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Influence of Substrate Bias Voltage on Structure, Morphology and Mechanical Properties of AlCrN Coatings Synthesized Using Cathodic Arc Evaporation

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ABSTRACT

AlCrN is one of the most widely studied hard coatings, especially if it is about their thermal resistance and mechanical properties. However, adhesion and wear resistance of AlCrN coatings synthesized from an Al-rich AlCr (80:20) cathode has not been studied yet. The influence of substrate bias voltage on the properties of coatings formed by cathodic arc evaporation was investigated. The morphology, phase and chemical composition, hardness, adhesion as well as wear of the coatings were analyzed by XRD, EDX, SEM, nanoindenter, scratch and ball-on-disc testers. It was found that as the negative substrate bias voltage (U_B) increased, the rate of deposition and the macroparticle number on the surface of the coating decreased, mainly due to the resputtering phenomenon. X-ray diffraction showed that the intensity of h-AlN diffraction lines decreases and the intensity of the cubic CrN diffraction lines increases with the increase of the negative substrate bias voltage. The hardness of the coatings increases and critical load Lc₂ decreases with negative substrate bias voltage. The lowest wear rate, about 1.1×10^{-16} m³/Nm, was observed for coating deposited at bias of -100 V.

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1. INTRODUCTION

The coatings of transition metal nitrides formed using various PVD (physical vapor deposition) processes find applications for almost every demand. They are characterized by good mechanical properties, as high hardness, and wear resistance as well as corrosion resistance. Such coatings applied to the tool surfaces significantly improve its durability [1]. The most frequently applied coatings are based on TiN and CrN.

The durability and operational reliability of tools are the key to increase the efficiency of machining processes. CrN coatings are used

extensively, however, their relatively low hardness and oxidation resistance require improvement in order to satisfy the needs of modern applications. То improve the properties of the coatings, various alloying elements can be added. Among many elements, such as Si, B, C, Al, Ti and others, it is particularly attractive to add aluminum and form a three-component thin AlCrN coating. The tests confirmed their excellent hardness [2,3] and other mechanical properties [4], wear [5] and oxidation resistance [2,6] and application on cutting tools [1].

The concentration of aluminum in AlCrN coating has a great impact on its structure and properties [1]. Two phases of AlN dependent on Al concentration can be formed. It has been shown that even at very high concentration of Al, 65-75%. the cubic AlN phase can form. Above this value limit, more stable than cubic AlN hexagonal phase is synthesized. The AlCrN coating with such a structure is characterized by reduced mechanical properties [1]. The cubic - hexagonal phase transformation, especially at elevated temperatures, can occur spontaneously [3]. The coatings with the hexagonal structure are characterized by poor thermal stability and wear resistance compared to the coatings with cubic structure [7]. Nevertheless, the investigations performed on the coatings synthesized from cathode with very high Al concentration, $Al_{80}Cr_{20}$, at atmosphere of nitrogen in wide pressure range 1 - 5 Pa, indicate that wear resistance is comparable to cubic AlCrN [8].

AlCrN coatings have been widely investigated in the past decades in terms of the deposition parameters, growth models, structures, various properties including chemical inertness and thermal stability. The production of AlCrN coatings at various substrate bias voltage U_B and their study was realized by many researchers [9,10]. Based on the literature analysis, we can conclude that the adhesion and wear resistance of AlCrN coatings synthesized from an Al-rich AlCr cathode have not been studied yet. Therefore, by using cathodic arc evaporation we synthesized AlCrN coatings from $Al_{80}Cr_{20}$ cathode at different substrate bias voltages.

The presented research tries to evaluate effect of applied technological parameters on the

morphology, structure, mechanical and tribological properties of the coatings deposited.

2. EXPERIMENTAL DETAILS

2.1 Deposition of the coatings

The cathodic arc evaporation method was applied to synthesize AlCrN coatings. The TINA 900M system equipped with $Al_{80}Cr_{20}$ alloy cathodes of 100 mm in diameter with a purity of 99.99% were used. 32 mm in diameter HS6-5-2 (EN ISO 4957) steel substrates were polished using abrasive paper to the mesh of 2500 (Ra of approx. 0.02 µm) and then they were ultrasonically washed in alkaline bath and in deionized water. After drying, the substrates were placed on a planetary rotated table. A substrate-cathode distance was 18 cm.

The vacuum chamber was evacuated to pressure of 1 mPa. Before deposition two processes had been performed: heating of the substrates and their plasma-etching applying an argon and chromium ions. As an adhesive layer thin Cr layer was deposited to the substrate before proper coating. The experimental conditions and deposition parameters are gathered in Table 1.

2.2 Structural and mechanical characterization of the coatings

The phase identification of the coatings was performed using the grazing incidence X-ray diffraction (X'Pert PANalytical). The following parameters were applied: Cu-K α radiation (0.154056 nm), the grazing angle $\omega = 3^{\circ}$, the operating voltage - 40 kV, current - 35 mA, 2 Θ scanning range - 20-90°, step size - 0.05° and scanning speed - 20s/step. HighScore Plus with ICDD PDF 4+ Database software was applied for data processing.

The chemical composition was determined by Energy Dispersive X-ray Spectroscopy (Oxford Link ISIS 300 system) attached to Jeol JSM 5500 scanning electron microscope (SEM).

The morphology of the coatings was observed using the scanning microscope (Jeol JSM5500) and the optical microscope Nicon Eclipse MA200. The surface roughness measurements were realized by a Hommel Tester T8000 stylus profilometer.

Table 1. Technological conditions of deposition.

The stage of the process	Experimental conditions		
Substrate heating	Resistance heater	To about 350°C	
Ion etching	Argon pressure	0.5 Pa	
	Voltage	-600 V	
	Cr cathode current	80 A	
	Time	600 s	
Adhesive layer	Cr layer thickness	0.1 μm	
	Argon pressure	0.5 Pa	
	Cr cathode current	80 A	
AlCrN coating	Cathode	Al ₈₀ Cr ₂₀	
	Nitrogen pressure	4 Pa	
	Substrate bias voltage	from -50 V to -150 V	
	Cathode current	80 A	

The spherical grinding method (CALOTEST) was used to determine the thickness of the coatings.

randomly selected cross-sectional wear profiles were averaged to calculate the wear rate.

The coating hardness and Young modulus were evaluated from nanoindentation (Fischerscope® HM2000) under depth-control mode. To avoid the effect of the substrate The depth of indentation of about 0.2 μ m was applied. To determine above parameters for each sample 20 measurements were realized.

To evaluate an adhesion of the coating the Revetest Scratch tester (CSEM) equipped with Rockwell C type diamond indenter was applied. The indenter tip radius was 200 nm. Following parameters were applied: the loading speed - 100 N/min, scratch speed - 10 mm/min. Two critical loads were determined: Lc_1 for the first cracks of the coatings and Lc_2 for total delamination of the coating from the substrate. At least three measurements were performed for each sample. Additionally, the Daimler-Benz test was applied to evaluate the character of the failure of the coating near the indenter imprint [11].

The wear was studied with the help of ball-ondisc experiment. Following parameters were applied: normal load - 20 N, sliding speed - 0.2 m/s, sliding distance - 2000 m, counterpart - 10 mm in diameter Al_2O_3 ball, room temperature, humidity of about 40 %, dry sliding. The diameter of the track was 22 mm. According to Archard the wear rate kv was evaluated from the equation: kv = V/sL, where V is volume of the removed coating material, s is the sliding distance and L is the normal load [12]. Five

3. RESULTS AND DISCUSSION

The coating thickness decreases with negative substrate bias from 4.0 μ m (U_B = -50 V) and 3.9 μ m (U_B = -100 V) to 3.6 μ m (U_B = -150 V). It means that deposition rate calculated as a coating thickness divided by deposition time also decreases from about 44 nm/min to 40 nm/min.

In cathodic arc evaporation process two opposite processes: nucleation and resputtering, affecting the deposition rate can be mentioned. As a result of nucleation the growth of the coating from the particles evaporated from the cathode and transferred to the substrate are observed. Due to the resputtering effect the thickness of the coating reduces. Resputtering is associated with U_B. For low negative substrate bias voltage of 50 V, the particles move randomly or in small ordered in the plasma space. For this small substrate bias voltage the particles were characterized by relatively small kinetic energy. It significantly restricts the resputtering effect. Due to it there were no factors disordering the coating growth. It means that the rate of deposition can be relatively high because of a large number of particles deposited at the substrate and small resputtering effect. As negative U_B increases, the movement of the particles is more ordered, towards the substrate. A further increase in U_B results in an increase in the energy of the particles, which should lead to a further increase in the deposition rate. The observed decrease in deposition rate is due to the increased resputtering effect. An impinging of high energetic ions into the coating results in resputtering of condensed film and reduces its growth. The above mentioned effect was previously presented during deposition using Cr/Al target [3,9]. The application of two separate cathodes: Al and Cr to synthesize AlCrN coatings gives similar behavior [13]. All above mentioned deposition processes were arc processes.

An analysis of EDS results indicate that the coatings consist of nitrogen, aluminum and chromium, Fig. 1. For better tracking of the measured values, in this figure and others a dotted line is drawn between them. Small amount (about 1 at.%) of oxygen, as an unintentional effect of the applied deposition technique was also registered. The results obtained for investigated coatings indicate that nitrogen concentration is almost constant and aluminum ratio, Al/(Al+Cr) slightly decreases from 0.79 for coatings deposited at $U_B = -50$ V to about 0.77 for the $U_B = -150$ V. This effect can result in different sputtering efficiency of aluminum and chromium in AlCrN system.



Fig. 1. The variation of aluminum ratio Al/(Al+Cr) and elemental composition of AlCrN coatings synthesized at U_B ranged from -50 V to -150 V.

Above interpretation is confirmed by investigation of Romero et al [9]. The opposite effect is presented by Wang et al. [3], who observed significant decrease of nitrogen concentration from 42 at.% to 37 at.% when U_B changes from -100 V to -300 V. Additionally, aluminum ratio also increases. The slight increase in aluminum content with negative substrate bias voltage was presented by Wang et al. [14] who investigated AlCrN coatings deposited by magnetron sputtering from separate Cr and Al sources.

The XRD measurements revealed that AlCrN investigated coatings were well crystallized, Fig. 2. The diffraction lines were identified by comparison with International Centre for Diffraction Data (ICDD) reference patterns. A detailed analysis indicates mainly the presence of h-AlN hexagonal phase (ref. code 01-070-0354), especially at coatings deposited at $U_B = -$ 50 V. Simultaneously, diffraction lines from the Cr₂N (111) hexagonal phase and Cr (110) cubic phase of low intensity were recorded. The observed Cr-based diffraction lines have the highest intensity for these phases. An increase of U_B in coating deposition process, two opposite effects are observed. First, the intensity of diffraction lines from h-AlN hexagonal phase, and also Cr₂N and Cr phases decreases. Second, the intensity of diffraction lines originating from the cubic CrN phase (ref. code 04-004-6868): (111), (200), (220) and further increases. The increase in the intensity of the CrN line may be caused by crystallites growth [3].



Fig. 2. XRD pattern of AlCrN coatings synthesized at U_B : a) -50 V, b) -100 V, c) -150V.

The increase of U_B favors the transformation of $CrN \rightarrow Cr_2N$ [15,16]. This is due to the knocking out of light nitrogen atoms by high-energetic particles. This phenomenon was not recorded here due to the high pressure of nitrogen during the coating deposition.

For coatings synthesized at the lowest and the highest bias show the texture of about 60 % for

h-AlN (100) plane. The texture is defined as a ratio of intensity of preferential orientation to the standard intensity of the relevant lattice plane. The lattice parameters of two present in the coating phases changes with negative substrate bias voltage, Fig. 3.



Fig. 3. The lattice parameters of h-AlN and c-CrN phases in investigated coatings synthesized at different U_B .

Standard parameters for hexagonal AlN structure are: a=0.3135 nm and c = 0.4986 nm (ICDD 01-070-0354). One can see that lattice parameters for AlN phase are higher than standard. The values of AlCrN coating lattice parameters changes with increase of U_B, a parameter decreases and c parameter increases. The c/a ratio is the lowest for coatings synthesized at UB = -50 V and amounts to 1.577. The coatings formed at U_B = -150 V are characterized be c/a ratio equal 1.59, i.e. standard ratio. The second phase present in the coating, cubic CrN shows lattice parameter a lower than standard, a = 0.4145 nm (ICDD 04-004-6868). The lattice parameter also decreases with U_B.

The crystallite sizes in the coatings determined using Scherrer equation are summarized in Fig. 4. The results show the reverse behavior of both phases with the increase of U_B . The crystallite size of c-CrN phase increases and h-AlN phase decreases. The properties of the coatings, especially mechanical, can be related with crystallite size change.

Using Rietveld method the density of the coatings was evaluated, Table 2. The results show slightly lower density of both phases compared to standards. This may be related to the porosity of the coating. This is a characteristic feature of the applied deposition

method. The increase in voltage contributes to the increase in density of both phases.



Fig. 4. The crystallite size of h-AlN and c-CrN phases in AlCrN coating synthesized at different U_B .

Table 2. The density of phases in Al-Cr-N coatings synthesized at different U_B .

Substrate bias	h-AlN phase	c-CrN phase	
voltage [V]	Density [kg/m ³]		
-50	3120	6040	
-100	3160	6170	
-150	3170	6300	
standard	3255	6170-6300	

In case of CrN the density was the subject of many researches. The density of coatings is connected with the coating deposition conditions, including PVD method of its formation, substrate bias voltage and nitrogen pressure. The highest density of chromiumbased coatings is characterized by the Cr metallic coating - 7140 kg/m³. Hexagonal Cr₂N density is lower, about 6540 kg/m³ [17]. The CrN cubic phase is characterized by density ranged from 6170 to 6300 kg/m³ [17]. The CrN coatings with density lower than 6000 kg/m^3 were also described [18]. Cunha et al. [19] studied coatings formed by magnetron sputtering in a wide range of values for such parameters technological as power of magnetron, substrate bias voltage and substrate temperature. They found that the coating density was dependent on the above parameters and was of 55-85 % bulk density.

A great number of macroparticles loosely the coating surface adhered to is the disadvantage of cathodic arc evaporation. Macroparticles can change the properties of the coatings, both mechanical and tribological. Droplets emitted from target arc spots, as well as collisions of ions or atoms usually occurring in a high pressure atmosphere, cause that atoms or ions can cluster and form macroparticles before reaching the surface of the coating [15]. Therefore, the chemical composition of macroparticles is usually similar to the chemical composition of the target. Typical SEM photographs of the surface of AlCrN coatings synthesized at different substrate bias voltages and the same nitrogen pressure of 4 Pa are shown in Fig. 5. These micrographs confirm presence of a great number of macroparticles on the coating surface. They are characterized by different dimensions. The majority of particles have small sizes. The analysis of the surface of the coating (Fig. 5a) indicates an increase in the substrate bias voltage results in decrease of the number and size of the macroparticles. It had also been found previously [20]. Simultaneously, an increase in number of shallow, in most regular craters was observed. The formation of craters involves the removal of macroparticles from the surface by ions with energy related to the substrate bias voltage.

The high coating roughness may be explained by a great number of macroparticles deposited on the coating surface, Table 3. The highest roughness parameter Ra is for the coating synthesized at U_B =-50 V. For higher U_B substrate bias voltage a significant, even twice roughness decrease is observed. The similar trend is observed for roughness parameter Rz. The effect of surface roughness reduction together with U_B was presented earlier [21].

The substrate bias voltage strongly influences the growth and physical characteristics of AlCrN coatings synthesized using cathodic arc evaporation. For example, its increase results in decrease in deposition rate. The hardness increases from about 16 GPa to about 21 GPa, Table 3. This may be connected with refinement of the structure. The h-AlN phase crystallite size decreases from about 15 nm (U_B = -50 V) to about 6 nm (U_B = -150 V). For c-CrN phase the crystallite size slightly increases from 8 nm to about 10.5 nm, Fig. 5. This effect is confirmed by Sabitzer et al. [22]. The coating microstructure becomes denser. The increase in the compressive stresses generated by the higher negative substrate bias voltage may also contribute to the hardness increase. This effect was previously described by Wang et al. [3].



Fig. 5. SEM surface images of AlCrN coatings synthesized at U_B , a) -50 V, b) -100 V, c) -150 V.

		Substrate bias voltage		
	-50 V	-100 V	-150 V	
Roughness Ra [µm]	0.15	0.13	0.08	
Roughness Rz [µm]	1.2	1.1	0.6	
Hardness [GPa]	15.5±1.6	17.4±4.0	21.2±4.6	
Young's modulus [GPa]	210±14	229±19	247±21	
H/E	0,074±0.012	0,076±0.024	0,086±0.026	
H ³ /E ² [GPa]	0,084	0,100	0,156	
Critical load Lc1[N]	46±3	37±3	32±3	
Critical load Lc ₂ [N]	105±4	94±1	69±4	
Friction coefficient	0.63±0.03	0.60±0.02	0.59±0.04	
Wear rate [m ³ /Nm]	(1.7±0.3)×10 ⁻¹⁶	(1.1±0.2)×10-16	(2.1±0.4)×10 ⁻¹⁶	

Table 3. Surface, mechanical and tribological characteristics of AlCrN coatings.

During impinging of high energetic atoms into the surface of the coating some phenomena can be observed. The atoms can harden the coating in process similar to "shot peening". In ion bombardment the atoms can be knocked out from the lattice points. The change in the position of atoms in the lattice leads to increased stress [23]. The increase in the energy of incident atoms can also increase the temperature of the coating. As a result, the size of crystallites increases, which may limit the increase in stresses.

The selection of the technological parameters and method of coating synthesis has a great impact on coating properties. AlCrN coatings formed by High Power Pulse Magnetron Sputtering and magnetron sputtering from the Al₇₀Cr₃₀ cathode have the hardness of about 26 GPa [7] and 22 GPa [24], respectively. This property is strongly associated with U_B [4,6]. The hardness of AlCrN coatings strongly depends on the substrate polarization voltage and increases almost monotonically from about 10 GPa ($U_B = -50$ V) to about 26 GPa ($U_B = -260$ V) [14]. Similar effects were also found in similar Ti_{0.5}Al_{0.5}N coatings formed by magnetron sputtering by Aliaj et al. [25]. They confirmed the increase in hardness from about 21GPa (U_B = -25 V) to about 23 GPa ($U_B = -100$ V) but also increase in compressive stress and decrease in crystallite size. This means that the increase in hardness may be related both to decreasing crystallite size in accordance with the Hall-Petch relationship and increase in compressive stress in the coating [25].

It is known that coatings with lower concentration of aluminum in AlCrN show

higher hardness, about 30 GPa or even higher [9,10]. It can be connected with their density. The h-AlN phase is characterized by about 18 % lower volume density than c-AN [26].

In coatings obtained at various U_B ranged from -50 V to -150 V the critical load decrease is observed, Table 3. The highest critical load Lc_2 shows the coating formed at the lowest $U_B = -50$ V. With increasing in bias the adhesion of the formed coating deteriorates. Similar trend was observed by Wang et al. [3].

It is known that the adhesion determined using the scratch test is influenced by many factors connected with the coating and the substrate, as roughness, hardness [27], coating thickness, substrate elasticity, and measurement method, as the friction coefficient in the coating-stylus system and the wear of the stylus [28]. Due to it the roughness of the substrates was similar for all coatings. Thus, it is not the cause of significant differences in critical load Lc₂. A higher substrate bias voltage during the coating deposition may result in microstructure and stresses change [10]. It means that it can directly affect the adhesion.

During the scratch test, two mechanisms of coating damage may occur simultaneously: cracking of the coating and propagation of cracks in the coating and damage to the coating as a result of plastic deformation of the substrate. Oden et al. [21] indicate that cracks in the scratch test form and propagate more easily in coatings synthesized at higher U_B. This is probably the reason for the lower adhesion of coatings. To confirm the coating adhesion formed at different substrate bias voltages, the Daimler Benz test was also conducted. In Fig. 6a the small chippings around indentation for the coating synthesized at $U_B = -50$ V are present. According the standard VDI 3198 [11] the coating shows acceptable adhesion and allows to accept it into HF3 grade. Similar effect, but with significantly less chippings is visible for coating synthesized at higher bias ($U_B = -100 \text{ V}$), Fig. 6b. This coating can be accepted to HF2 grade. The last coating ($U_B = -150$ V) shows a great delamination around indentation and distinct image of substrate material pile-up, Fig. 6c. It suggests that this coating is both highly brittle and weakly adhesive - HF6.

Increase in substrate bias voltage should result in coating densification and smoothening of the coating surface [21]. The higher adhesion of the coatings does not have to be associated with a higher bias. Oden et al. investigated CrN coatings synthesized by arc evaporation [21]. They demonstrate that critical load decreases from 127 N ($U_B = -20$ V) to 107 N ($U_B = -400$ V) [21]. Similar effect was present by Wang and Weng [29]. The multi-arc ion plating method was applied by Wang et al. to deposit Cr-Al-N coatings [6]. They found the highest adhesion for coatings formed at at -100 V (about 85 N), and the lowest - about 75N (U_B = -300 V). Also investigations performed on C/Cr multilayer coatings indicate on reduction of critical load from 75 N ($U_B = -75$ V) to 20 N ($_{UB} = -350$ V) [30]. Above coatings were formed using two deposition techniques: unbalanced magnetron sputtering and steered cathodic arc. Similar effect was confirmed by our team on CrN coatings [31] and Zr-Si-N coatings [32].

One of the most important process parameter is substrate bias voltage. It determines the energy of the ions forming the coating and affecting the morphology, microstructure and mechanical properties of PVD coatings [21]. For arcevaporated TiN coatings low U_B values ranged from 0 to -100 V favor an increase of the compressive intrinsic stresses from 1.9 GPa (U_B = -5 V) to 6.5 GPa (U_B = -100 V) because of the increase in density of the defects. At higher bias, ion bombardment increases atomic mobility. This can cause a reduction in defects, which affects the lower stresses, and as a result also reduces the hardness [33].



Fig. 6. The Daimler–Benz indents performed for coatings synthesized at: a) $U_B = -50$ V, b) $U_B = -100$ V, c) $U_B = -150$ V.

The maximum value of stress is not always calculated for coatings formed at the $U_B = -100$ V. TiN-MoSx coatings formed using the pulsed DC magnetron sputtering method at U_B =-40 V show the highest critical load and hardness as well as the smallest wear rate [34]. The coatings deposited for other substrate bias voltages show worse properties.

Lower negative bias voltage during coating deposition favors lower compressive stresses [10]. Therefore, they show good adhesion. Higher compressive stresses may cause cracking of the coating, which affects the lower adhesion.

Tribological properties of coatings can be determined using various methods, test parameters and various counterparts. The results depend on many factors related to both the tested coating and the counterpart, including their chemical and phase composition of both, as well as test parameters [35]. To evaluate the tribological properties (friction and wear) of AlCrN coatings, a ball-on-disk system equipped with 10 mm in diameter Al₂O₃ ball was applied. The tests were conducted at ambient temperature without lubrication. Presence of coating debris and counterbody residues in the friction track, i.e. the "third body" can contribute to increasing the friction coefficient. The average friction coefficient for all coatings is about 0.6 with visible decreasing trend with substrate bias voltage.

The friction coefficient estimated for measurements between 600 m and 2000 m of friction distance decreases slightly from $0.63 \pm$ 0.03 ($U_B = -50 \text{ V}$) to 0.59 ± 0.04 ($U_B = -150 \text{ V}$). It is rather constant and don't show decreasing or increasing trend. The substrate bias voltage ranged from -50 V to -150 V applied for the AlCrN coatings deposition does not cause a significant change in the friction coefficient. Similar conclusion is presented by Romero et al. [9]. It is typical coefficient of friction for coatings investigated against Al₂O₃ counterpart [8,35]. In friction investigations of Al_{0.6}Cr_{0.4}N coatings made in sliding speed ranged from about 0 to 1.458 m/s and temperature of the test about 20 °C almost constant coefficient of friction, about 0.65 [35] was found. Increase in temperature to about 800 °C results in the friction coefficient decrease to 0.4-0.45. Mo and Zhu investigated Al₇₀Cr₃₀ coating formed using multi-arc ion plating technique [36]. They found for this coating the value of friction coefficient is slightly higher - 0.75. Application of other counterparts in tribological system significantly changes the coefficient of friction. For ZrO_2 counterpart the coefficient of friction tested at temperature of 20 °C increases with sliding speed from 0.3 (0.002 m/s) to about 0.65 (1.458 m/s). For Si₃N₄ tested at 20 °C the friction coefficient is much higher, about 0.85 (0.002 m/s), and even above 0.9 for sliding speed ranged from 0.006 to 0.054 m/s [35].

In Fig. 7 are presented the micrographs of wear tracks after friction tests against Al₂O₃ counterpart for AlCrN coatings formed at various substrate bias voltages. The coatings were gradually worn during the wear test. The surface of wear tracks is rather smooth, the smoothest is the coating deposited at $U_B = -$ 150 V, Fig. 7c. Inside the wear track the failure of the coating was not observed, but one can see the presence of numerous craters in the wear tracks. No damage of the coating was observed inside the wear track, but there are numerous small craters ranging in size from tenths to single micrometers. These craters are from macroparticles removed during the friction process.

During sliding various chemical reactions may occur on the rubbing surfaces due to high local pressure (Hertzian stresses of about 1.5 GPa) and flash temperature. They can change the chemical and phase composition of the outer surface layer as well as its mechanical properties. There is mainly oxidation of coatings and formation of thin microfilms on hard coatings. The EDX analysis of selected areas in tracks indicate increased wear oxygen concentration. The concentration of coating elements don't change significantly, and aluminum ratio Al/(Al+Cr) is about 0.8 and correspond to cathode composition. An analysis of wear track composition indicate on oxidation process during wear test. In coatings deposited at increasing substrate bias voltage the oxygen concentration increases, Fig. 7. The wear rate of AlCrN coatings investigated is almost independent on substrate bias voltage during deposition, Table 3. The wear depth of the coatings was similar and about 0.6 µm. In EDX measurements the elements of the substrate (mainly iron) were not observed.





b) Еlement¤ Atomic-%й N-К# 37½ O-К# 18й Al-К¤ 35,4ж Cr-К# 9,6ж Spectrum 2 600µm Electron Image 1 C)

Fig. 7. SEM images with worn morphologies with chemical composition of selected wear track for AlCrN coatings synthesized at: a) U_B =-50 V, b) U_B =-100 V, c) U_B = -150 V. Applied load - 20 N.

AlCrN coating containing about 40 at.% of Al synthesized using cathodic arc evaporation at various U_B tested at normal load of 6 N are characterized by an almost constant wear rate, around 3×10^{-16} m³/Nm, irrespective of the

deposition conditions and applied counterpart - 6 mm in diameter tungsten carbide and sintered alumina balls [9]. About one order of magnitude higher wear rate, from about 2×10^{-15} m³/Nm to about 5×10^{-15} m³/Nm were found by Reiter et al. [1] for coatings with an aluminum concentration ranged from 21 at.% to 83 at.%. AlCrN coatings with about 80 at.% of Al show relatively low wear rate ranged from about 8×10^{-16} m³N⁻¹m⁻¹ [8].

Magnetron sputtered coatings are characterized by higher wear rates. Investigations of Lin et al. of $Cr_{0.77}Al_{0.23}N$ coatings indicate a wide range of wear rate against Al_2O_3 ball ranged from about 16×10^{-15} to 3.4×10^{-15} m³/Nm [37].

The wear tests performed against other counterparts: Si₃N₄, ZrO₂, WC, steel ball etc. show different values. For example, the investigations of Al_{0.6}Cr_{0.4}N coatings against Al₂O₃, Si₃N₄ and ZrO₂ counterparts indicate that the lowest wear rate from 3×10^{-15} m³/Nm, to 1×10^{-16} m³/Nm was for Al₂O₃. In the test of the same coating against ZrO₂ ball as a counterpart the wear rate was the highest, from 9×10⁻¹⁴ m³N⁻ $^{1}m^{-1}$ to $4 \times 10^{-15} m^{3}N^{-1}m^{-1}$ [35]. The same wear rate of 3.5×10⁻¹⁵ m³N⁻¹m⁻¹ for Al_{0.7}Cr_{0.3}N against an Si_3N_4 ball was presented by Du et al. [7]. Significantly lower wear rate was found for Al_{0.7}Cr_{0.3}N formed using high power impulse magnetron sputtering at different process parameters. In wear tests against WC-6%Co ball the wear rate ranged from 1.9×10⁻¹⁶ m³N⁻¹m⁻¹ to 6×10⁻¹⁷ m³N⁻¹m⁻¹ [38].

The high coefficient of friction usually results in the high wear rate [35]. For investigated coatings the difference in coefficient of friction is very low. Due to it the difference in wear rates should be also small. The only minor wear of the coating is observed. In the wear track the formation of tribolayer is possible. In the track is observed increase in oxygen concentration. Because of it the formation of Cr_2O_3 and Al_2O_3 is possible. Due to the presence of aluminum in both the counterpart (Al_2O_3) and the coating (AlCrN), it is difficult to prove the transfer of the counterpart material to the coating.

The oxidation of the coatings, especially in contact area, can be related to severe friction test conditions, mainly normal load of 20 N. Due to it and relatively low thermal conductivity of

AlCrN coatings so called flash temperature in friction pair can be high. According the equations [39]:

$$\Delta T = \frac{\mu P v}{4(K_1 + K_2)\alpha} \tag{1}$$

$$\alpha = \left(\frac{P}{\pi H}\right)^{\frac{1}{2}} \tag{2}$$

the contact radius of the real contact area (α) and the flash temperature (ΔT) and can be calculated. The analyze of the equations indicate that other parameters of friction test, except normal load, as the friction coefficient (μ) and the sliding speed (v) have a key role in calculations. Due to low thermal conductivity of the coating (K₁ - 5 Wm⁻¹K⁻¹ [40]) and the Al₂O₃ counterpart (K₂ - 34 Wm⁻¹K⁻¹ [41]) the flash temperature can be significant. Due to hardness increase the contact radius α decreases and the flash temperature increases. Really, the calculations indicate that it is about 800 K (U_B = -50 V) and increases to about 870 K for coatings deposited at U_B = -150 V.

Antonov et al. presented similar results [35]. They applied a normal load of 3 N to the friction tests. It was significantly lower than our investigations (20 N) and calculated rise in flash temperature for AlCrN - Al₂O₃ system was about 300 K. For other systems including Si_3N_4 and ZrO₂ counterparts the rise in flash temperature was about 560 K and 1900 K, respectively, mainly due to their lower thermal conductivity. It means that applied counterpart in friction test has significant impact on the different phenomena at the contact area including also the flash temperature. Lin et al. [39] indicate that also applied normal load and sliding speed significantly affect on flash temperature.

During friction test especially at elevated temperatures the surface oxidation may occur and Al_2O_3 and Cr_2O_3 films can form. Aluminum concentration is a key element in oxidation behavior of AlCrN [5], because the Al_2O_3 top layer prevents diffusion of oxygen into the coating. Cr_2O_3 phase (Gibbs free energy is -252.9 kcal/mol) is less stable than Al_2O_3 phase (-378.2 kcal/mol [42]).

As mentioned above in tribology contact area two oxides can form, Cr_2O_3 and Al_2O_3 . According crystal-chemical approach [43] the main considered parameter is so called the ionic potential φ of an oxide defined as φ =Z/r, where Z is cationic charge and r is the radius of the cation. Based on results of many investigations and references it was stated that small ionic potential of oxides or oxide mixture is responsible for high friction.

Investigations of CrN coatings in ball-on-disc tribotester equipped in Al₂O₃ ball (10 mm in diameter) under a typical sliding velocity of 0.2 m/s and relatively low normal load of 5 N were performed by Ozturk et al. [44]. Based on the Raman's investigations they determined the phase composition of CrN debris as a mixture of CrO₂ and Cr₂O₃. Chim et al. investigated a thermal stability of Cr- based coatings (CrN and CrAlN) [45]. They found that CrN coating oxidation starts at 700 °C and CrAlN about 1000 °C. EDX tests carried out in a CrN coating at 900 °C showed the presence of a small residual amount of nitrogen. It means that CrN was almost totally oxidized. CrAlN coatings are more resistant to oxidation. After annealing at 1000°C, the concentration of oxygen was significantly lower, only about 19 at.% [45]. When the friction during sliding is performed in the air, tribo-oxidation of the AlCrN coating can occur already at 300 °C. Various chromium oxides, such as CrO₂, Cr₂O₅ and CrO₃, may then be formed [3]. The sliding tests conducted at room temperature are also favorable for oxidation [35]. For coatings with Al ratio (Al/(Al+Cr) higher than 60 % the polishing is the main type of wear mechanism and the main oxide formed is Al_2O_3 [5].

The ionic potential for Al_2O_3 , Cr_2O_3 and CrO_2 are 4.4, 4.0 and 7.3, respectively. It is known that Al_2O_3 is strongly abrasive and its presence in tribological contact can lead to increase the probability of abrasive wear [35]. The formation of Cr_2O_3 , serving as a solid lubricant, provides reduction in friction coefficient while Al_2O_3 leads to higher CoF [35].

An increase in hardness and related to it increase in flash temperature and Cr_2O_3 formation can lead to friction coefficient decrease. The low wear rate is probably connected with the smoothening of the coating.

4. CONCLUSION

Al-Cr-N coatings synthesized using cathodic arc evaporation at different substrate bias voltage

were investigated. The $Al_{80}Cr_{20}$ cathode was applied to check the rare reports on poor wear resistance of coatings with hexagonal AlN structure. The structural, mechanical and tribological properties of the coatings were also studied. Test results allow to present the following conclusions:

- Deposition rate of the coatings decreases with negative substrate bias voltage increase. Due to higher particles energy the resputtering of condensed film reduces their growth.
- The coatings are a mixture of two phases the hexagonal phase of AlN and the cubic phase of CrN. The intensity of diffraction lines of c-CrN increases and h-AlN decreases. This may be associated with decreasing concentration of aluminum in the coating, as a result of resputtering and different Al and Cr efficiency of sputtering in the AlCrN system.
- The density of both phases increases with substrate bias voltage, as a result of higher energy of particles incident to a substrate.
- A crystallite size of h-AlN phase decrease and c-CrN phase slightly increase can explain the hardness increase with substrate bias voltage. Additional reason is the density of the coatings increase.
- Despite the deterioration of the adhesion their wear resistance is relatively high. The coating synthesized at a substrate bias voltage $U_B = -100$ V is characterized by a lowest wear rate of $(1.1\pm0.2)\times10^{-16}$ m³/Nm. The coating formed at $U_B = -150$ V show the highest wear rate - $(2.1\pm0.4)\times10^{-16}$ m³/Nm. This means that the lower adhesion of the coating is responsible for its lower wear resistance.
- The "flash temperature" depends on the hardness of the coating, and increases with increasing hardness of the coating. The "flash temperature" increase may result in more intense the coating surface oxidation process in tribological contact. This is demonstrated by increasing, with coating hardness, the concentration of oxygen in their wear tracks.

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