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Tribological properties of CrN_x coatings

B. Warcholinski*, A. Gilewicz
Institute of Mechatronics, Nanotechnology and Vacuum Technique,
Koszalin University of Technology, ul. Raclawicka 15-17, 75-620 Koszalin, Poland
* Corresponding author: E-mail address: bogdan.warcholinski@tu.koszalin.pl

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Properties

ABSTRACT

Purpose: The purpose of this work is the characterization of the tribological properties thin Cr-N coatings, both monolayer Cr_2N, CrN coatings and multilayer Cr/CrN, Cr_2N/CrN coatings, deposited by cathodic arc physical vapour deposition (CAPVD).
Design/methodology/approach: The deposition parameters of Cr_2N and CrN were determined. Structure of the coatings were investigated using the scanning electron microscopy (SEM). The XRD examination was carried out to specify the phase structure, EDS to define the chemical composition of the coatings. The investigation includes also microhardness, roughness tests, adhesion, friction coefficient and wear rate.
Findings: Basing on the scratch test it was shown that the influence of the architecture on the coating' adhesion is dominant. It was found that the all tested coatings show high critical load Lc_2 >70 N. The multilayer coatings show higher critical load when compared to monolayer coatings.
Research limitations/implications: The main limitation of this work is linked to the deposition technique itself. It is difficult to avoid surface defects and pinholes that strongly influence the tribological results.
Practical implications: Chromium based coatings present good mechanical properties which allow them to be used in several applications; from decorative to protective coatings.
Originality/value: The comparison of adhesion and wear resistance of mono- and multilayer coatings based on chromium. The deposition technology enable to obtain the coatings with high adhesion to the substrate. This may be important to advanced coatings industry.
Keywords: Tool Materials, Mechanical properties, Wear Resistance, PVD, CrN, Scratch test; Tribological test

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1. Introduction

The application of CrN and other coatings obtained by means of the PVD methods is becoming increasingly popular in industry [1-4]. This stems from their good tribological properties. These are characterised by a relatively low friction coefficient, good wear resistance and a high corrosion resistance. Due to its exceptional abrasion resistance, chrome nitride is used as a coating in cutting, milling and screw-threading tools for the elements made of titanium and its alloys, brass, copper and other non-ferrous metals. It is also employed in covering moulding forms, punches and parts of machines. Chrome nitride shows high chemical resistance and exceptionally little affinity to the machinated non-ferrous metals. These coatings may be deposited by various PVD techniques, both magnetron and arc [5].

The coatings obtained by means of the arc method are characterised by a varied phase composition and crystallographic orientation, depending on the deposition conditions. Oden [6] points to the fact that, with the bias voltage at -300 V and the nitrogen pressure larger than 5 Pa, the CrN coatings obtained by means of the arc method show a privileged orientation (220). He also points out that hardness of such coatings is strongly depend on their internal stresses. The tribological properties of the coating-substrate system are connected with the hardness, elastic module and the coatings' adhesion to the substrate. These are influenced by the chemical and phase composition, microstructure, stress and architecture of coating in the case of multilayer coatings (module's thickness and the thickness ratio in the module's layers). All these results are determined by the conditions of coating deposition (gas composition, bias, temperature of the substrate and the discharge parameters).

In the binary Cr-N system there may be a hexagonal Cr_2N phase and the regularly centralised CrN. The conditions of depositing coatings have a considerable effect on the type of phases that are developed in them.

Due to their mechanical properties, hardness and crack resistance, multilayer coatings are subject to numerous examinations. The fact that their results are better than those of single-layer coatings is connected with the limitation of dislocation movements on the margin of layer divisions. The deformation of multilayer coatings is markedly different from that of the single-layer ones due to the fact that the former have interfaces [4].

The aim of this research is to specify the tribological properties of thin CrN_x coatings deposited by cathodic arc physical vapour deposition (CAPVD). It contains information concerning the deposition technology of CrN_x coatings, results of structural analysis and chemical composition as well as microhardness and coefficients of wear and dry friction in the ball-on-disk system.

2. Technology and testing methods

Single-layer CrN, Cr_2N coatings and multilayer Cr/CrN, CrN/Cr_2N coatings were deposited by cathodic arc physical vapour deposition onto polished substrates (R_a<0,02 μm) made from HS 6-5-2 steel and a 32 mm of diameter. The substrates were cleaned in alkaline baths by means of ultrasounds. Such prepared substrates were assembled on a rotating table in a chamber, 18 cm from the sources. The vacuum system allowed to reach the final pressure of $1x10^{-3}$ Pa. The substrates were radiatively heated up to the temperature of 300^0C. All the processes of coating depositions were preceded by a 10-minute etching of metal ion with the voltage at -600 V and the argon pressure in the chamber at 0.5Pa. A thin chromium layer of about 0,1μm thick was used as a sublayer in order to improve the adhesion of coatings to the substrate. The process of deposition of layers was performed with the substrate bias at -70 V, and arc current of 80 A for the Cr target in the nitrogen atmosphere. The rotating speed of the samples was 2 min^{-1}. The processes were carried out with the nitrogen pressure in the technological chamber ranging from 0.2 Pa to 2 Pa.

For the nitrogen pressure about 0.2 Pa we obtained hexagonal Cr_2N, while at 1.8 Pa, cubic CrN. Multilayer coatings were obtained as a combination of the above single-layer coatings. The multilayer coatings consisted of 7 Λ modules, i.e. the recurring double layers of constant thickness. The thickness of layers was regulated by the time of their deposition.

The composition of the coatings was determined by means of the EDX method, while their structure by means of the method of XRD diffraction of Co-K_α radiation. The thickness of coatings was measured by means of the wear method (Calotest). The hardness was measured by means of the Vickers method, using the Hannemann's attachment to the Neophot 2 microscope. The applied pressure ranged from 0,1 to 1,0 N. The morphology of the coating layer and the dimension of impresses were measured with a scanning electron emission microscope JSM5000. The hardness was determined using the Jönsson-Hogmark method [7].

The adhesion of coatings to the substrate was determined using the Daimler- Benz method [8] and the scratch method performed on a CSEM Revetest® Scratch-Tester with a diamond type C Rockwell indenter. The indenter was moved with the speed of 10 mm/min, linearly varying the pressure force from 0 to 200 N with the speed of 200 N/min. In the Daimler-Benz method adhesion is determined by means of a 6-degree scale. According to this scale, the marks HF1 to HF4 mean good adhesion with small cracks or delamination of the coating in its contact with the Rockwell indenter. The HF5 and HF6 marks indicate poor adhesion with considerable cracks of the coating. In the crack method, the critical force L_{c2} was defined as a force of detaching the coating from the substrate.

The friction coefficient measurements were performed in the ball-on disk device (T-01M) with the load of 30 N and the speed of ca. 60 mm/s in the dry friction conditions on a distance of 1000 m. Alundum sphere with the diameter of 10 mm and R_a < 0,03μm was used as counterpart. The measurements were performed in the air atmosphere with the humidity of ca. 50 % in the ambient temperature. The profile of sample wear was measured by a T 8000 Hommel-Werke profile meter. The wear rate was determined as the volume of the material removed during the friction test divided by a product of the distance of friction test and the load [9].

3. Results and discussion

3.1. Thickness and composition of the coatings

The entire thickness of coatings for all the samples was determined by means of the Calotest method and amounted to ca. 2.5 μm, including the sublayer thickness of 0.1 μm. Endler et al. [10] found that the cutting tools' edges become rounded when the layers they cut are too thick, which is the reason for the increase in their wear. At the same time, the hardness of the CrN coating on the substrate from sintered carbides reaches its maximum value with the thickness at 2 μm [11].

The composition of layers was measured using the EDX method. The results of these measurements confirm that in the coating obtained with the nitrogen pressure at 1.8 Pa the chrome to nitrogen ratio amounts to 53% to 47 % at. This ratio is typical for the CrN phase [12]. The appearance of this nitride was consequently confirmed in the XRD examinations. The coating obtained with the nitrogen pressure at 0.2 Pa contains ca. 70 % at. of chrome and 30 % at. of nitrogen. It needs to note that the results of ca. 0.5 % at. of oxygen in the coating were to be found in all tested samples.

The multilayer coating consists of 7 Λ modules, each of them being 340 nm thick. The thickness of particular Cr_2N and CrN coatings in module are 170 and 170 nm, respectively. Fig. 1 illustrates the morphology of the surfaces of CrN and Cr_2N coatings. The profilemeter measured the roughness of Ra and Rz which amount to 0,6 and 2,8 µm respectively for CrN as well as 0,6 and 2,6 µm for Cr_2N.

In Fig.1 one can see a considerable number of microdroplets and their craters which constitute their remains typical for cathodic arc physical vapour deposition. This results in a substantial (ca. 4-5 times) increase in the coating's roughness in comparison with the roughness of the substrate. Some droplets are placed right on the substrate and extend throughout the whole thickness of the coating.

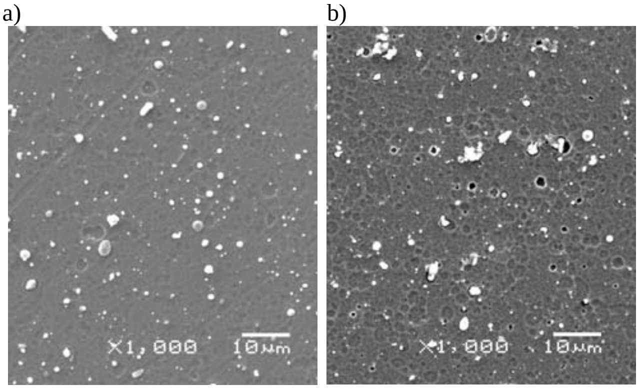

Fig. 1. SEM images of CrN (a) and Cr_2N (b) coatings

3.2. XRD analysis of the phase composition

Fig. 2 shows the diffraction patterns of the obtained CrN_x coatings. The reflexes which can be seen there stem from the substrate and indicate the existence of various phases of nitrogen and chrome compounds. These also point to dominating crystallographic orientations with a change of nitrogen pressure during the deposition process.

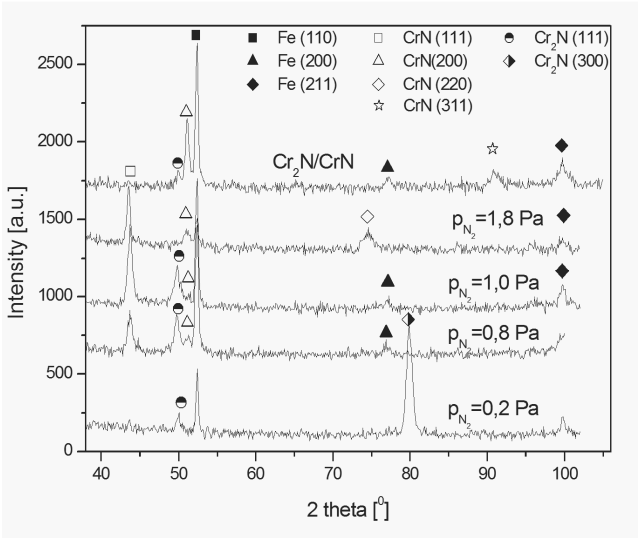

Fig. 2. X-ray diffraction patterns for the CrN_x coatings deposited at different nitrogen partial pressure

When analysing the half width value of the Cr_2N phase peak (111) one can assume that along with the increase of nitrogen in the application (amount of nitrogen in the coating) there appears a broadening of the diffraction line. This happens as a result of an introduction of free nitrogen atoms to a crystallographic lattice, which leads to its non-uniform deformations and impose of reflexes. Substrate reflexes from the planes (110), (200) and (211) show low intensity. This stems from the masking of the substrate by the chrome nitride coating. At the pressure of 0.2 Pa there appears a Cr_2N phase with a dominating peak (300). The base diffraction line (111) is also registered. Along with the increase in pressure there appear base peaks (111), (200) and (220), which is typical for the CrN phase. At the pressure of 1.8 Pa there appear only CrN phase peaks with a dominating orientation (111). For the pressure values of 0.8 and 1.0 Pa the XRD data point to the appearance of both phases of chrome nitride. The multilayer Cr_2N/CrN coating reveals peaks of both phases with a change in the CrN texture and a dominating peak which derives from the plane (200).

The observed reflexes are moved to a low diffraction angles when compared to the table data. This results from the compressive stresses which appear in the layer and are caused by ion bombardment during the process of deposition. A similar diffraction pattern may be seen in other papers [2, 3, 13, 14].

Depending on the technological conditions of the process of CrN coating deposition in the wide range of nitrogen level, there may also appear pure chrome [3, 9, 13, 15]. Since the iron reflexes (the substrates are from HS 6-5-2 steel) and chrome are situated in close proximity and have the same intensity, it was necessary to perform the XRD test of the coatings deposited on the silicon substrate. It did not reveal any presence of pure chrome in the examined coatings.

3.3. Hardness

Hardness results for the examined coatings deposited at the temperature of 300ºC can be seen in Fig. 3. The hardness of chromium nitride, CrN and Cr_2N, amount to 18 and 21 GPa, respectively, and comply with the date found in literature. As demonstrated by the Hall-Petch formula [16]:

$$H_{mc} = H_0 + \frac{k_{HP}}{\Lambda^{0.5}} \quad (1)$$

where H_{mc} is the hardness of a multilayer coating, H_o, k_{HP} are constant and Λ is the thickness of the module,

This means that the most significant parameter which improves the hardness of the coating is the module thickness. By reducing the module thickness, one improves its hardness, yet only up to its critical thickness value beyond which the hardness either remains constant or is reduced.

The hardness of multilayer Cr/CrN and Cr_2N/CrN coatings is not considerably higher than that of Cr, Cr_2N and CrN. A similar effect has already been observed [17, 18]. The hardness depends on a number of factors, including the density of coating and lattice defects, size and distribution of grain, phase composition and crystal structure. The appearance of a base peak (311) for CrN in a multilayer coating attests to a different texture of the coating when compared to a single-layer CrN coating and can be the reason for the varied values of hardness.

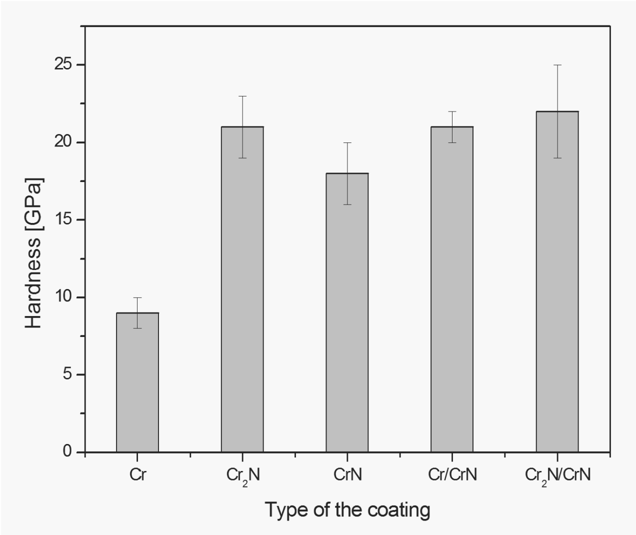

Fig. 3. The hardness of tested films

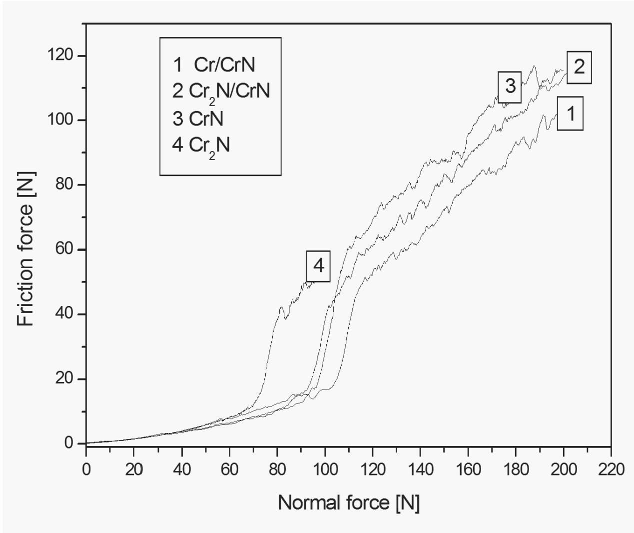

Fig. 4. The friction force as a function of normal force in scratch test for different coatings

3.4. Adhesion

In the scratch method a diamond indenter scratches the surface of the coating which moves at a constant speed and with a linearly increasing load over it. The damage to the coating may have different forms: cohesive, adhesive and conformal breaks, delamination of a coating from the substrate, chipping, flaking etc. A big number of possible coating damages in a scratch test makes it difficult to interpret the results with certainty. Critical force is often associated with adhesion whenever the coating is damaged. Its chipped or flaked elements are removed by the moving indenter outside the scratch, revealing the substrate. However, they are also sometimes pressed into the coating. When the fragments of the coating removed on top of the track do not reveal the substrate, the critical force is not related to adhesion, but to the mechanical properties of coating. The factors affecting the value of critical load in the scratch test include: adhesion and cohesion of coating-substrate system, hardness and roughness of the substrate, hardness and roughness of the coating, thickness of the coating, friction coefficient between the substrate and the indenter as well as the coating stress and that on the edge between the coating and the substrate.

The adhesion is high for all of the analysed coatings. Fig. 4 shows a change in the friction force as opposed to the normal force (scratch test) for the examined coatings. The course of changes in friction force in the load function for the CrN coating and multilayer Cr/CrN coatings as well as Cr_2N/CrN are very similar. A high adhesion of the coating to the substrate is connected, among other things, with the applied chromium interlayer.

The listing of adhesive properties in the analysed coatings is presented in Fig. 5. As can be seen, pure chromium is characterised by a very good adhesion to steel surfaces and its application as an intermediate layer may be beneficial.

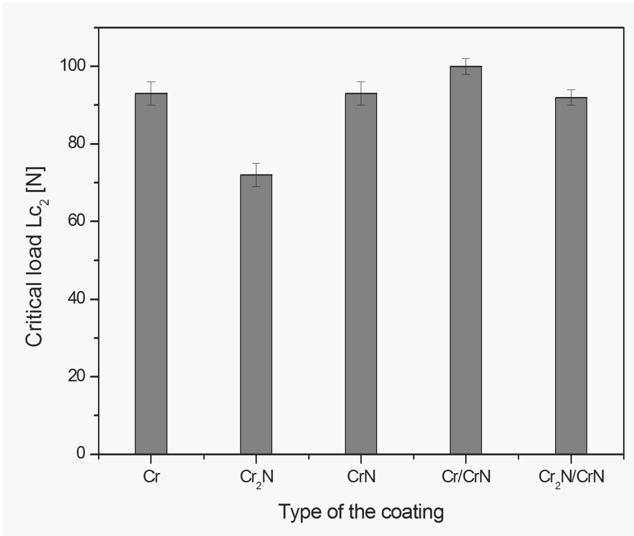

Fig. 5. Critical force Lc_2 for tested coatings

Fig. 4 and 5 demonstrate that the multilayer Cr/CrN coating shows the best adhesion among the analysed coatings. However, its lower hardness results in its anti-wear properties being not so good. One can see no cracks or delamination in the wear picture obtained in the course of thickness measurements of the Cr_2N/CrN coating – Fig 6a. In the whole trace of wear there can be seen microdroplet voids loosely connected with the coating. In the picture which shows an impression left by the Daimler-Benz test on the Cr/CrN coating there can be seen several radial cracks and chippings on the edge of the indenter-coating interaction. This coating could be classified as class HF4. Similar character of adhesion and wear is presented in [19-21].

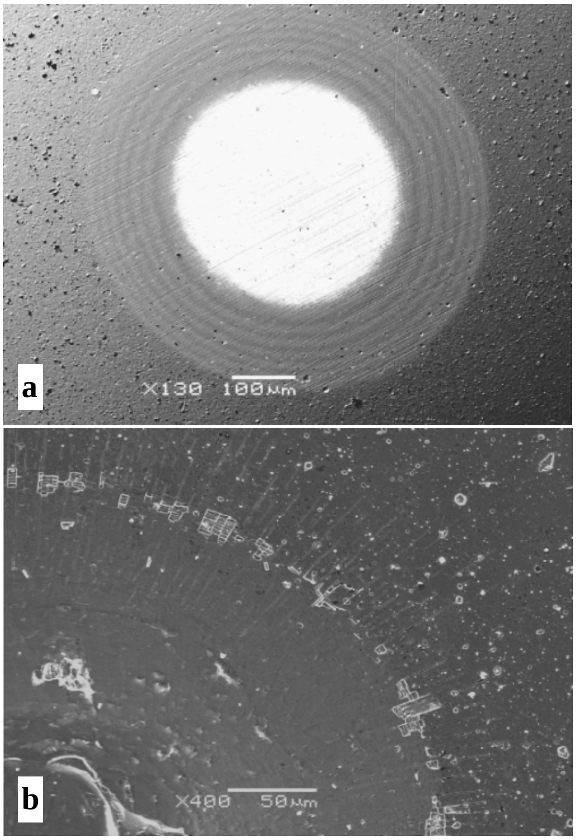

Fig. 6. Optical micrograph of ball crater thickness tester Calotest for Cr/CrN coating (a) and of Rockwell C indentation print on Cr/CrN coating (b)

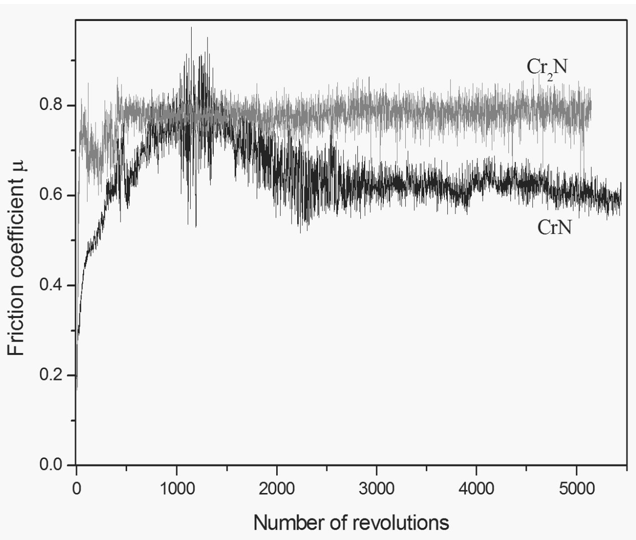

Fig. 7. The friction coefficient plotted versus the number of revolutions of Cr_2N i CrN coatings

3.5. Friction

There are a number of factors which affect the tribological properties of the coatings. These are, among others, their density and microstructure, size of grain, residual stresses as well as the interfacial surface between the substrate and the coating. These factors are related to the method of coating deposition. One of the parameters which determine the friction coefficient is the roughness. Those coatings which are rougher are normally characterised by a smaller critical force and a larger friction coefficient [22]. On account of the method that the examined coatings were obtained, they are characterised by a relatively high roughness, which is corresponding for this deposition method. This could be the reason why the friction coefficient shows a higher value. The friction coefficient values are presented in Figs. 7 and 8 are slightly higher from those that can be found in literature.

3.6. Wear

A reduction in a friction coefficient is often accompanied by a reduction in the wear rate. Highly significant here is the shear strength for its low value results in a low friction coefficient. Those coatings which, apart from the hardness, are characterised by w high shear strength normally show a low wear rate [24]. A higher friction coefficient reflects the boundary lubrication in which there is a larger contact field of the abrasive faces [23]. This leads to an appearance of a mechanical wear mechanism, elastic and plastic strains of the coating and its substrate, cracking the coatings as well as a propagation of cracks [24]. This wear mechanism is responsible for a significant wear of the CrN coatings. On the other hand, a low friction coefficient points to a smooth and flat coating. The tribochemical wear, which appears as a result of the chemical processes which take place on the surface of the coating in tribological contact [23], dominates. Fig. 9 presents a wear profile for the Cr_2N/CrN coating following a friction test on the distance of 1000 m. The architecture of the coating presented here is in the same scale as the wear profile.

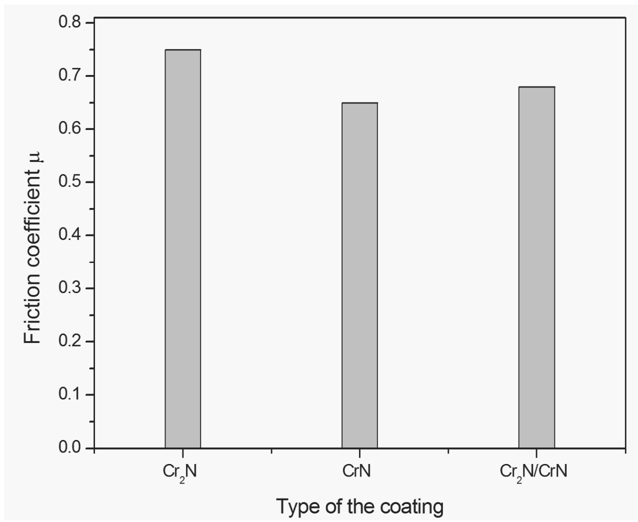

Fig. 8. The friction coefficient for tested coatings

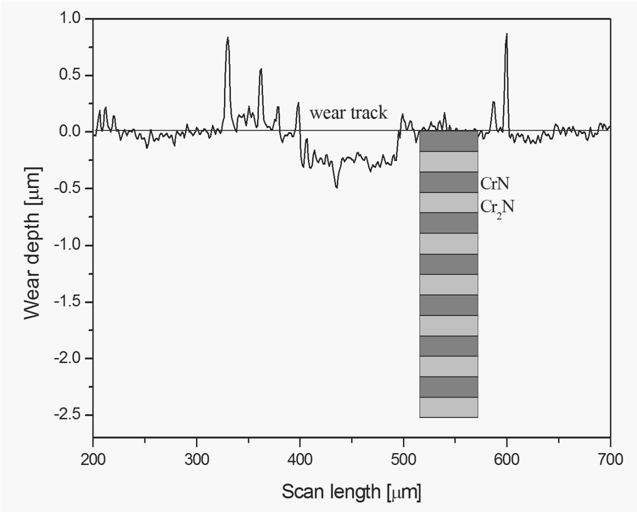

Fig. 9. Depth profile of Cr_2N/CrN coating after 1000 m wear distance

The hardness of the coating and the friction coefficient combined with an counterpart are not the only coefficients in its evaluation. One needs to take into consideration its adhesion and, in particular, the wear rate against different counterparts. Fig. 10 presents the wear values of the k_{mc} coating for different coatings.

The coating with Cr_2N is characterised by a considerably better wear coefficient as opposed to the multilayer Cr/CrN coating whose wear coefficient is considerably higher and amounts to $k_{mc}=4x10^{-5}$ mm^3/Nm. At the same time, the CrN coating, in particular Cr_2N/CrN, is characterised by a considerably lower wear rate. It amounts to $5.7x10^{-7}$ mm^3/Nm for CrN and $3x10^{-7}$ mm^3/Nm for Cr_2N/CrN.

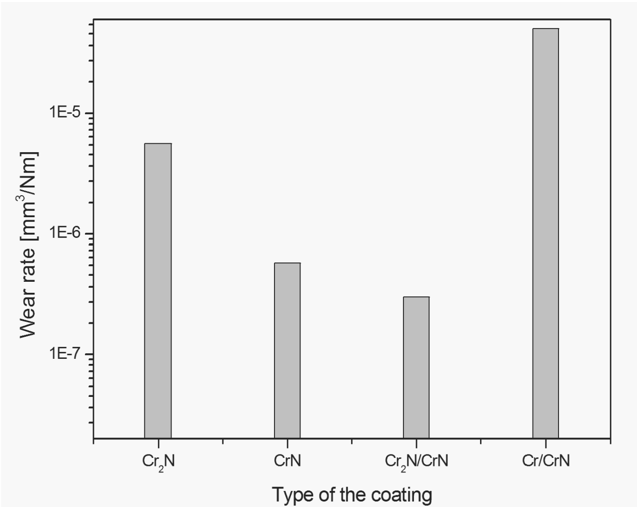

Fig. 10. The wear rate for different coatings

During the friction test of a ceramic sphere of Al_2O_3 with a CrN_x coating, one of the types of wear, often dominating and dependent on the test conditions is the tribochemical wear, acting as oxidisation of both friction faces and chemical interaction between them. In the ambient temperature CrN and Cr_2N react with oxygen, thus resulting in the creation of chromium oxides [23]. One can assume, by studying the works of Zhou et al. [23], that CrN reacts with oxygen easier than Cr_2N. There appears a Cr-Al-O-N tribolayer with a lower shear strength. This results in a typical abrasive wear with a tribolayer as a third face, which reduces wear. One of the effects which came about in the process of wear examination is the polishing of surfaces which takes place in all temperatures [23,25].

The friction measurements were carried out in the ambient temperature and in the air atmosphere and humidity of ca. 50%, i.e. with a water vapour in the air. Here again it is easier to oxidize the CrN coating which leads to its lower wear.

4. Conclusions

- Single-layer and multilayer chrome- and nitrogen- based coatings were obtained using cathodic arc physical vapour deposition. The technological deposition conditions of stoichiometric Cr_2N and CrN layers were also determined.
- Both phases are characterised by high hardness, although CrN is more resistant to wear than Cr_2N.
- Worth noting is the high critical force exceeding 70 N, characteristic to all of the examined coatings.
- The multilayer Cr_2N/CrN coatings are characterised by a low wear rate, 10 times lower than the Cr_2N and 100 times lower than the Cr/CrN ones. This stems from a difference in the wear mechanisms of single- and multilayer coatings.

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