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STRUCTURE, COMPOSITION AND MECHANICAL PROPERTIES OF MULTI-LAYER VACUUM-ARC NITRIDE COATINGS

Abstract. *The conditions of application of multilayer vacuum-arc nitride coatings on a substrate made from polycrystalline cubic boron nitride (PCBN) are considered using the samples of (TiAlCrY)N/ZrN, (TiZr/TiSi)N, (TiAlSiY)N/CrN compositions. A schematic diagram of a vacuum-arc installation for applying similar coatings is presented, and the technological conditions of coating formation are considered. The structure and composition of the coatings were studied during diffractometric studies, and the performance of coated tools was examined when turning hardened steel. A large amount of the droplet phase in the (TiAlCrY)N/ZrN coating was established. The lattice parameters of two nitrides with an fcc crystal lattice were determined: ZrN – 4.590 Å, TiAlCrYN – 4.203 Å. CSR (coherent-scattering region) of the ZrN phase is 5.4 nm at the microstrain level* $\varepsilon = 4.79 \cdot 10^{-3}$*. High homogeneity and low defects in the thickness of the (TiZr)N/(TiSi)N coating were established – the amount of droplet phase is insignificant. The CSR of the coating is 24.2 nm at the level of microstrain* $\varepsilon = 5.76 \cdot 10^{-3}$*, and the predominant texture orientation is (111). A small amount of the droplet phase was found in the (TiAlCrY)N/CrN coating. Both coating layers are characterized by the formation of phases with a cubic (fcc) crystal lattice, and a strong (111) texture occurs. The crystallographic planes (111) of the phase grains are mainly oriented parallel to the coating interface. The size of the CSR is 14.6 nm. It is shown that multilayer vacuum-arc coatings lead to an increase in the tool life of PCBN cutting tools by reducing the effect of adhesive sticking of the processed material and reducing the intensity of chemical interaction in the cutting zone.*

Keywords: *vacuum-arc technology, multilayer nitride coatings, composition and mechanical properties of coatings, PVD coatings, PCBN cutting tool.*

Introduction. In the engineering industry one of the most important priority directions is surface strengthening and the application of strengthening protective coatings on machine parts, cutting and forming tools, and technological equipment [1]. Increasing the volume of surface strengthening treatment is one of the trends in world practice.

Analyzing modern materials for PVD coatings can be identified two trends in the development of materials for coatings [2–4]. The first consists of creating multi-layer coatings. Each layer performs its own function and ensures a smooth transition of the physical and mechanical properties of the coating from the surface to the base. The second trend is to create multi-component layers.

Protective coatings make it possible to repeatedly increase the durability of machine parts, providing the possibility of intensification of many production processes [5].

Vacuum-arc technologies make it possible to apply hard, dense coatings on the surface of various materials, including non-metallic ones, with high adhesion [6]. The technology allows the application of multi-layer coatings (with a total thickness of up to 50 μm) with unique properties. At the same time, corrosion and erosion resistance, wear and heat resistance, and fatigue strength of products increase [7].

Multi-layer coatings can enhance the stability of tools by 25–200% compared to single-layer TiC and TiCN coatings [8].

During the intermittent cutting of difficult-to-process materials, tools with multilayer coatings, in which «soft» and «hard» layers alternate, showed the best resistance [9].

Multilayer coatings are generally multifunctional [10]. They combine high hardness, wear resistance, resistance to oxidation and adhesive interaction with the contacting material, low friction coefficient, and increased resistance to abrasive wear and oxidation at elevated temperatures.

A new generation of multilayer coatings, consisting of a large number of very thin (~ 10 μm) layers with a composition that continuously changes in thickness and properties, allow solving the problem of the difference in coefficients of thermal expansion and the effect of residual stresses, therefore, avoiding adhesive peeling from the substrate [11, 12].

Multilayer nitride coatings, along with high hardness, have greater plasticity compared to single-layer coatings, making them effective when working under dynamic contact load conditions [13].

The presence of protective coatings on the contact surfaces of products leads to changes in the mechanics and physico-chemistry of the contact interaction [14]. The first is determined by the redistribution of stresses on the surfaces of the parts, a change in the friction coefficient and, as a result, acting forces and temperature. The second is related to the fact that in order to ensure the most optimal conditions for the operation of parts or tools, in each specific case it is necessary to choose such a coating that ensures the minimization or absence of effects that negatively affect their performance. The protective coating should also play the role of a passive protector, which prevents the mechanical interaction of the product and the tool in the contact zone or play a certain role, changing the conditions of direct chemical interaction of their materials [15].

In this regard, the composition and properties of protective coatings can affect the conditions of interaction in the contact zone and thus increase the efficiency of the coated products [16].

In this work, on the example of the compositions (TiAlCrY)N/ZrN, (TiZr)N/(TiSi)N, (TiAlSiY)N/CrN, the conditions for the formation of vacuum-arc multilayer nitride coatings on a substrate of polycrystalline cubic boron nitride (PCBN) are considered, and they are investigated composition and properties.

Methods of research. Vacuum-arc nitride coatings were applied in a modified BULAT-6 installation, the schematic diagram of which is shown in Fig. 1. RNUN 070300 indexable inserts made of polycrystalline cubic boron nitride (PCNB) of the «Borsinit» brand as substrates for deposition. The samples were placed on a metal flat holder located at a distance of 500 mm from the evaporator.

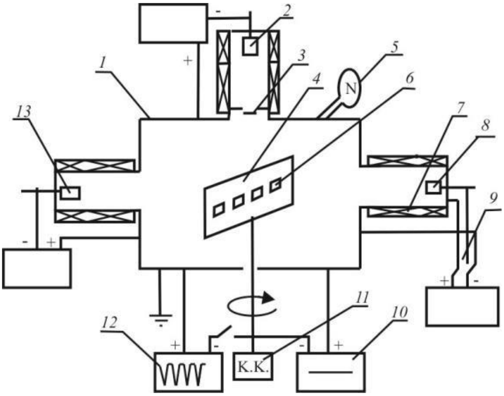


Figure 1 – Schematic diagram of a vacuum-arc installation of the "BULAT-6" type for deposition of nitride coatings with preliminary cleaning in a gas discharge: 1 – vacuum chamber; 2 – vacuum-arc evaporator; 3 – a metal screen that does not allow vaporized metal ions to pass through; 4 – screen-holder of substrates; 5 – nitrogen injector; 6 – samples; 7 – vacuum-arc evaporator housing – anode for gas discharge; 8 – cathode of the same material; 9 – switching relay; 10 – constant voltage source; 11 – command-controller; 12 – pulse voltage source; 13 – cathode of the second material

The vacuum chamber was previously pumped to a pressure of $P = 0.3 \cdot 10^{-3}$ Pa, and ion cleaning and surface activation of the substrates were performed in a gas vacuum-arc discharge. Electrical indicators during the preparation of the substrate for deposition: – current on the cathode I_k = -70 A, current on the anode I_A = 100 A, voltage on the rotary mechanism U_P = -1100 V, voltage from the high-voltage pulse source U_I = -2000 V, frequency 7– 12 kHz. Nitrogen pressure in the vacuum-arc chamber during cleaning P_H = 0.6 Pa. The temperature on the samples was 550–590 °C, the cleaning time in all experiments was 10 min.

After cleaning in a vacuum and heating the samples, a layer of clean cathode material was applied for 1 min.

Deposition of vacuum-arc nitride nanolayer coatings was performed within 60 min. Nitrogen pressure in the vacuum chamber during deposition of coatings P_N = 0.05–0.60 Pa, and the negative potential on the substrate U_P = -100– -200 V was used. Deposition of nanolayer vacuum-arc coatings was carried out using a command-controller. The vaporizers work simultaneously for 7 seconds and will periodically turn off during the 180° rotation of the substrate by the electric motor. This mode is intended for applying two-phase coatings on flat substrates. Both evaporators, operating for a given time, are turned on at the same time, which determines the thickness of the coating nanolayer, and the rotation system is turned off. On the surface of the substrate, nitrides of the material of cathode 1 are deposited on one side, and materials of cathode 2 are deposited on the other side.

Diffractometric studies were carried out on a DRON-4-07 X-ray diffractometer in copper Cu-Kα radiation using a nickel selectively absorbing filter. The diffracted rays were recorded by a scintillation detector. The characteristics of the diffraction maxima – angular position 2θ, the intensity I, and integral half-width B, were determined.

The analysis of the substructural characteristics (the size of the regions of coherent scattering L and the level of microdeformations ε) was carried out by the integral width of the diffraction lines.

A scanning electron microscope LYRA 3 XMU FEG/SEMxFIB (Tescan, Czech Republic) equipped with an EDS analyser Ultimmax with software Aztec (Oxford Instruments, UK) was used for microstructure observation and elemental analysis of coatings. The surface roughness was calculated from 3D reconstructed surfaces measured by a laser confocal microscope Lext OLS3100 (Olympus, Japan).

Mechanical properties of the coatings (determined by indentation of the interface of the coatings in the polished state) – microhardness and Young's modulus were determined using a universal nanomechanical testing machine Zwick ZHN (Zwick/Roell, Germany) at a load on the indenter of 490.3 mN.

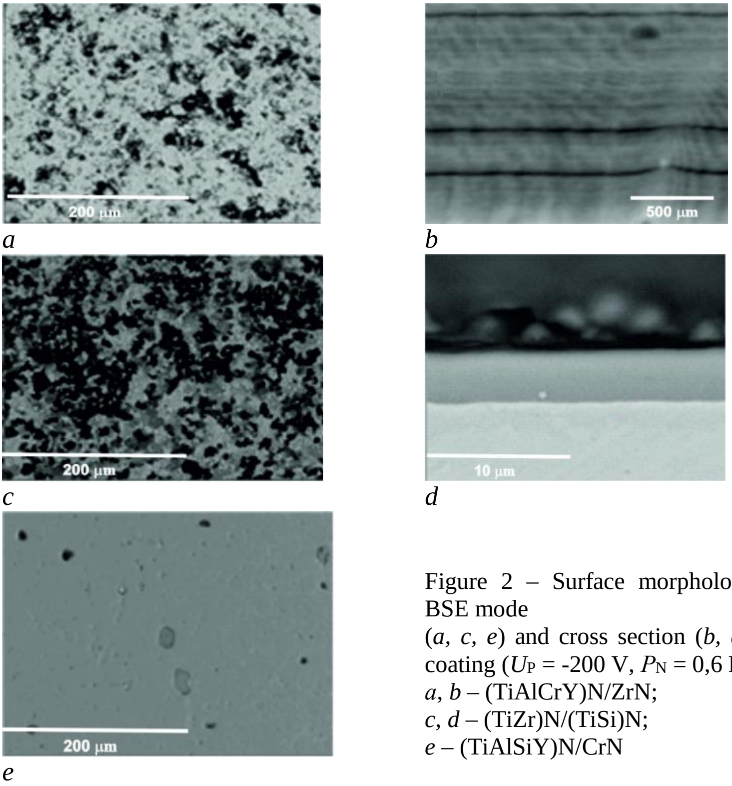
Polishing of the coating interface was performed using a suspension based on ASM 1/0 synthetic diamond powder to obtain a roughness of R_a 0.05.

Testing of cutting tools with polished coatings was carried out during finishing turning with an impact of a sample made of ShKh15 steel (60–62 HRC). Cutting modes: cutting speed $v = 140$ m/min, feed and cutting depth $S = 0.06$ mm/rev, $t = 0.15$ mm. The rake angle of the cutting tool $\gamma = -10°$. The width of the flank wear chamfer on the rear surface was measured with a microscope installed on the machine bed with an error of ± 4 µm.

Results and discussion

(TiAlCrY)N/ZrN coating. The surface morphology of the vacuum-arc nanolayer (TiAlCrY)N/ZrN coating shows a rather large amount of the droplet phase of the cathode material (Fig. 2, *a*, *b*). Such a large number of droplets is due to the relatively poor thermal conductivity of the TiAlCrY cathode/target.

A large amount of the droplet phase leads to an increase in the percentage content of elements Ti, Al, Cr, and Y in the coating. At the same time, a bcc structure was formed that did not form a nitride, which is unfavourable for the coating working on the tool. Likewise, the droplet phase creates difficulties when conducting mechanical tests, in particular, microhardness.



a *b*

c *d*

e

Figure 2 – Surface morphology SEM BSE mode (*a, c, e*) and cross section (*b, d*) of the coating (U_P = -200 V, P_N = 0,6 Pa):
a, b – (TiAlCrY)N/ZrN;
c, d – (TiZr)N/(TiSi)N;
e – (TiAlSiY)N/CrN

In Fig. 3, the characteristic energy dispersive spectr a of the coating is given. As can be seen, the entire elemental composition of the two cathodes is revealed in the coating.

Considering that the concentration of yttrium in the target was about 1%, this element is not observed in the spectrum of the coatings, since its concentration is most likely below 0.1%.

The microgeometry of the coating interface after its formation (from R_a 0.59 to R_z 3.48) (Fig. 4, *a*), due to the droplet phase, leads to limitations and accuracy of microhardness measurement and research by scratch testing.

Such a developed surface, due to the droplet phase, can negatively affect the wear resistance of a cutting tool with such a coating due to brittle destruction by softer drops.

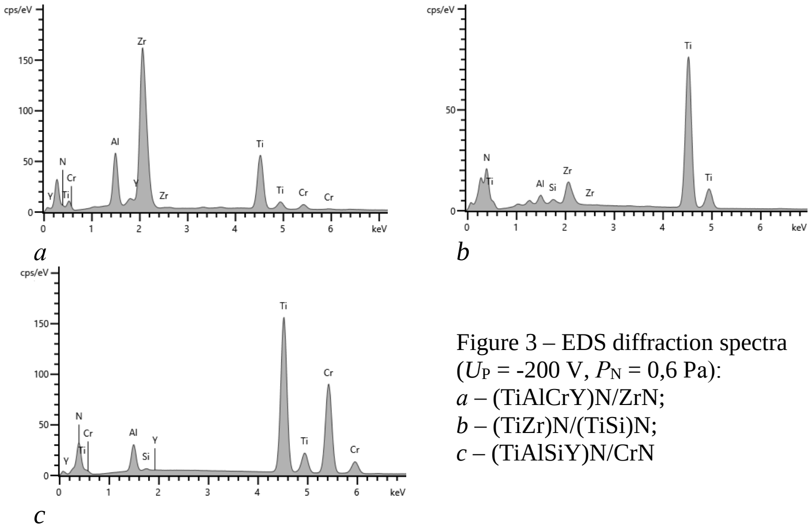


Figure 3 – EDS diffraction spectra (U_P = -200 V, P_N = 0,6 Pa):
a – (TiAlCrY)N/ZrN;
b – (TiZr)N/(TiSi)N;
c – (TiAlSiY)N/CrN

The results of X-ray structural studies and the phase composition of (TiAlCrY)N/ZrN coatings showed the presence of two nitrides with an fcc crystal lattice, ZrN and TiAlCrYN (Fig. 5, *a*). The lattice parameter of ZrN nitride a = 4.590 Å, the size of the coherent-scattering regions of this phase is D = 5.4 nm, and the level of microstrain $\varepsilon = 4.79 \cdot 10^{-3}$. The lattice parameter of vacuum-arc coating TiAlCrYN a = 4.203 Å.

(TiZr)N/(TiSi)N coating. Vacuum-arc deposition of multilayer nitride (TiZr)N/(TiSi)N coatings was carried out from two different TiZr and TiSi cathodes. The period of the (TiZr)N/(TiSi)N layers is 20–30 nm with a total coating thickness of ~ 4 μm. Cathode materials have good thermal conductivity, so the amount of droplet phase on the surface of the tested sample is insignificant. However, the use of silicon in the cathode leads to possible inhomogeneities on the surface of the coating, which is shown in Fig. 2.

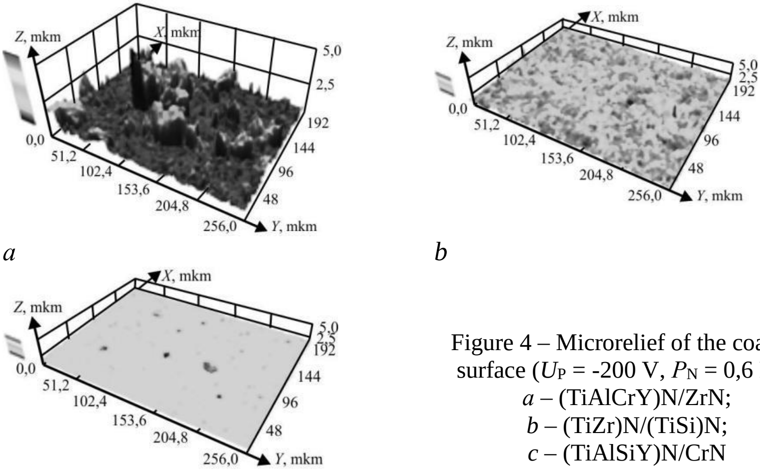


Figure 4 – Microrelief of the coating surface (U_P = -200 V, P_N = 0,6 Pa):
a – (TiAlCrY)N/ZrN;
b – (TiZr)N/(TiSi)N;
c – (TiAlSiY)N/CrN

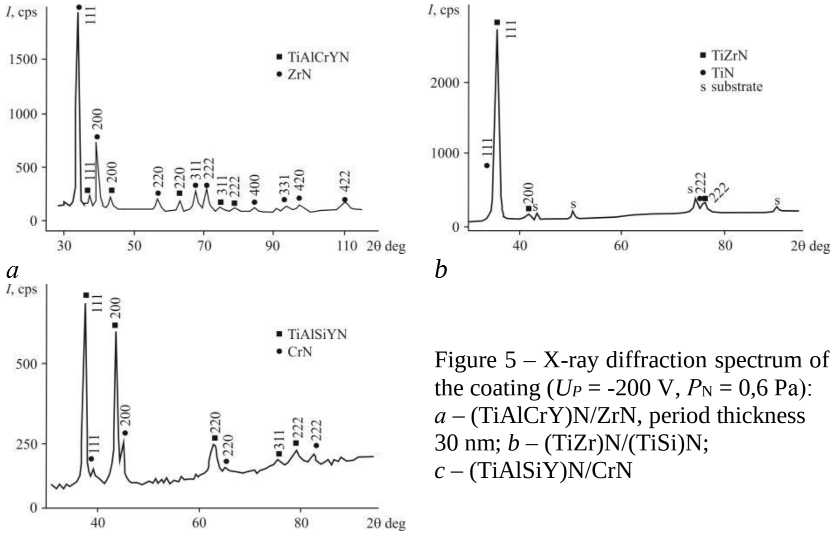


Figure 5 – X-ray diffraction spectrum of the coating (U_P = -200 V, P_N = 0,6 Pa):
a – (TiAlCrY)N/ZrN, period thickness 30 nm; *b* – (TiZr)N/(TiSi)N;
c – (TiAlSiY)N/CrN

As can be seen from fig. 3, *b*, the composition of the coating includes all components of cathodes.

The image of the polished cross-section of the vacuum-arc (TiZr)N/(TiSi)N coating shows high uniformity and low defects throughout the thickness of the coating (Fig. 2, *d*). This is visible from the analysis of the microrelief of the coating interface after its formation (from R_a 0.1091 to R_z 0.8365) (Fig. 4, *b*).

A decrease in the concentration of lighter elements, especially silicon, was determined in the coating material (Fig. 5, *b*). The CSR size for such a coating is 24.2 nm at the level of microstresses $\varepsilon = 5{,}76 \cdot 10^{-3}$. The intensity analysis and the results of structural studies indicate the predominant orientation of the texture [111], the silicon nitride phase was not detected.

(TiAlSiY)N/CrN coating. On the surface of the (TiAlSiY)N/CrN coating, an insignificant content of the droplet phase was determined, which was deleted after polishing (Fig. 2, *e*).

In Fig. 3, the characteristic energy dispersive spectrum of the coating is shown. It was determined that the formed coating has an almost stoichiometric structure. The chemical composition of the coating corresponds to the elements included in the cathode material, except for yttrium, which was not detected (the reason is described above).

The roughness of the (TiAlSiY)N/CrN coating interface after its formation is low (from R_a 0.0628 to R_z 0.5638) (Fig. 4, *c*), due to the use of cathode materials with good thermal conductivity.

Analysis of the diffraction spectrum (Fig. 5, *c*) shows that the resulting coating is characterized by the formation of phases with a cubic (fcc) crystal lattice in both layers of the multilayer coating.

A disordered solid solution (TiAlSiY)N with crystal lattices of structural type NaCl and CrN is formed in the nitride coating layers. The intensity of the lines in the X-ray spectrum indicates the presence of a strong (111) texture in multi-element nitride and chromium nitride. The grains of these phases are mainly oriented so that their crystallographic planes (111) are parallel to the surface of the sample. The size of the CSR is 14.6 nm.

Mechanical properties of coatings. The microhardness and Young's modulus of coatings are given in the Table. 1.

Table 1 – Mechanical properties of coatings

Coating	Microhardness, GPa	Young's modulus, GPa
(TiAlCrY)N/ZrN	32,3–38,0	395–415
(TiZr)N/(TiSi)N	26,5–28,2	380–430
(TiAlSiY)N/CrN	30,4–36,0	300

Depending on the deposition conditions, the microhardness of the investigated coatings varies in a wide range. It should be noted that the microhardness of coatings can be significantly greater than the microhardness of nitrides (single-layer coatings) included in them. For example, TiAlSiYN coating has a microhardness of 34 GPa, CrN coating – 26 GPa.

When examining the surface of the coatings, no chips or cracks were detected, which reduces the likelihood of defects and cracks forming during thermobaric loading of the coatings when they are used in a cutting tool.

Testing of coatings in a cutting tool. To determine the most promising composition for further research, testing of tools with vacuum-arc coatings of compositions (TiAlCrY)N/ZrN, (TiZr)N/(TiSi)N, (TiAlSiY)N/CrN was carried out. The test results are shown in Fig. 6, where the results obtained for the uncoated tool are also presented for comparison.

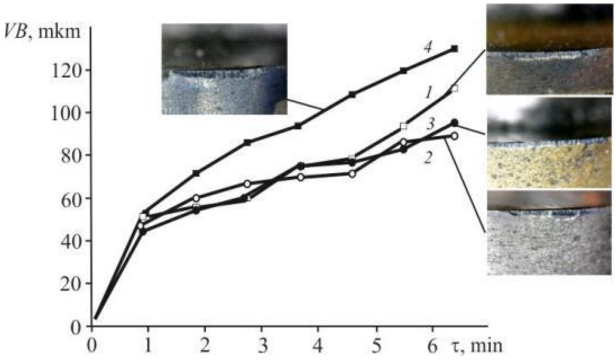


Figure 6 – Dependence of the tool wear on cutting time and contact areas of coated tools (cutting time 6.5 min): *1* – (TiAlCrY)N/ZrN; *2* – (TiZr)N/(TiSi)N; *3* – (TiAlSiY)N/CrN; *4* – without coating

As can be seen, all multi-layer vacuum-arc coatings deposited on the PCBN leads to an increase in the tool life compared to a cutting tool without coating. Coatings perform the role of protection against abrasion, they reduce the effect of adhesive sticking of the processed material, decline chemical interaction intensity in the cutting zone at high temperature conditions, most often protective coating efficency is associated also with a decrease in the coefficient of friction due to formation of thin oxide films on its surfaces. Moreover, they reduce the probability of tool breakage under dynamic load conditions, especially at the stage of the cutting tool penetration into the processed part. Fig. 6 shows the worn areas of the tools, where the width of the flank wear zones of the tools without coating and with nano-layer vacuum-arc coatings is visually different.

Conclusions. On the example of the compositions (TiAlCrY)N/ZrN, (TiZr)N/(TiSi)N, (TiAlSiY)N/CrN, the formation of vacuum-arc multilayer nitride coatings on a polycrystalline cubic boron nitride substrate was considered, their structural features, composition and mechanical properties, the possibility of use in cutting tools when processing hardened steel.

The selection of components for multi-layer coatings allows the development of protective wear-resistant layers on the surface of the cutting tool, the system of which has a hardness of up to 38 GPa.

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СТРУКТУРА, СКЛАД ТА МЕХАНІЧНІ ВЛАСТИВОСТІ БАГАТОШАРОВИХ ВАКУУМНО-ДУГОВИХ НІТРИДНИХ ПОКРИТТІВ

Анотація. *Розглянуто умови нанесення багатошарових вакуумно-дугових нітридних покриттів на підкладку з полікристалічного кубічного нітриду бору (ПКНБ) на прикладі композицій (TiAlCrY)N/ZrN, (TiZr/TiSi)N, (TiAlSiY)N/CrN. Наведено принципова схема вакуумно-дугової установки для нанесення подібних покриттів, розглянуто технологічні умови формування покриттів, запропоновано діаграма режиму роботи випарників та обертання підкладки. Структура і склад покриттів вивчено при дифрактометричних дослідженнях, механічні властивості оцінені з використанням нанотвердоміру «Micron-gamma» з індентором Берковича, працездатність інструментів з покриттям розглянута при точінні загартованої сталі. Встановлено велика кількість краплинної фази у покритті (TiAlCrY)N/ZrN. Визначено параметри гратки двох нітридів з ГЦК кристалічною решіткою: ZrN – 4,590 Å, TiAlCrYN – 4,203 Å. ДКР фази ZrN 5,4 нм при рівені мікронапружень* $\varepsilon = 4{,}79\cdot10^{-3}$. *Встановлено висока однорідність і мала дефектність по товщині покриття (TiZr)***N***/(TiSi)N – кількість краплинної фази незначна. ДКР покриття становить 24,2 нм при рівні мікронапружень* $\varepsilon = 5{,}76\cdot10^{-3}$, *переважна орієнтація текстури (111). Встановлено незначна кількість краплинної фази у покриття (TiAlCrY)N/CrN. У обох шарах покриття характерно утворення фаз с кубічною (ГЦК) кристалічною решіткою, має місце сильна текстура (111). Кристалографічні площини (111) зерна фаз переважно орієнтовані паралельно інтерфейсу покриття. Розмір ДКР становить 14,6 нм. Показано, що багатошарові вакуумно-дугові покриття призводять до збільшення ресурсу роботи різальних інструментів з ПКНБ за рахунок зниження впливу адгезійного налипання оброблюваного матеріалу та зниження інтенсивності хімічної взаємодії в зоні різання та впливі кисню воздуху.*

Ключеві слова: *вакуумно-дугова технологія; багатошарові нітридні покриття; склад і механічні властивості покриттів.*