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TRIBOLOGICAL PROPERTIES OF TiAlCrN THIN FILMS

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Abstract. The dry sliding wear of monolayer TiAlN, TiAlCrN and multilayer TiAlN/CrN coatings have been investigated against alumina counterpart. All tested films were deposited using cathodic arc evaporation with Ti/Al and Cr cathode. All coatings were deposited on Cr and CrN sublayers, which reduces stresses between film and substrate and causes adhesion increasing. Coatings with chromium show lower friction coefficient when compared with TiAlN film and meaningful lower wear rate of the coating. Increasing the normal force and bilayer thickness of multilayer coating causes reduction the friction coefficient from 0.85 to 0.77 and from 0.90 to 0.77 respectively. Wear rate for TiAlN was measured as 5×10^{-6} mm^3/Nm, for TiAlCrN 5×10^{-7} mm^3/Nm, for TiAlN/CrN 3×10^{-6} mm^3/Nm. Wear rate for alumina counterpart was at least an order of magnitude lower than tested coatings.

1. INTRODUCTION

End users of cutting tools require better efficiency for complex cutting operation, high speed, lack or minimum lubrication and highly abrasive materials. The use of TiAlCrN coatings for cutting tools both mono- and multilayer films has increased rapidly. This coating is very promising for its wear resistance caused its excellent high temperature corrosion and oxidation resistance which results in higher chemical stability when compared to TiN.

Deposition of thin films based on TiAlCrN using cathodic arc evaporation enables creation coatings with excellent adhesion and dense structure. These features are base of its application reducing production costs and increasing the output in many high speed or dry machining.

Ti(X)N coatings where X stands for metallic element introducing to the TiN lattice have been subjected to great interest. The group of titanium nitride coatings can be divided in three generations [1]. The first generation, titanium nitride monolayer coatings show many industrial applications connected with their attractive properties – high hardness, chemical stability, good wear resistance [2]. The second generation forms by introducing metallic element(s) to TiN coatings. The most important of them are TiAlN [3-6], TiAlCrN [7-9] showing excellent wear and oxidation resistance when compared with TiN [6]. These coatings predominantly shows higher hardness when compared with first generation films. Multilayer coatings are frequently named as the third their generation. With this group of coatings is connected technological progress because of their very high hardness [1,9].

Multilayer coatings show high hardness and toughness when compared with monolayer coatings. The latter of these features is very important because in many applications the cracking of the coating is unacceptable. Metal - ceramic composite multilayer coating show higher toughness and crack resistance as compared with single layered ceramic coatings. This has been at the expense of a reduced hardness and wear resistance [10].

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Table 1. Deposition parameters for CAE coatings.

Parameters	Monolayer coating Values	Multilayer coating Values
Partial pressure of N_2 [Pa]	1.0	1.0 /1.8
Target diameter [mm]	100	100
Target – surface distance [cm]	18	18
Etching voltage [V]	-600	-600
Argon pressure during ion etching [Pa]	0.5	0.5
Etching time [min]	10	10
Bias voltage [V]	-70	-70
Number of layers		8 (25)
Deposition rate [μm/min]	~ 0.04	~ 0.03
Arc current [A]	60	60 - $Ti_{50}Al_{50}$ 80 - Cr

TiAlN/CrN coating is an example of multilayer coating characterizing by higher hardness and oxydation resistance as compared with TiAlN. It can improve tribological properties of these films.

In this paper tribological results of investigated TiAlN, TiAlCrN monolayer and TiAlN/CrN multilayer coatings are shown. All coatings were deposited using cathodic arc evaporation.

2. EXPERIMENTAL RESULTS

Thin monolayer TiAlN and TiAlCrN and multilayer TiAlN/CrN coatings were deposited using cathodic arc evaporation. The substrate of 28 mm in diameter and 3 mm thick were made from hardened and annealed HSS steel. Before deposition each substrate was mechanically polished to R_a ~0.02 μm. Then they were ultrasonically cleaned in the series of hot alkaline cleaning bath for 10 min and finally dried in hot air to remove the residual solvent. Afterwards the samples were mounted on rotating substrate holder in vacuum chamber.

The chamber was evacuated to the pressure about 1 mPa and then back-filled with argon to 0.5 Pa. The next step was sputter cleaning for 10 min using bias voltage - 600 V and next they were radiationally heated to about 300 °C. A thin layer of chromium and chromium nitride were deposited to improve adhesion of the coating to the substrate. The thickness of this sublayer was about 0.4 μm and it was deposited using bias voltage -70 V and arc current 80 A in presence of high purity nitrogen gas.

The chamber was equipped in four arc sources, two with AlTi (50:50 at.%) targets and two with Cr (99.8% pure) targets placed alternate with the angle between TiAl and Cr cathodes of 60°. The gases, argon and nitrogen, were introduced into the system equipped with the flowmeters to control the gas flow, through a pipe mounted in neighbourhood each target to enhance the reaction of the plasma.

TiAlN and TiAlCrN monolayer coatings were deposited using $Al_{50}Ti_{50}$ target and two targets $Al_{50}Ti_{50}$ and Cr respectively using under the nitrogen pressure 1 Pa. TiAlN/CrN coating was deposited using two different nitrogen pressures, 1 Pa for TiAlN and 1.8 Pa- sufficient to result in nearly stoichiometric CrN phase. Substrate bias voltage -70 V and arc current 80 A for both layer in multilayer coating were applied.

The coating thickness was controlled by time of deposition. The periodic thickness of the multilayered TiAlN/CrN coating was controlled by the rotational speed of the substrate holder. The experimental parameters of the deposition process are shown in Table 1.

Composition of the deposited film was evaluated by EDX. Thickness was tested with Calo- test method, SEM was also used. Friction and wear tests were carried in ball-on-disc tribotester using the normal load from the range 5-20 N with the constant sliding speed 60 mm/s. A total sliding distance of 1000 m (13000 revolutions) was used in each case. The test was performed in open air of about 50% relative humidity at room temperature and without lubrication. The counterpart material was 10 mm diameter alumina ball polished to less

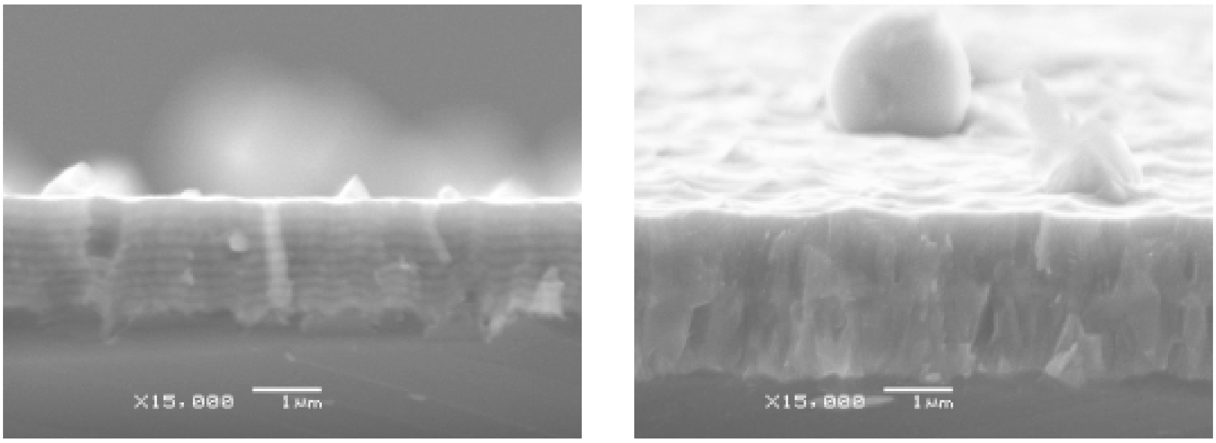

Fig. 1. Cross-section micrograph of TiAlN/CrN multilayer coating of bilayer thickness $\Lambda = 0.234$ μm (a) and TiAlCrN monolayer coating (b).

than $R_a < 0.03$ mm. The wear scar of the ball was measured using Hommel Werke T2000 profilograph to calculate wear coefficient, i.e. volume loss at unit normal load and unit sliding distance [11]. The measurements were realized for five samples of each coating.

3. RESULTS AND DISCUSSION

3.1. General characterization of deposited coatings

Coating's composition was determined from EDX analysis. Composition of the CrN sublayer deposited from Cr cathode material was 53 at.% of Cr, 46 at.% of N and 1 at.% of oxygen. The composition of TiAlN coating deposited from $Ti_{50}Al_{50}$ target was about 17 at.% of Ti, 11 at.% of Al, 71 at.% of N and 1 at.% of oxygen.

Chromium amount in TiAlCrN and TiAlN/CrN coatings was determined as about 10 at.% with comparable amount of Ti and Al in monolayer TiAlN coating. An atomic ratio of Ti:Al in TiAlN coating was changed to 60:40 compared with the $Ti_{50}Al_{50}$ cathode material and it is in accordance with results presented in works [3,12]. It can be connected with the lower atomic mass of Al that causes higher scattering in the collisions with nitrogen, and leads to a lower volume density in the vapor [13].

Fig. 1 shows the cross-section SEM images of multilayer TiAlN/CrN coating with bilayer thickness $\Lambda = 0.234$ μm (photo a) and monolayer TiAlCrN coating (photo b). The thickness of all investigated films are about 2 μm as shown below. The number of bilayer in the multilayer coating depends on bilayer thickness. For bilayer thickness of 0.234 μm it was 8 bilayers; for bilayer thickness 0.068 μm it was 25 alternating bilayers.

The microscopic analysis pointed out that investigated coatings show the same thickness in all deposition area. They show high adhesion and compact structure and big density without visible voids and delamination. Presented multilayer coatings didn't show columnar texture, typical for monolayer coatings (as shown on Fig. 1b), but it probably can exist in nano-scale [12]. The scratch test revealed cohesion critical load L_{c1} for all coatings as 20-30 N and adhesion critical load L_{c2} as 75-90 N. This good adhesion can be caused by chromium nitride sublayer.

3.2. Friction

The hardness is very important property of coating from tribological point of view. Hardness isn't the only property which provide low friction coefficient in kinematic pair. High temperature and stresses which appear there can change the structure, composition and other properties of hard coatings. In this kinematic pair three objects: the coating, workpiece and environment are important. They decided about friction coefficient and wear of the coating. The friction coefficient for investigated coatings are shown in Fig. 2 and friction coefficient as a function of bilayer thickness in multilayer TiAlN/CrN coating are shown in Fig. 3.

Presented above values are average of five samples of each coating. This values are close

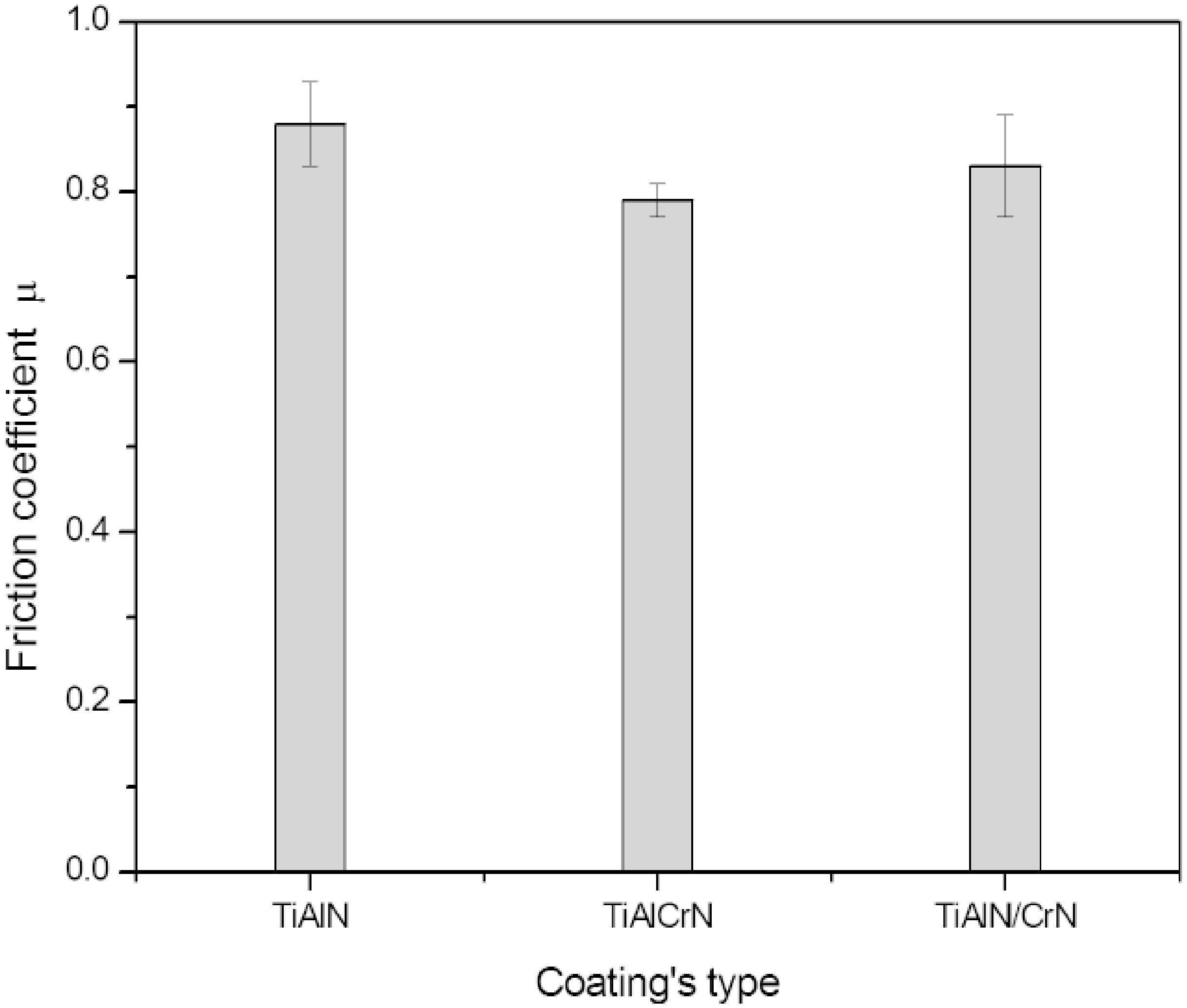

Fig. 2. Friction coefficient of investigated coatings.

together but chromium based coatings show slightly lower friction coefficient in applied measurement conditions. Friction coefficients (Fig. 2) are close to published in [1,14] for TiAlCrN and TiAlN/CrN coatings and in [3] for TiAlN coatings.

From tribological point of view, all the coatings show different friction and wear behavior. The character of material removed from wear scar is important to determine the tribological behavior of sliding system. The chemical structure cognition of this debris formed during sliding can help in explanation the friction and wear of different materials. Öztürk [15] connects good tribological behavior of CrN coatings with forming of a chromium oxides with high ionic potential [16] during wear processes. This potential described as $\varphi = Z/r$, where Z refers to formal cationic charge and r refers to the radius of the cation. The cations with small radius are efficiently screened by the surrounding oxygen which causes their large ionic potentials. Such oxides are soft, susceptible to distortion and shear during sliding. The oxides with high ionic potentials are expected to operate as lubricious compounds [16]. Higher ionic potential of CrO_2 forming during CrN sliding when compared with TiO_2 forming during TiN sliding causes better tribolological behavior of CrN.

Decrease of bilayer thickness in multilayer coatings causes increase of hardness [14]. Increase the hardness for many coatings lead to decrease the friction coefficient, but not only hardness exerts influence on friction coefficient of the coating. The deposition of multilayer coating is connected with total stress escalation when compared to deposition of monolayer coating.

Hovsepian [14] points that increase of the friction coefficient can be correlated with the increase in the residual stress in the coatings, which pro-

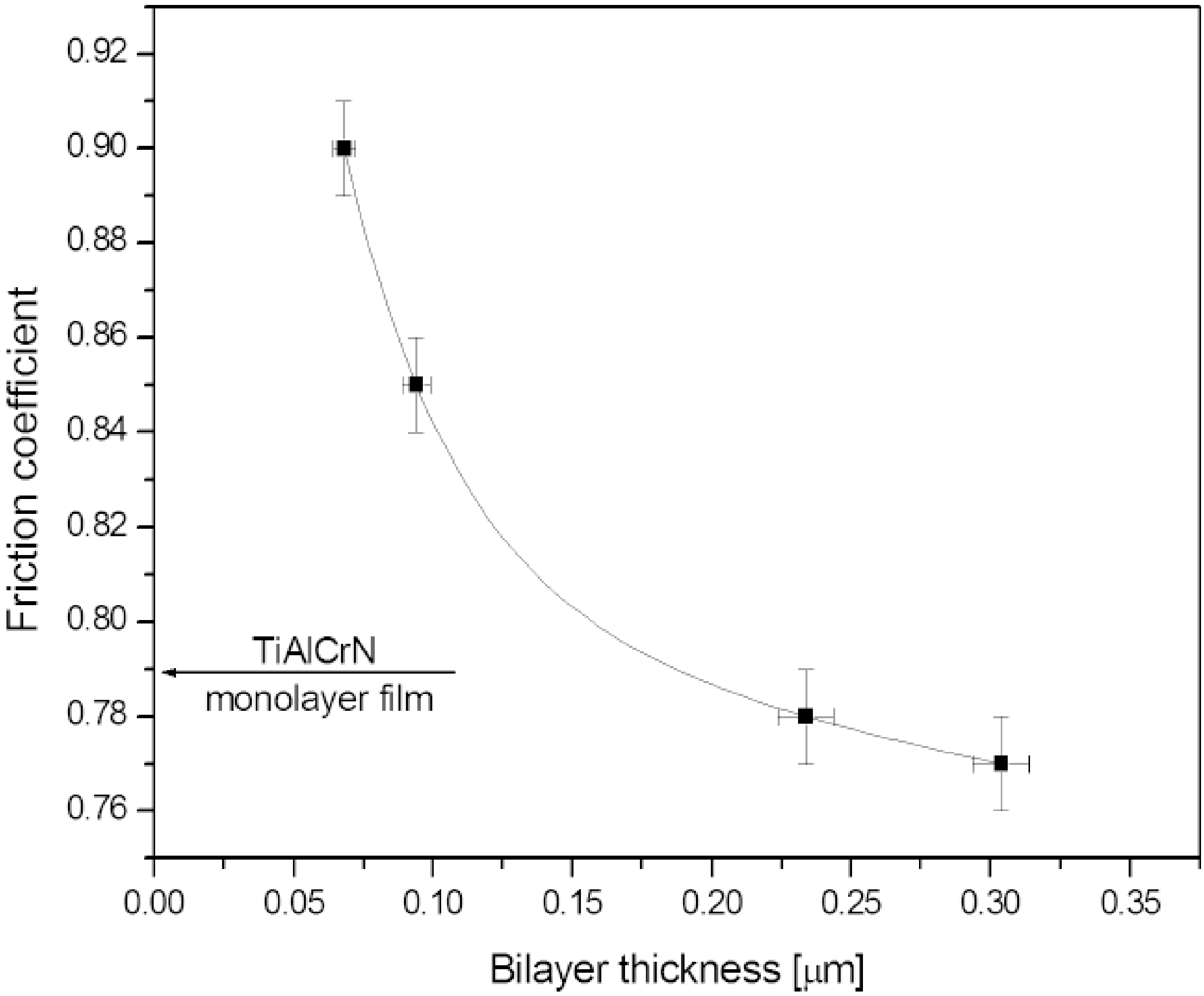

Fig. 3. Friction coefficient as a function of bilayer thickness of TiAlN/CrN multilayer coatings.

motes brittle fractures. In dry sliding conditions small debris from materials are forming, leading to a three-body tribological contact and micro-abrasive wear mechanism. This third body characterized by irregular shapes and high hardness are additional and effective agent leading to raise of coating wear.

Increasing the normal load causes a slight decrease in the average friction coefficient (Fig. 4). The variation of the friction coefficient for investigated coatings is typical and similar to each film. Earlier published data [1,9] are close to those presented in this work.

3.3. Wear

The wear of hard coatings has depended on, among others, normal force in tribological contact and its geometry, relative humidity, sliding speed, lubricity of the contact. At low sliding speeds and low loads, it is assumed that dominant wear mechanism in dry running conditions is smoothing the surface of the coating and forming the metal oxides as a consequence of high temperature in tribological contact. Increase of the load or sliding speed causes that abrasion and microshearing appears as dominant wear mechanism in these coatings [17].

Hovsepian et al. [14] presents mechanical wear behavior of multilayer TiAlN/CrN coating stating qualitatively different to that of the columnar monolithically grown TiAlCrN hard coating. The individual columns in latter coating deform plastically under high mechanical loads results in delamination and crack formation about 0.2 µm deep below the surface. The fine scale delamination was observed on the surface of multilayer TiAlN/CrN coating with no evidence of plastic deformation or crack

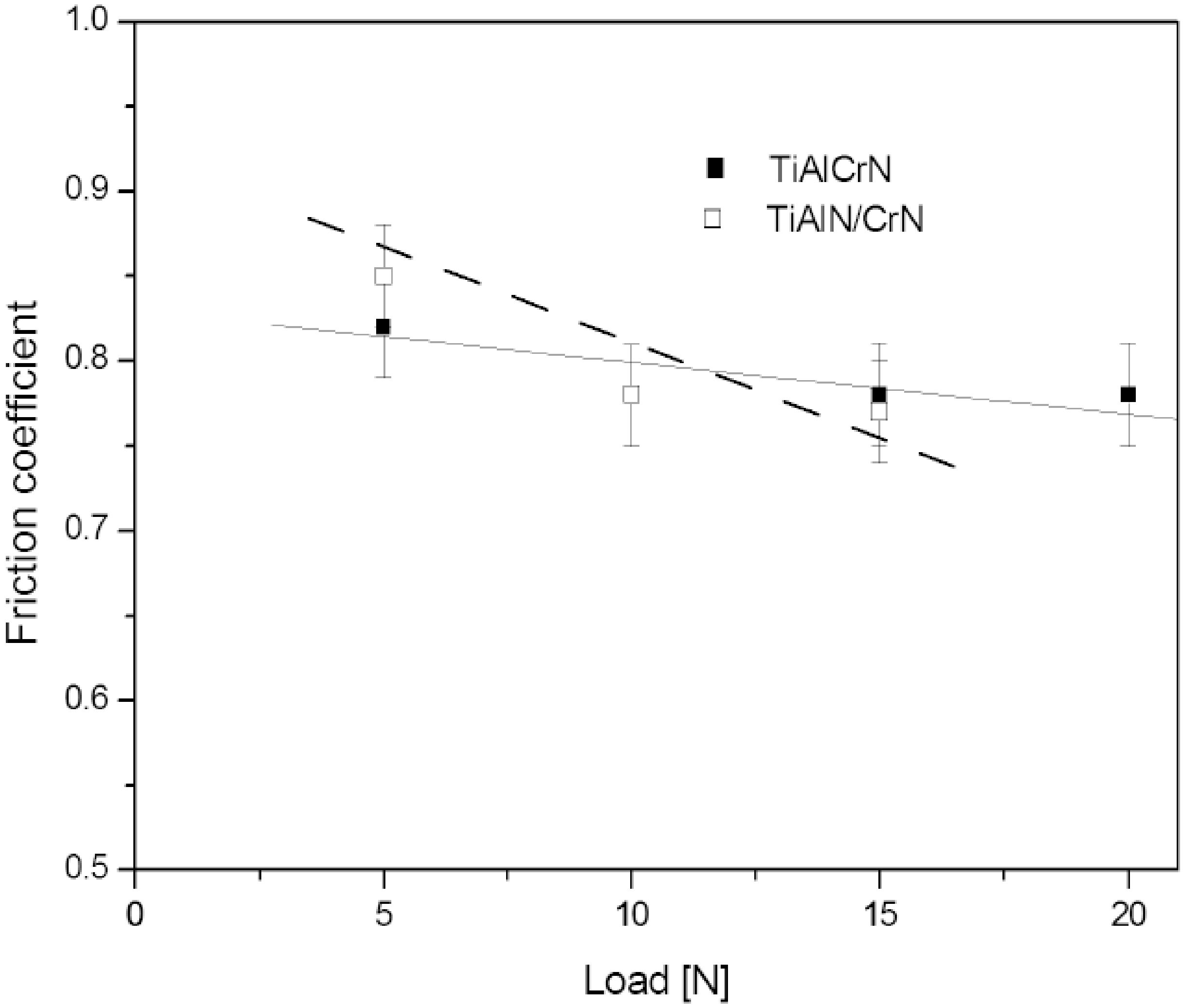

Fig. 4. Friction coefficient as a function of load in TiAlN/CrN multilayer coatings.

propagation. It can be the reason of high wear resistance of multilayer coatings.

The wear mechanism of the coatings consisting of tribo-chemical and mechanical part, contains among other things polishing, cohesive spalling and adhesive spalling [1,9]. The wear mechanisms, at low load, for mono and multilayer coatings are similar. It can be confirmed by comparable wear rates and friction coefficients of monolayer TiAlCrN and multilayer TiAlN/CrN coatings. At higher load, when mechanical degradation of the coating dominates, multilayer coatings show higher wear resistance than the monolayer [1].

Presented in this paper coatings show lower wear rate as described in [18] for TiAlN and in [1] for TiAlCrN and TiAlN/CrN. In Fig. 5, a large difference can be seen in wear rate for monolayer TiAlN and the coatings with chromium. It can be caused by much higher wear rate for TiN when compared to CrN coatings [15].

The investigated coatings show relatively high adhesion critical force L_{c2} although cohesion critical force L_{c1} is not so high – 20-30 N. This low cohesion critical force is directly related to fracture toughness and coating's cracking and is often observed with covalently-bonded materials [19]. This cracking is blocked on the nearest interface and small delamination can be visible. The debris from delaminated coating can indicate on raise the friction coefficient. Simultaneously residue coating is no failure. This contributes to high adhesion critical force.

The wear mechanism can be following. In the beginning stage of friction process the smoothing

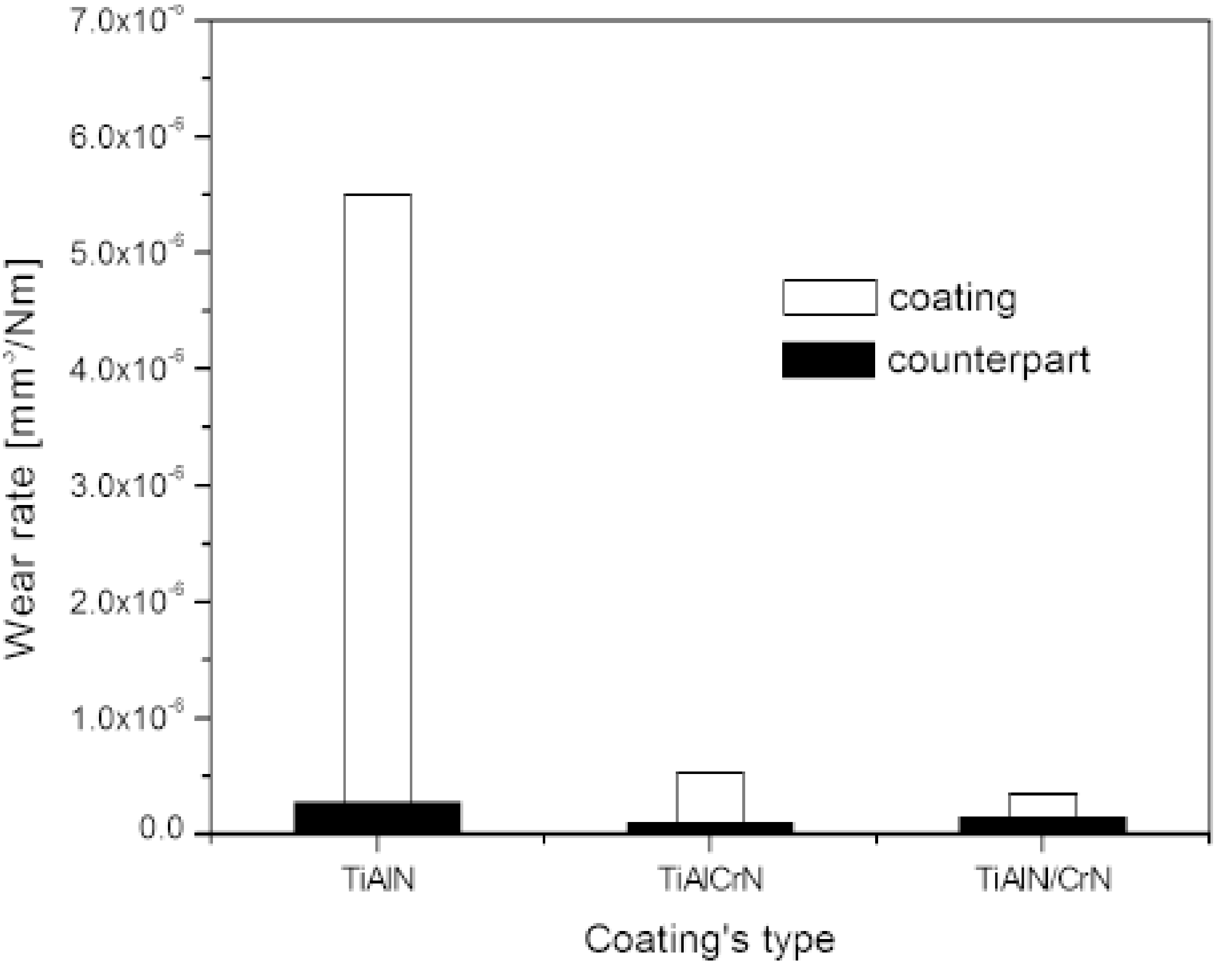

Fig. 5. The wear rate for different coatings.

of the surface is proceeded and afterwards the spalling of the coating with low toughness are removed. This debris are in tribological contact and raise the friction coefficient and wear rate of the coating.

4. CONCLUSIONS

- Coatings based TiAlN namely TiAlN and TiAlCrN monolayer coatings and TiAlN/CrN multilayer coatings were deposited using cathodic arc evaporation with Ti/Al (50/50 at.%) and chromium cathodes.
- Addition of chromium to TiAlN coating causes increase of the hardness.
- Reduction of friction coefficient and wear rate when compared to TiAlN are registered.
- Increase of bilayer thickness for TiAlN/CrN multilayer coatings causes friction coefficient decrease.
- The problems with surface – coating adhesion caused by stresses can be solved by addition stress reducing interlayer to this system.
- Wear rate of TiAlN/CrN multilayer film ($3.3 \bullet 10^{-7}$ mm³/Nm) is lower than TiAlCrN monolayer film ($5.3 \bullet 10^{-7}$ mm³/Nm) for about 60% and about 20 times lower when compared to TiAlN film ($5.5 \bullet 10^{-6}$ mm³/Nm).
- Increase of friction coefficient with bilayer thickness decrease of multilayer films is difficult to explain and other tests of this effect are planned.

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