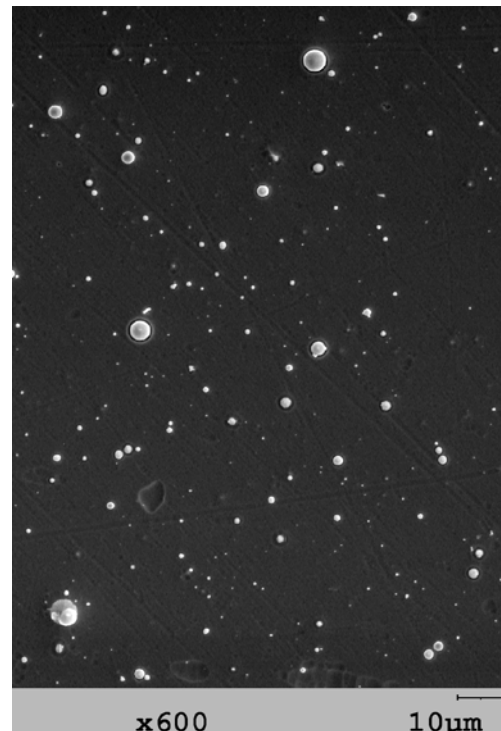
### 3. Results and Discussion

Research of morphology coatings surface ZrN been revealed that coatings, which obtained at relatively low constant potential of bias  $-40$  V have as in volume, than also on surface sufficiently large number of droplet phase (Fig. 1a, b). Herewith the structure hasn't pronounced columnar structure of growth of crystallite. Increasing of the bias potential leads to a decrease droplet phase and to appearance of columnar structure. Surface morphology and fracture pattern of coatings that deposited at feed

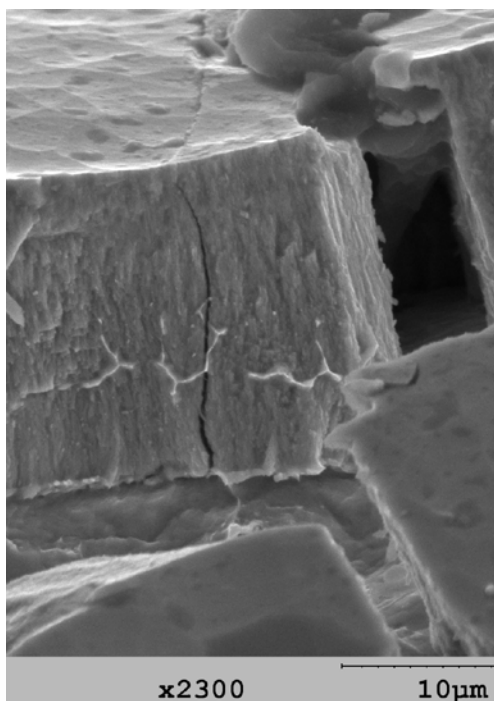
of bias potential with magnitude  $U_b = -220$  V is shown on Fig. 1 c, d. It is seen that microparticles of droplet phase in volume and also on the surface practically absent in coatings and structure of coating growth has columnar appearance (Fig. 1 c). Such considerable decrease in the content of droplet phase can be explained by that droplet component, also as any other accumulation of atoms that placed in plasma acquires a negative (floating) potential and is repelled by surface, on which negative potential (in this case by substrate surface) is served [4].



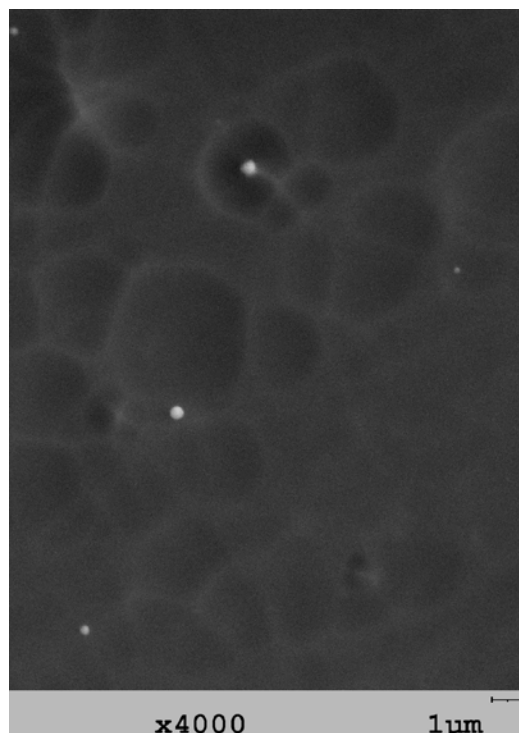
a



b



c



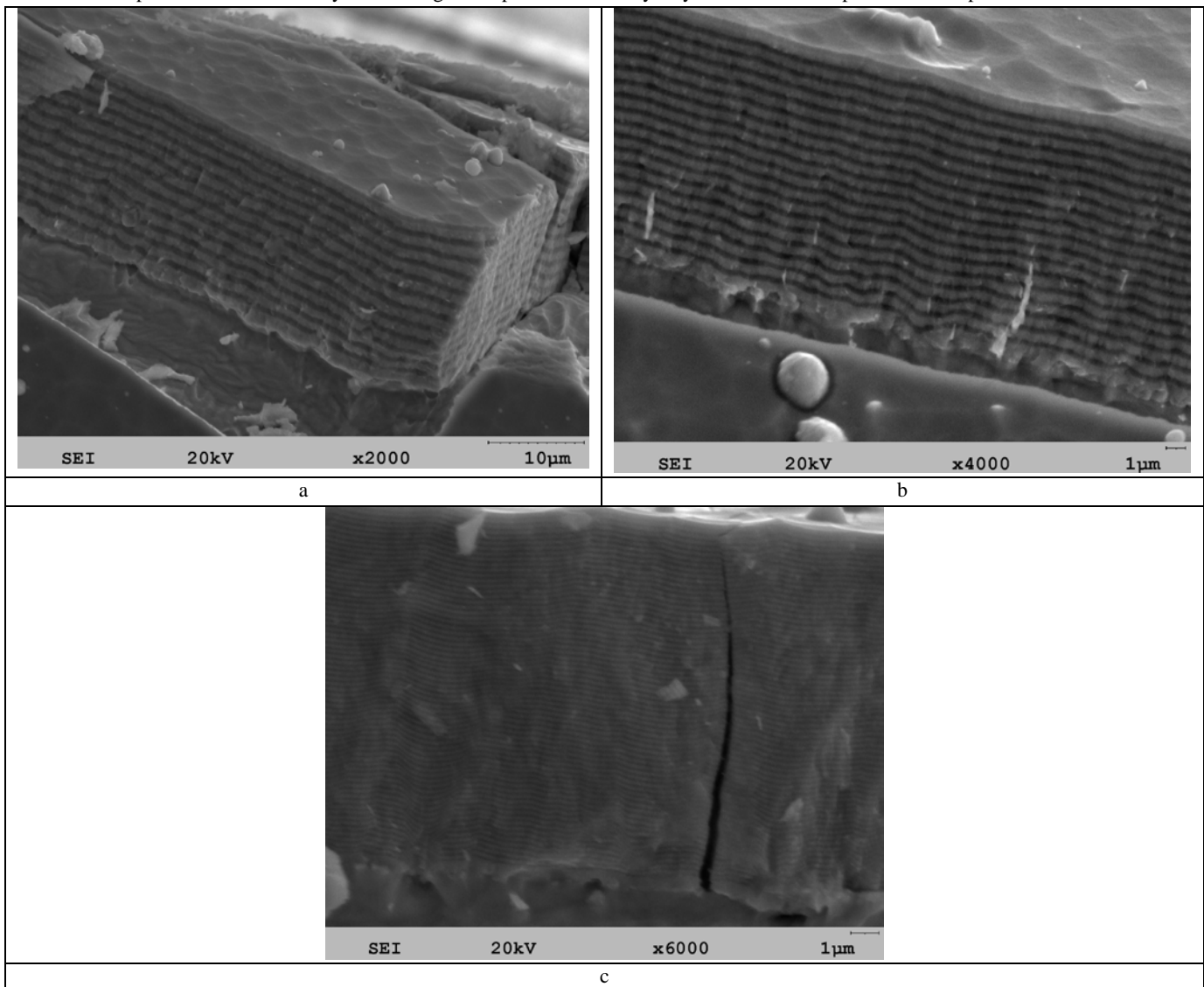
d

Fig. 1 – Surface morphology and fraktogramma of fracture coatings ZrN ( $P_N = 4,7 \cdot 10^{-3}$  Torr): a, b –  $U_b = -40$  V; c, d –  $U_b = -220$  V

Impact of constant potentials of displacement with magnitude -200 V and -110 V is considered in article for multilayer coatings ZrN/TiN.

Images of fracture morphology of coatings with maximum thickness of layers with bilayer period about 1.5 microns (Fig. 1 a) and with lesser periods of 0.8 microns (Fig. 3 b) and 0.2 microns (Fig. 3 c).

It is seen that planarity and uniformity by thickness of layers is observed and appearance of drop phase inside layers is not observed irrespective of number of layers and magnitude period of multilayer systems at constant potential of displacement -200V.



**Fig. 2** – Fracture morphology of coatings with 26 layers (13 periods by two layers with average thickness of period 1.5 microns) (a), b – 36 layers (18 periods by two layers with average thickness of period 0.8 microns) and c – 134 layers (67 periods by two layers with average thickness of period 0.2 microns)

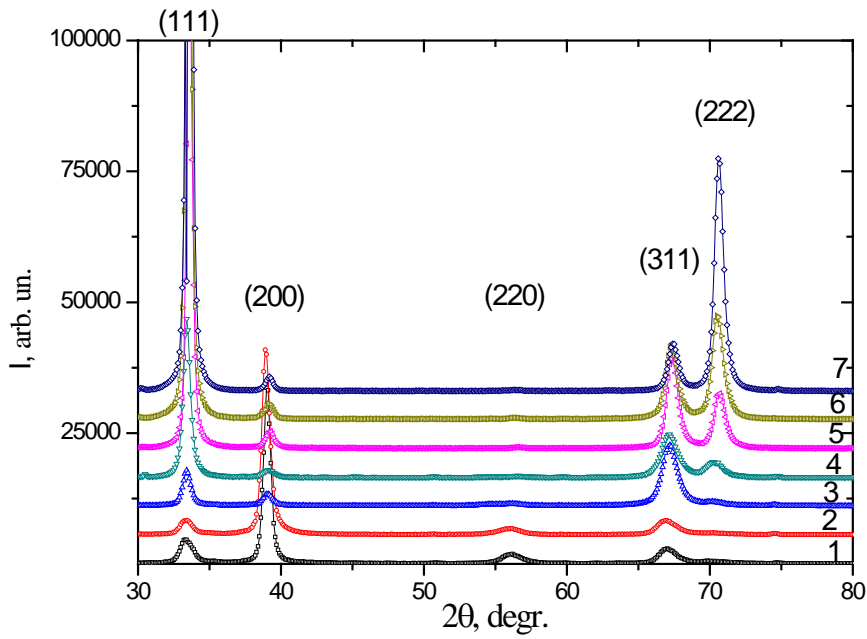
Lighter layers – ZrN, which are obtained by 1.5 times thicker, than TiN. I.e evaporation rate TiN lower than zirconium nitride. At total coating thickness 734 about 17 microns (13 layers of titanium nitride and 13 layers of zirconium nitride) – layer thickness of zirconium nitride - about 900 nm and a titanium nitride – about 600 nm. Despite the fact that time of deposition of each layer were about 300 seconds – deposition rate of zirconium nitride 3 nm/s and the titanium nitride – 2 nm/s. Then obtain at minimum deposition time 10 s – will layer thickness of zirconium nitride about 30 nm and titanium nitride – about 20 nm.

Results of X-ray diffraction research were obtained in basis of structural engineering.

Diffraction spectrums of coatings that obtained at different meanings  $U_b$  are shown on Fig. 3. It is seen that forming

single-phase structural state that typical for ZrN with face-centered cubic lattice (structural type NaCl) is happening throughout the range of submitted displacement potential (-27...-300 V). In this case attitude of intensities reflections from different planes is changed depending on magnitude of supplied negative potential of displacement that evidence of appearance texture (preferential orientation of crystallites). Large intensity of peak from the plane (200) at low bias potential (27 ... 40 V) indicates on texture with axis [100] that perpendicular to plane of growth.

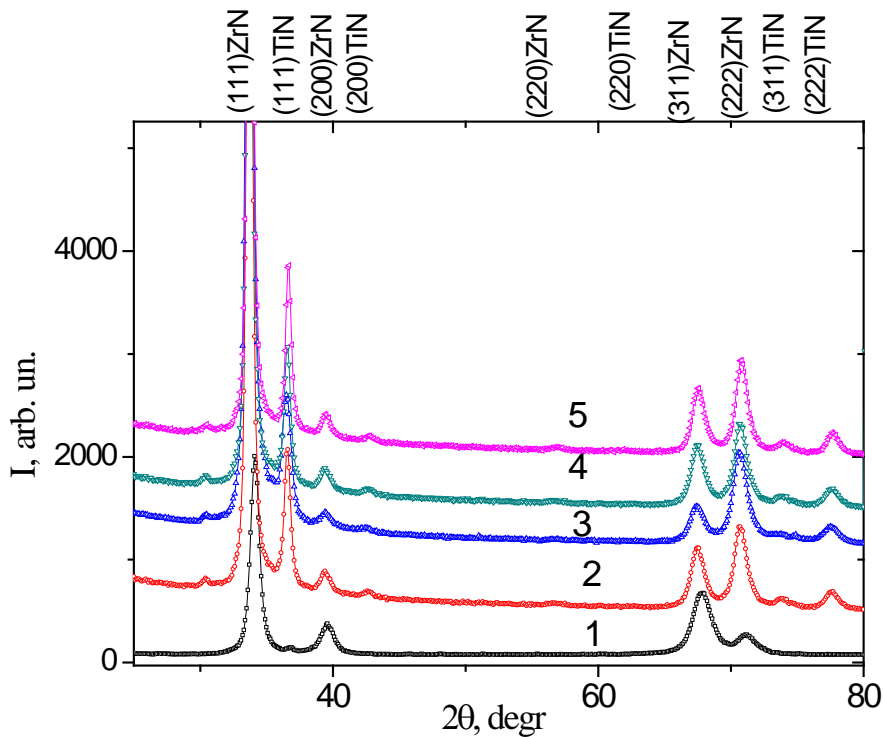
Changing texture is happening with increasing  $U_b$ ; at  $U_b = (-70 \dots -150 \text{ V})$  – on bi textured with preferred orientation of crystallites with axes [311] and [111] that perpendicular to plane of growth and at  $U_b$ , which exceeding by meaningfully -150 V to almost uniaxial texture with axis [111] (Fig. 3, spectrums 6 and 7).



**Fig. 3** – Sectors of X-ray diffraction spectrums of coatings ZrN that were obtained at  $P=4,7 \cdot 10^{-3}$  Torr,  $U_b$ : 1 – 27 V; 2 – 40 V; 3 – 70 V; 4 – 100 V; 5 – 150 V; 6 – 220 V; 7 – 300 V

X-ray diffraction (XRD) spectrums of coatings of multiperiod system ZrN/TiN are shown on Fig. 4. Is seen that at smallest  $\Lambda = 10$  nm (spectrum 1, Fig. 4) phase is formed based on ZrN of crystal lattice with reduced (as compared with tabulated

values for ZrN) period of 0.4523 nm. This is determined by smaller atomic radius of titanium, due to which period of isostructural lattice TiN phase is small and amounts to 0.4241 nm (card PDF 38-1420).



**Fig. 4** – Sectors of diffraction spectrums coatings ZrN/TiN that are obtained at  $U_n = -110$  V, with different  $\Lambda$ : 1 – 10 nm; 2 – 20 nm; 3 – 80 nm; 4 – 150 nm; 5 – 300 nm.

Increasing thickness of  $\Lambda$  for this system leads to forming similar phases ZrN and TiN at crystal lattices with same type of preferential orientation (axis [111]) of crystallites in layers.

Supply of constant potential of displacement on substructural level leads to increasing crystallite size at meanings  $U_b$  is less -200 V (Fig. 5). Increasing degree of interaction between metal atoms and nitrogen atoms that were activated by increasing

energy are one of main causes of this process. Decreasing crystallite size when submitting higher potential may be associated with process of polygonization under impact high compressive stresses that are reaching magnitude  $\sigma = -6,7$  GPa (critical magnitude for displacement of dislocations in ZrN). Observed decreasing of microdeformation can associate with this process (Fig. 5 b).

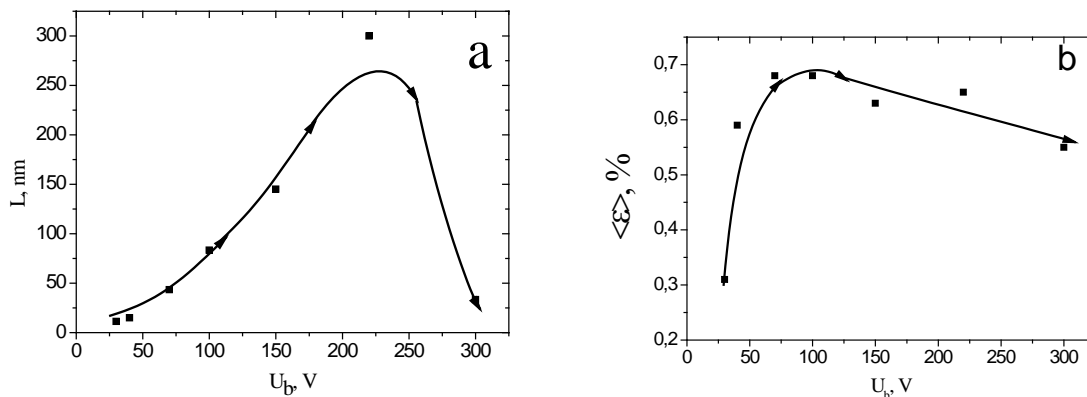


Fig. 5 – Dependency of crystallite size (a) and microdeformation (b) from constant potential by  $P_N = 4.8 \cdot 10^{-3} Topp$

Increasing constant potential of displacement in multilayer systems ZrN/TiN on substructural level leads to decrease microdeformation and to decrease crystallite size in TiN component and to increasing sizes in ZrN component (Fig. 6).

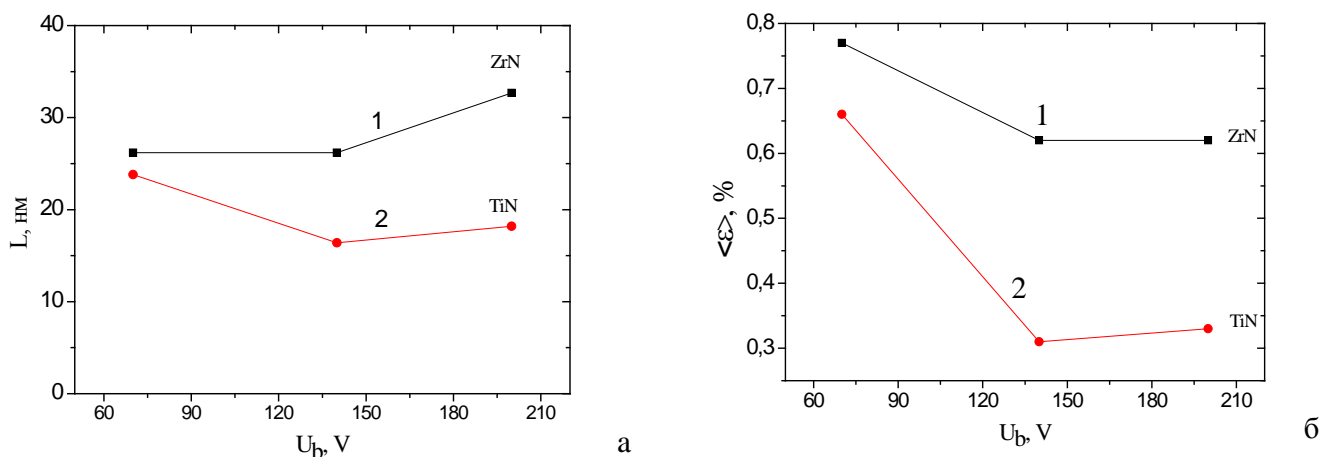


Fig. 6. Changing substructural (crystallite size,  $L$  (a) and microdeformation,  $\langle \epsilon \rangle$  (b)) characteristics on the magnitude supplied bias potential  $U_b$ . 1 – relates to layers ZrN, a 2 – to layers TiN

Reason of observed non-uniform changes can be associated with more strong radiation damageability ZrN layers due to large mass Zr atoms that bombarding surface during the growth of these layers. Decreasing microdeformation and increase of medium crystallite size at maximum  $U_b = -200V$  can be associated with larger average energy of deposited particles and with

temperature of heating the surface. First and second – allows increasing surface diffusion and correspondingly more uniform filling surface plane by atoms. This defines larger average crystallite size. Herewith period grating decreases as a result of compaction coating as ZrN, than also in TiN layers that is shown on Fig. 7.

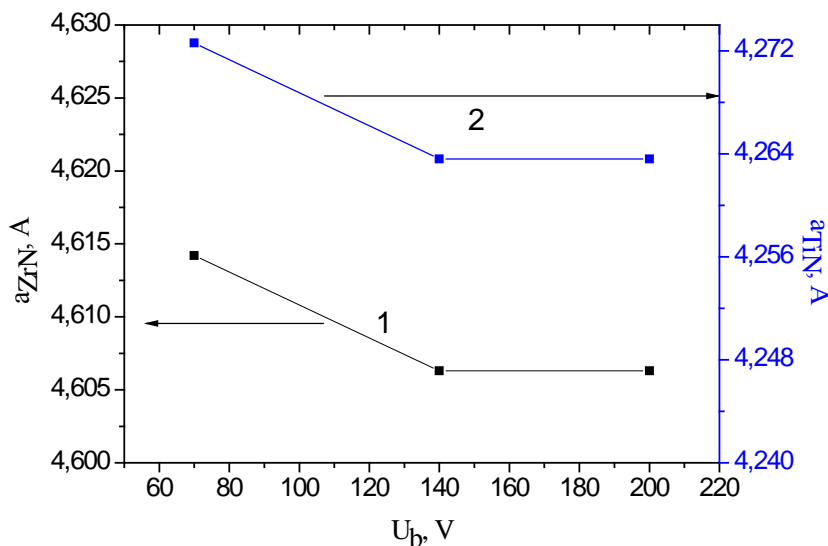


Fig. 7 – Dependencies of changing periods grating on the magnitude supplied bias potential  $U_b$ , 1 – relates to layers ZrN, and 2 – to layers TiN

Macrostress state changed by not monotonically: increases with decreasing  $\Lambda$  to 25 nm with subsequent fall at lower period (Fig. 8).

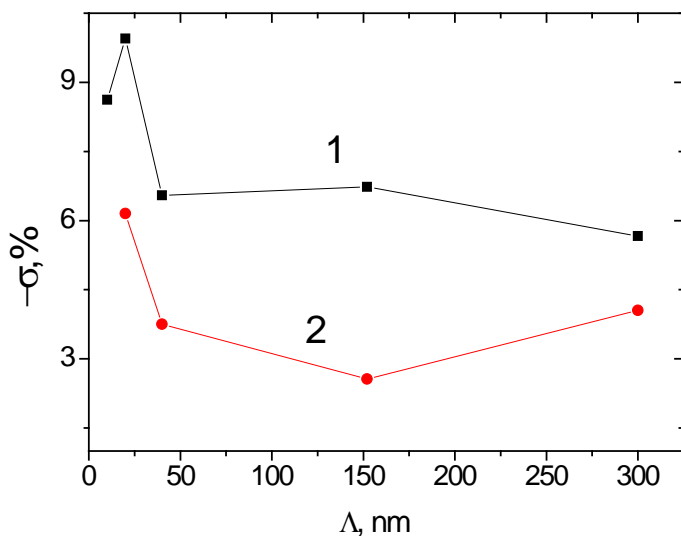


Fig. 8 – Dependence of magnitude compression stress ( $-\sigma$ ) from period of multilayer coatings  $\Lambda$  system ZrN/TiN for components: 1 ZrN, 2 -TiN ( $U_b = -110$  V)

This reason is because in system ZrN/TiN the depth of maximum penetration of ions Ti→ZrN about 0.8 nm and total depth of impact (where penetrating ions are identified) are ≈2,1 nm. The total depth of impact ions Zr→TiN about 2 nm.

Thus layer with thickness about 2 nm, in which radiation stimulated stirring affects by decisively is formed during deposition of coating on borders. Total depth of impact at period is about 4 nm, because in period  $\Lambda$  are two such boundaries.

Hardness at indentation is most universal express characteristic to determining the mechanical properties. The obtained results are show that largest hardness in single ZrN coatings is 40.5 GPa and achieved at  $U_b \approx -100$  V. Hardness is

approximately 33 GPa at a large  $U_b \approx -200$  V. Hardness is lower and its magnitude is determined by  $\Lambda$  for multilayer system ZrN/TiN at  $U_b \approx -200$  V. Hardness decreases from 31 to 25 GPa at decreasing  $\Lambda$  from 50 to 10 nm. Considerably higher hardness of coatings that obtained at a lower  $U_b \approx -110$  V. Hardness reaches 44.8 GPa at  $\Lambda \approx 20$  nm. But hardness of multilayer coatings ZrN/TiN decreases to 40 GPa also in this case, at reduction of  $\Lambda \leq 20$  nm.

#### 4. Conclusion

Impact negative potential  $U_b$  on surface morphology at deposition affects to decrease of droplet phase. This is determined by the acquisition of drops with negative charge and by repulsion it from negatively charged surface of substrate at deposition.

Supply  $U_b$  leads to forming preferential orientation of crystallites at structural level. Supply of small in magnitude  $U_b$  (to -50 V) in single-layer ZrN coatings leads to preferred orientation of crystallite growth with axis [100]. Forming texture [311] that passes into texture with axis [111] at  $U_b = (-150 \dots -300 \text{ V})$  is happening at higher  $U_b = (-50 \dots -100 \text{ V})$ .

Supply  $U_b$  in the interval of (-100 ... -250 V) on substructural level in single layer ZrN coatings leads to decrease average crystallite size and relaxation of microdeformation. Supply  $U_b$  in multilayer systems ZrN/TiN leads to decrease microdeformation and decrease of crystallite size in TiN layers and increasing of sizes in ZrN layers.

Highest magnitude of hardness in single layer ZrN coatings is 40.5 GPa and achieved at  $U_b \approx -100 \text{ V}$ . Using higher in magnitude  $U_b$  leads to increased density of defects and to decrease of hardness. Changing of hardness has nonmonotonic character depending on  $U_b$  in multilayer coatings ZrN/TiN (with  $\Lambda \approx 50\text{-}100 \text{ nm}$ ). Maximum hardness 44.8 GPa is achieved at lower  $U_b = -110 \text{ V}$ . Decrease of hardness is happening at low  $\Lambda$  as a result of mixing. Herewith ratio  $H/E$  (hardness/modulus of elasticity) reaches 0.14 in hardest coatings that complies to high relaxation characteristics of material.

Correlation between increased magnitude of compressive stresses that are developing in coating and increasing hardness is revealed. Compressive stresses are stimulated by higher specific atomic density and contribute to increasing strength of relations and hardness.

#### 5. References

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