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PROPERTIES OF TOOL STEEL WITH Cr/CrN TYPE HYBRID COATINGS, OBTAINED BY PVD METHOD

The paper discusses the results of investigations of material, tribological and anti-corrosion properties of hybrid coatings of the Cr/CrN type, consisting of chromium and chromium nitride, formed on the surface of alloy tool steel by the Arc-PVD method. Investigations of the morphology and microstructure of hybrid coatings, as well as of their phase composition were carried out. The studies on mechanical properties included tests on hardness and Young's modulus using the nanoindentation method. Tests on adhesion were conducted using the scratch-test method. Tribological properties of the obtained coatings were evaluated by the pin-on-disc method. Resistance to corrosion was determined by electrochemical methods. It was shown that hybrid coatings of the Cr/CrN type are characterized by good adhesion to the substrate and very good tribological properties, as well as by very good resistance to corrosion in a solution containing chlorine ions.

Keywords: hybrid coating, PVD treatment, wear, corrosion

1. Introduction

Hybrid technologies, consisting of a combination of different methods of surface treatment into one complex technological process, constitute currently one of the most advanced trends of investigations in the field of surface engineering [1-4]. This paper pertains to hybrid coatings of the Cr/CrN type, consisting of chromium and chromium nitride, formed on the steel surface by means of arc evaporation method, called Arc PVD (Arc Physical Vapour Deposition).

PVD processes, carried out with the participation of plasma in conditions of lowered pressure, are characterized by a big concentration of ions, electrons and excited atoms [5-7]. Owing to the above, crystallization in a plasma environment is a more advantageous process than crystallization from a non-ionized gas [8-10], because ions in plasma may be controlled by an external electric or magnetic field. As a result, the coating deposited in a plasma environment is characterized by a significantly higher density, as well as better adhesion to the substrate, in comparison to coatings deposited from a non-ionized gas [11-12]. Additionally, due to the presence of ions, electrons and excited atoms it is possible to obtain metastable microstructures, impossible to obtain in processes which are activated solely by heat.

Among the disadvantages of the arc evaporation method is the formation of micro-droplets of vaporized material in the generated plasma flux [13-15]. These droplets are deposited on the substrate and become a part of the newly formed coating. The presence of micro-droplets deteriorate the homogeneity of chemical composition and of the microstructure of the created coating. In order to limit the undesired effect of micro-droplets building themselves into the microstructure of the coating, various technical solutions are employed, among other: electrostatic separation, mechanical separation and magnetic separation [14-16].

Currently, the main activity in the field of surface engineering are aimed at the development of technology of forming layers and coatings which are functional, that is designated to carry out certain functions in the process of service, e.g. reduction of friction, reduction of the effect of thermal shock, enhancement of corrosion resistance, etc. [17-19]. Among the latest solutions in this field are the hybrid technologies which allow the possibility of adapting machine components and tooling to work in very adverse conditions, by the formation of multi-component, multi-layered and gradient coatings, etc. [20-22].

The subject of the research in this paper was to assess the possibility of increasing the durability of tools, e.g. disc-cutters for cutting rubber, by the application of hybrid technology.

The appearance of the disc-cutter, made from alloy tool steel, as well as a fragment of its cutting blade is shown in Fig. 1. As is common knowledge in the majority of cases, the destruction of material in service conditions is initiated and is concentrated in the surface layer of the material.

Therefore, the study of the working surface of the disc-cutter was carried out, in order to establish the factors, which destroy it during the cutting of rubber [23]. Photographs of the working surface of the disc-cutter, taken after a half-year service time, with the aid of a digital microscope (KEYENCE VHX 1000), as

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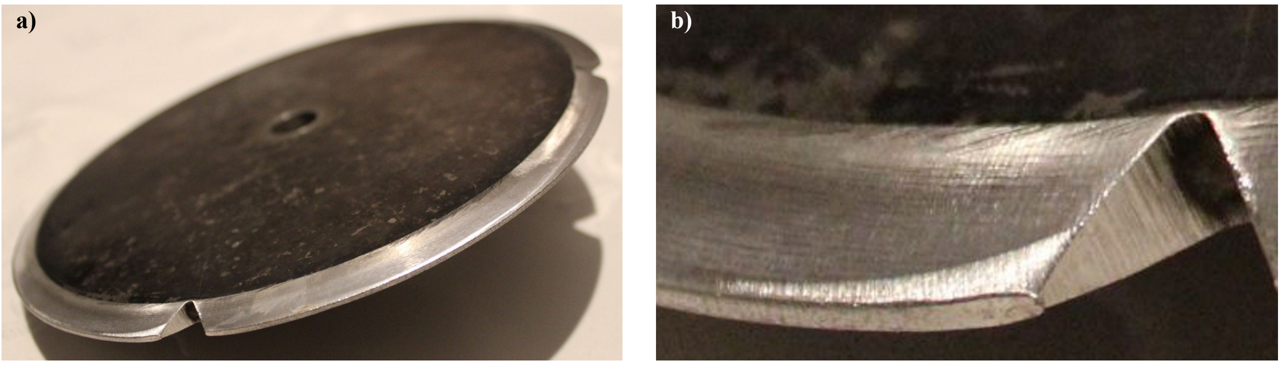

Fig. 1. Disc-cutter for cutting rubber (a) and a fragment of the cutting blade (b)

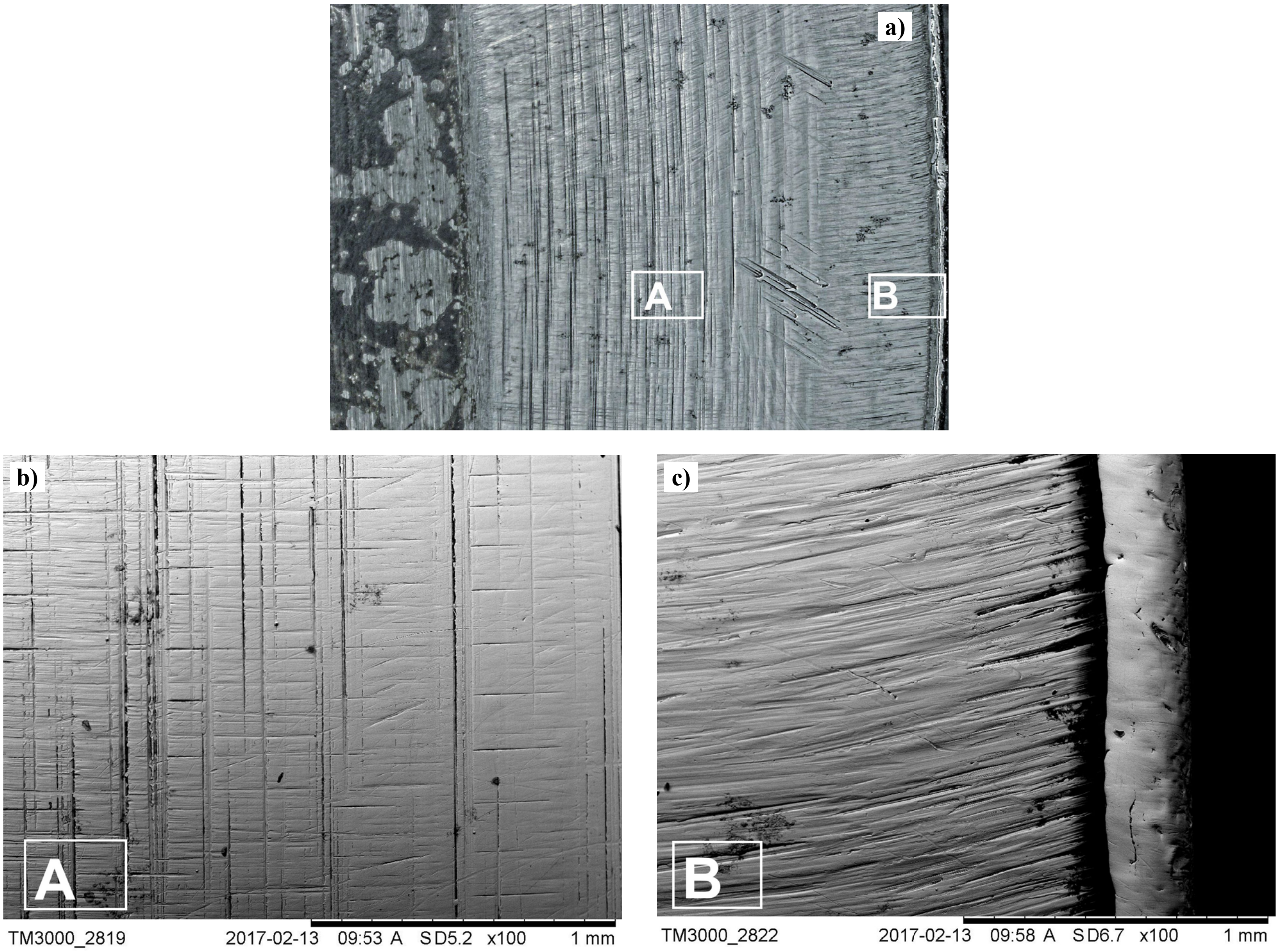

Fig. 2. Appearance of working surface of the disc-cutter for cutting rubber after service (a), with visible scratches (KEYENCE VHX 1000) and scanning electron images (b, c) of marked fragments of the cutter (HITACHI TM 3000), illustrating the mechanism of wear.

well as scanning electron images (made by HITACHI TM 3000) of selected fragments of the surface of the cutter, revealed the presence of a network of scratches, characteristic of the mechanism of abrasive wear by furrowing, as seen in Fig. 2.

The formation of scratches on the working surface of the cutter during the cutting of rubber causes a deterioration of the quality of that cutter and, in consequence, disqualifies it from further service. Based on obtained results of investigations it is possible to assume that the main destructive factor in this case is tribological wear. The second factor causing destruction of disc-cutters, following a long time of service, is corrosion because in the process of cutting rubber, the tool is sprayed by cold water to counteract the excessive heat.

Especially good tribological properties are exhibited by coatings composed of the CrN chromium nitride, whose hardness is in the range of 2000÷2400 HV, [20]. The field of application of CrN as anti-wear coatings includes cutting tools for cutting colored metals (e.g. copper alloys), tools for cold forming, as well as forming tools used in the manufacture of plastics and pressure die castings of aluminum alloys [12,18,24]. At the same time coatings made of chromium nitride exhibit high corrosion resistance, as well as resistance to brittle fracture [25].

Chromium nitride belongs to the PVD coatings group, of which the technology of its formation by the Arc Evaporation method is known and well controlled [26,27].

Also well known is the technology of formation of hybrid coatings of the CrC/CrN type which, besides exhibiting very good tribological and anti-corrosion properties, are characterized by very good adhesion to the steel substrate [4,12].

The Cr/CrN hybrid coatings, obtained by the Arc PVD deposition of a CrN coating on the surface of the chromium coating, consisted of two separate sub-zones: the first (outer sub-zone), containing the CrN nitride, and the second (inner sub-zone), containing chromium, sandwiched between the CrN coating and the tool steel substrate [12,28,29]. A direct effect on good adhesion of these hybrid coatings to the steel substrate is exerted by the thin chromium coating deposited on its surface, prior to the deposition of chromium nitride [18,28].

Investigations pertaining to hybrid coatings of the Cr/CrN type, composed of chromium and chromium nitride, have been conducted by Bayon et al. [28-30].

The article discusses the results of the investigation of mechanical, tribological and corrosion resistance of the Cr/CrN type hybrid coatings produced by Arc PVD on the surface of steel. The investigations were carried out for alloy tool steel of the X210Cr12 grade, used, among others, for disc-cutters for cutting rubber.

2. Experimental procedure

The Cr/CrN hybrid coatings, consisting of chromium and chromium nitride, were formed on samples made from alloy tool steel of the X210Cr12 grade (containing 1.90% C, 12% Cr). The hybrid coating deposition process was carried out by means of the arc-evaporation method (Arc PVD), utilizing a Standard 1 device at the Institute for Sustainable Technologies – NRI in Radom.

The vacuum chamber of the equipment had 3 sources of arc, a modern power system, a system of polarization of the substrate, as well as a system monitoring of substrate temperature and of pressure of process gases. For the formation of Cr and CrN coatings, arc sources with pure chromium cathodes were used.

Prior to the beginning of each process, the samples, placed inside the vacuum chamber, were initially preheated with the help of resistance heaters to a temperature of T ≈ 300°C, under a pressure of $p = 5.0\times10^{-5}$ mbar. The surfaces of steel samples were cleaned by etching, first by argon ions, and next by chromium ions.

The process of deposition of the Cr/CrN type hybrid coating was started by the deposition of a thin coating of chromium, of a thickness below 1 μm, which served to enhance its adhesion to the steel substrate. Next, the chromium nitride coating was deposited. The processes were carried out employing technological parameters given in Table 1.

TABLE 1

Parameters of the chromium and chromium nitride deposition processes

Type of process	Substrate temperature T [°C]	Substrate polarization voltage U_{BIAS} [V]	Pressure p [Pa]	Atmosphere
Heating	300	—	$<1\times10^{-3}$	—
Etching by Ar ions	300	–300	5.0×10^{-1}	Ar
Etching by Cr ions	400	–300	5.0×10^{-1}	Ar
Deposition of Cr	400	–50	5.0×10^{-1}	Ar
Deposition of CrN	380	–150	3.5	N_2

3. Methods of investigation

In order to analyze the structure and surface morphology of the Cr/CrN type hybrid coatings, microscopic observations were carried out by scanning electron microscopy. Investigations of structure were carried out on polished metallographic cross-sections of steel samples with coatings. The X-ray phase analysis was carried out with the aid of a Philips PW-1710 diffractometer operated at 40 kV and 40 mA with CuKα X-rays.

Scanning electron microscope studies of hybrid coatings, in conjunction with the analysis of chemical composition in micro-areas was carried out with the aid of a Hitachi TM-3000 scanning electron microscope, equipped with a BSE detector and an X-ray spectrometer with EDS.

Hardness and Young's modulus of investigated hybrid coatings were measured by means of the nanoindentation method, employing the Nano-Hardness Tester of CSM Instruments. Measurements were carried out with the Berkovich indenter using the following parameters: $F = 10$ mN, $dF/dt = 20$ mN/min.

The testing of adhesion of coatings to steel substrate was carried out using a scratch test made with REVETEST tester from CSM. This tester is equipped with a measuring head with a Rockwell indenter, an optical microscope with high resolution video imaging system, a sensor of acoustic emission, a penetration depth sensor, as well as a sensor of friction and normal forces. The scratch test was carried out using load forces from 0 to 200 N, increasing at a rate of 100 N/min. The rest of process parameters like normal force range, scratch length or sensitivity of acoustic emission system, were selected during examinations.

The tribological tests were performed using the ball-on-disc tribometer designed by DUCOM Instruments with a Al_2O_3 ceramic ball of 6 mm diameter according to the following parameters: ball load forces $F = 10$ N, sliding distance $s = 100$ m, and velocity $V = 0.2$ m/s. During the tests, the friction coefficient was measured. After the tests, the wear tracks were analyzed with the use of an MG140 confocal profilometer by DUCOM and Surface Imaging & Metrology Software Mountains Map 7.0. Based on the volume of removed coating material, the wear index W was calculated, according to the following formula (1):

$$W = V/(F \times s) \tag{1}$$

where V – volume of removed material [mm^3], F – ball load force [N], and s – length of wear track [km],

Electrochemical corrosion measurements of steel samples with hybrid coatings were performed in 0.5 M NaCl solution at a temperature of 24°C. The solution was open to air. The exposed area of the sample was 1 cm^2. Potentiometric testing was employed to determine the time dependencies of the open circuit potential of the samples in the corrosive solution.

4. Results and discussion

4a. Characterization of hybrid coatings

X-ray phase analysis of tool steel with a Cr/CrN hybrid coating, consisting of chromium and chromium nitride, exhibited the presence of Cr, CrN nitride with a body centered cubic lattice, and traces of the Cr_2N nitride with a hexagonal lattice. Additionally, the analysis detected the presence of Fe iron which constitute a component of the steel in which the coating was deposited (Fig. 3). Similar results of X-ray phase analysis were obtained in other reports [3,4].

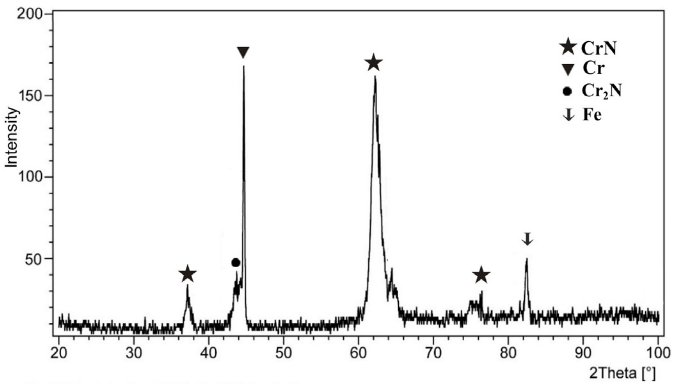

Fig. 3. X-ray diffraction pattern (CuKα) of the X210Cr12 steel surface with the Cr/CrN type hybrid coating

An analysis of surface morphology of a sample with a hybrid coating, carried out with the help of scanning electron microscope (Hitachi TM-3000), revealed the presence of a homogenous, very fine microstructure with a small amount of a droplet phase, characteristic of the Arc PVD method [4]. Similar scanning electron microscope images of the surface of CrN coatings were also observed in other papers [19-22], (Fig. 4).

Scanning electron microscope images (SEM+BSE+EDS) of tool steel with a hybrid coating, obtained on metallographic cross-sections, are shown by Figs 5 and 6. The dark gray Cr/CrN hybrid coating, of about 4 μm thickness, adheres uniformly to the steel substrate.

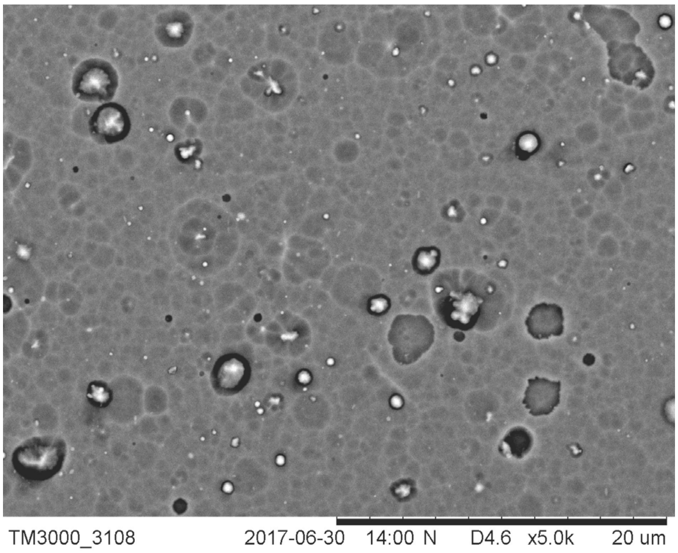

Fig. 4. The SEM image of the surface of the tool steel sample with the Cr/CrN hybrid coating

The Cr/CrN hybrid coating, obtained by Arc PVD deposition of a CrN coating on the surface of the chromium coating, consisted of two separate sub-zones: the first (outer sub-zone), containing the CrN nitride, and the second (inner sub-zone), of a thickness below 1 μm, containing the chromium, sandwiched between the CrN coating and the tool steel substrate. However, the boundary separating the very thin inner sub-zone of the hybrid coating, containing chromium, from the outer sub-zone, containing the CrN nitride, was not observed.

The boundary between the sub-zones Cr and CrN in the hybrid coating was revealed using a microscope with much higher resolution and higher magnification by Smolik [4]. Similar results were reported in other papers [12,28].

The chromium carbides (gray precipitations) are visible in the steel substrate, constituting the structural component of the X210Cr12 tool steel.

An analysis of elements concentration (chromium and nitrogen) in selected micro-areas of this coating, marked with points 1-3 on Fig. 6, is shown in Table 2.

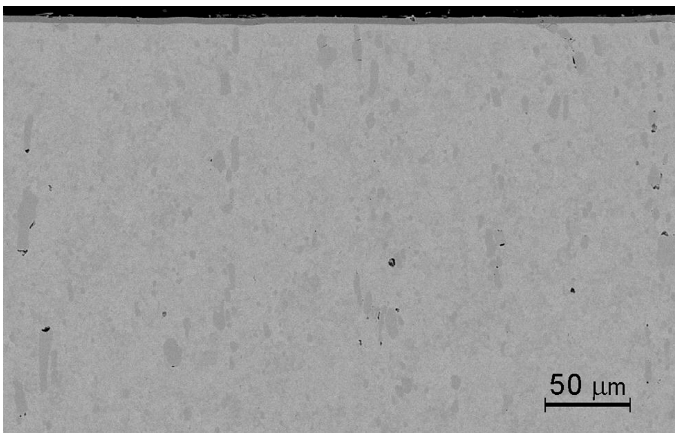

Fig. 5. The SEM image of the X210Cr12 tool steel with the Cr/CrN hybrid coating

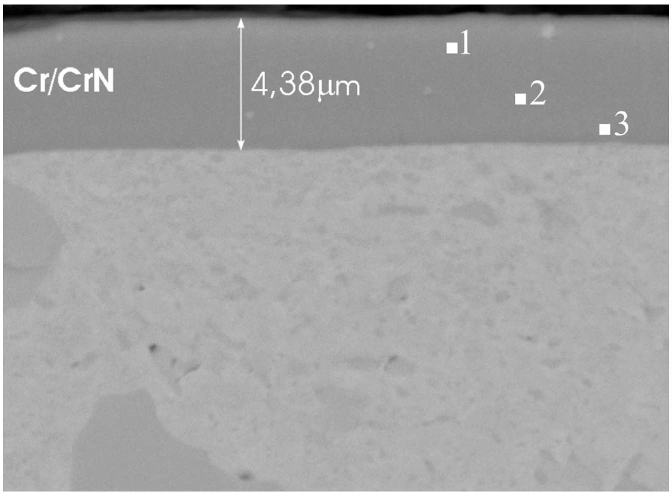

Fig. 6. Scanning electron image (SEM+BSE+EDS) of the Cr/CrN hybrid coating, produced on the surface of the tool steel, with micro-areas of the coating, marked by points 1-3 on the image, analyzed by EDS (Table 2)

TABLE 2

Concentration of elements in micro-areas of the Cr/CrN hybrid coating, marked by points 1-3 on the SEM image, Fig. 6

Chemical composition [weight %]		
Number of the point	**Cr**	**N**
1	68	32
2	64	36
3	73	27

An analysis of the chemical composition shows the presence of the CrN chromium nitride in the hybrid layer, because its main components are nitrogen and chromium (point 1-3 in Fig. 6 and Table 2). An enhanced concentration of chromium (approx. 68 wt.% Cr) relative to the concentration of nitrogen (approx. 32 wt.% N) in point 1 may be caused by the presence of the droplet phase, containing chromium, which is formed at the surface of the CrN coating, obtained by the Arc PVD method, [13-15]. An enhanced concentration of chromium (approx. 73 wt.% Cr) relative to the concentration of nitrogen (approx. 27 wt.% N) near the steel substrate (in point 3) may be caused by the presence of a thin chromium coating, which is deposited on the steel surface prior to the chromium nitride deposition.

4b. Hardness and Young's modulus

Hardness measurements of the Cr/CrN hybrid coatings, characterized by small thickness (about 4 μm) carried out by classical methods, are encumbered with big errors due to the significant effect of the substrate on results. Because of this, measurements of coating hardness and their Young's modulus were made with the help of the Nano-Hardness Tester which enables a selection of test loads from 0.05 to 500 mN, as well as a precise selection of penetration depth of the indenter into the material being tested, eliminating the influence of the substrate on the obtained results. Measurements of hardness and of Young's modulus of the Cr/CrN hybrid coatings were made maintaining the maximum penetration of the indenter within <10% of the coating thickness. Results of measurements are given in Table 3.

TABLE 3

Results of measurements of hardness and Young′s modulus

Coating type	**Thickness g [μm]**	**Hardness H [GPa]**	**Hardness HV [Vickers]**	**Young's modulus E [GPa]**
Cr/CrN	4.38	26 ± 2.8	2475 ± 260	309 ± 38

An analysis of results of the hardness measurements showed that the Cr/CrN hybrid coating is characterized by high hardness, 2475 HV, while its Young's modulus is similar to values determined in other reports pertaining to this type of hybrid coatings [20,21].

4c. Adhesion

The examination of adhesion of coatings to the steel substrate was carried out using a scratch test, with gradual increase of the normal force loading the penetrator which scratches the surface of the sample. Due to the pressure of the indenter, increasing elastic-plastic deformations of the coating arise until the appearance of damages that result from the loss of adhesion or decohesion of this coating. The measure of adhesion was the critical force, i.e. the lowest normal force causing loss of adhesion of the coating with the substrate [31].

To assess the value of the critical force, the record of changes in acoustic emission signals (AE) and tangent force (Ft) and microscopic observations allowing for the location of damage caused by loss of adhesion of the coating with the substrate and the nature of these damages were used.

The effect of the penetrator loading on three different adhesion parameters was analyzed: Fc1, at which first cracks in the tested coating are formed; Fc2, where local adhesion loss of the coating occurs in the area of the scratch and its edge, and Fc3, where the decohesion of the entire coating from the substrate occurs. Three scratches were made on each sample.

Diagram of variations of the tangent force (Ft), acoustic emission signals (AE) and friction factor (μ) in function of load (a) and the SEM images of scratch (b, c, d), obtained during the scratch test of the tool steel samples with the Cr/CrN hybrid coating are shown in Fig. 7. Adhesion parameters determined during the scratch test are given in Table 4.

The first cracks of the Cr/CrN hybrid coating were observed under a load Fc1 = 18 N (Table 4). The local adhesion loss of the coating, occurring in the area of the scratch and its edge, appeared under a load Fc2 = 29 N. The total decohesion of the coating from the substrate came about only under a load Fc3 = 102 N.

The obtained test results show very good adhesion of the hybrid coating to the steel surface. Similar results were obtained in other papers related to chromium nitride base hybrid coatings [4,20].

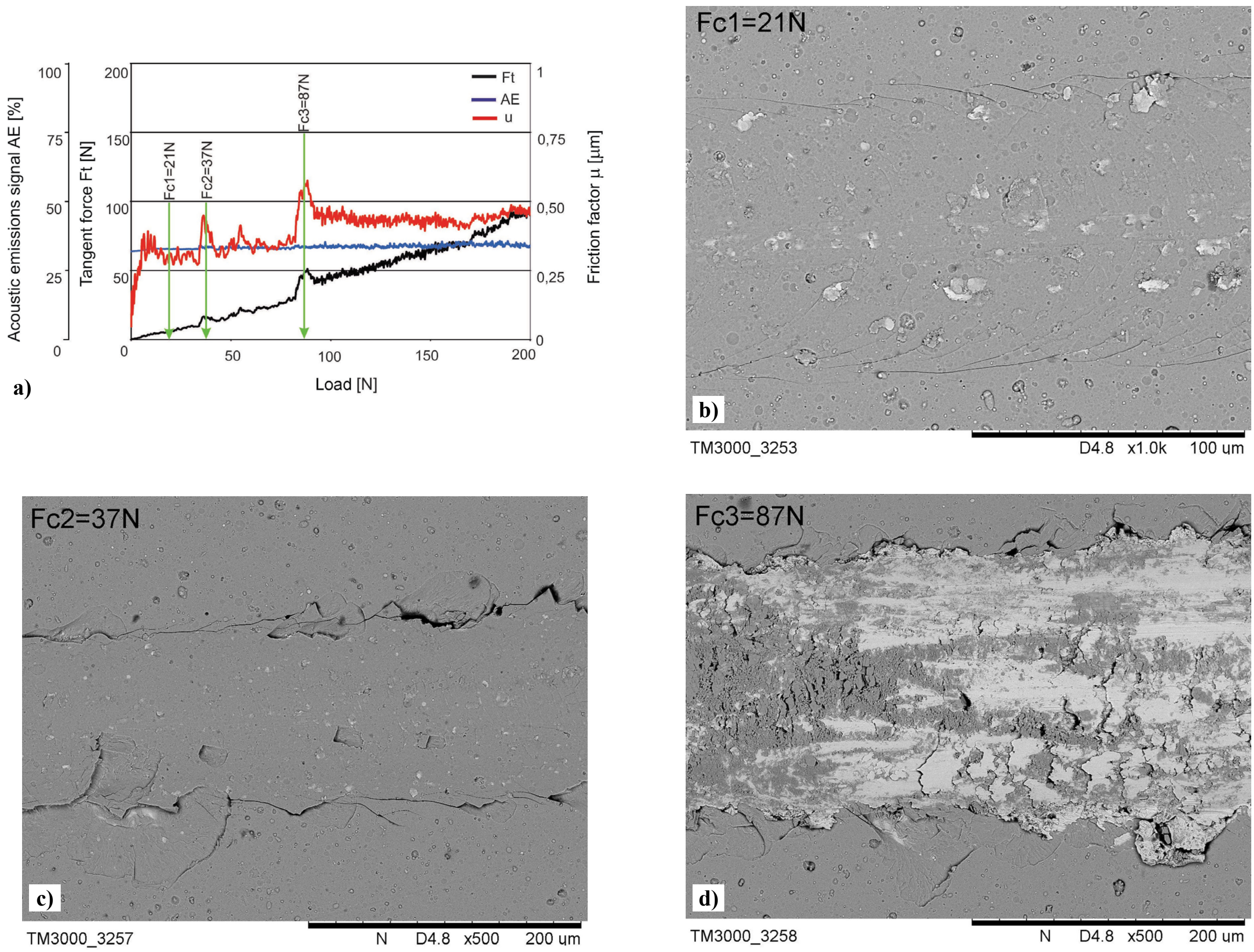

Fig. 7. Diagram of variations of the tangent force (F_t), acoustic emission signals (AE) and friction factor (μ) in function of load (a) and the SEM images of scratch (b, c, d), obtained during scratch test of the steel samples with the Cr/CrN hybrid layer

TABLE 4

Critical load values determined during scratch test of the Cr/CrN hybrid coating

Coating type	Adhesion parameter	Critical load value, [N]			
		Scratch 1	Scratch 2	Scratch 3	Average
Cr/CrN	Fc1	21	20	13	18
	Fc2	37	34	17	29
	Fc3	87	103	116	102

4d. Tribological properties

Tribological properties of samples of tool steel with hybrid coatings were evaluated based on wear resistance tests by the ball-on-disc method. Tribological tests were carried out on samples of X210Cr12 grade steel with Cr/CrN type hybrid coatings, and, for comparison, on samples of the same steel without any coating. The appearance of the wear track on the surface of tested samples (KEYENCE VHX 1000) following the ball-on-disc test, as well as wear profiles for both cases, are shown in Figs. 8 and 9.

An analysis of the appearance of wear tracks on the surface of samples allowed a diverse mechanism of their destruction. The zone of wear of the Cr/CrN coated sample exhibits a uniform surface, as seen in Fig. 8. Within the scratch made on the Cr/CrN hybrid coating one can observe a small damage of the coating, typical of abrasive wear.

On the other hand, an analysis of the appearance of the wear track on the surface of steel without any hybrid coating points to a completely different mechanism of damage of that material in wear tests, as shown in Fig. 9.

Numerous furrows, as well as recesses, characteristic of the mechanism of abrasive wear by furrowing were observed. As a result of this phenomenon, there occurs a significant deterioration at the interface of the mating surfaces, conducive to faster damage of the material.

In accordance with the assumed method of investigation, the maximum depth of the wear track h_{max}, the volume of removed material V_a, as well as wear index W were determined. Table 5 gives the results of the tests, being the average value of the measurements made for three samples.

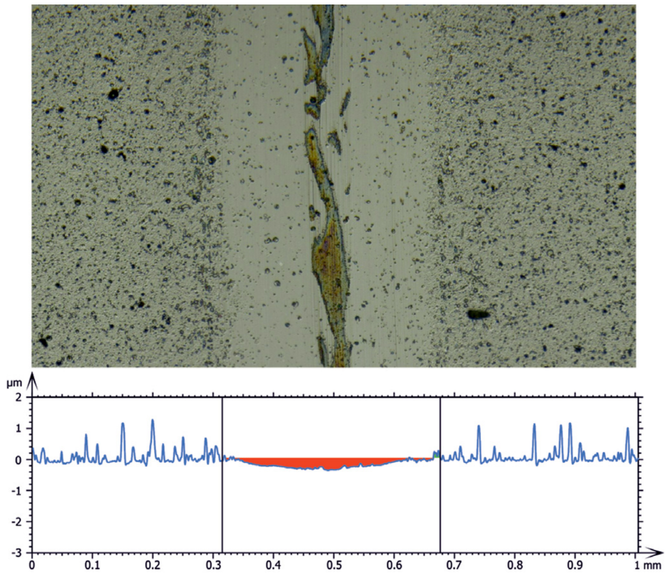

Fig. 8. Appearance of the wear track on the surface of tool steel sample with Cr/CrN hybrid coating after a ball-on-disc test, and the wear profile

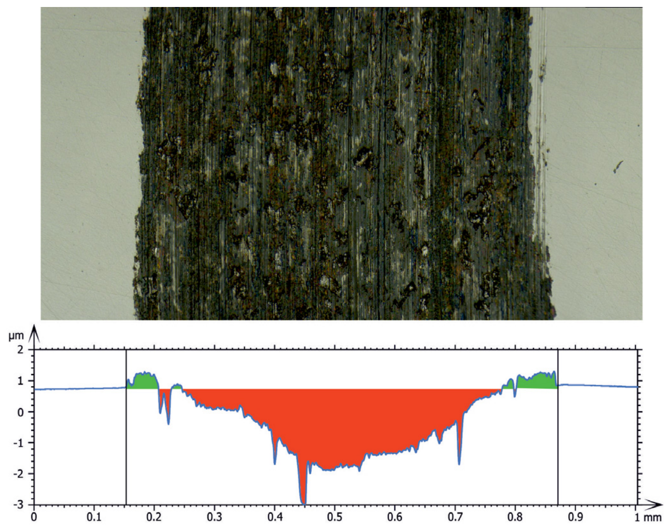

Fig. 9. Appearance of the wear track on the surface of a sample of tool steel without a hybrid coating after a ball-on-disc test, and the wear profile

TABLE 5

Results of tribological tests obtained by the ball-on-disc method

Samples type	**Maximum depth of wear h_{max}, [µm]**	**Average volume of removed material V_a, [mm^3]**	**Wear index W [mm^3/N× km]**
Tool steel with the Cr/CrN coating	0.43	6.50×10^{-4}	1.30×10^{-8}
Tool steel without coating	3.84	6.47×10^{-3}	1.29×10^{-7}

The mean value of the volume of removed material, as well as maximum depth of the wear track for samples with the Cr/CrN hybrid coating were accordingly: $V_a = 6.50\times10^{-4}$ mm^3 and $h_{max} = 0.43$ µm, which indicates low wear of this coating.

In the case of wear of steel samples without the hybrid coating, the mean value of volume of removed material was greater by an order of magnitude and was equal to: $V_a = 6.47\times10^{-3}$ mm^3. Also, the maximum depth of the wear track, which equalled $h_{max} = 3.84$ µm, was almost ten times greater.

The wear index determined for samples made from the X210Cr12 tool steel with the Cr/CrN hybrid coatings, $W = 1.30\times10^{-8}$ mm^3/N×km, indicate that that these samples are ten times more resistant to abrasive wear in comparison with samples of the same steel but without the hybrid coating, for which $W = 1.29\times10^{-7}$ mm^3/N×km.

4d. Corrosion resistance

Corrosion tests were performed on the following samples:

- Cr/CrN hybrid coating on the tool steel surface,
- tool steel, without coating.

Electrochemical studies revealed significant differences in the corrosion behavior of the samples tested. The bare steel samples exhibited very negative potentials below E = - 580 mV. Higher values of the open circuit potential E = - 320 mV were observed for the steel with the Cr/CrN hybrid coating. This indicates a significantly higher corrosion resistance of steel with a hybrid coating. The course of anodic polarization curves confirmed this view, see Fig. 10.

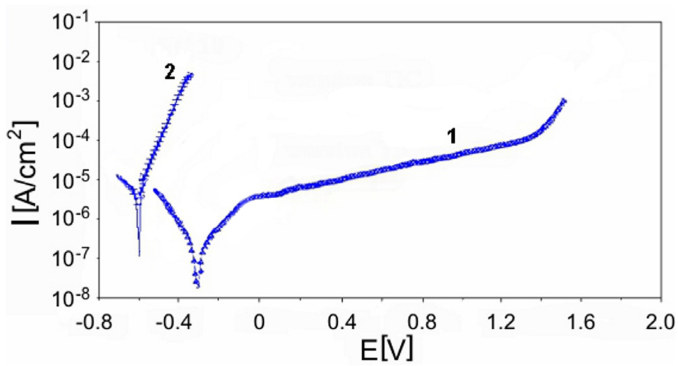

Fig. 10. Anodic polarisation curves of steel samples with the Cr/CrN hybrid coating (curve 1) and of bare steel (curve 2)

The shape of the curves for bare steel (a fast increase in anodic current) indicated an intense active dissolution of the steel samples. The steel samples with hybrid coatings exhibited spontaneous passivation and remained passive in wide ranges of potentials, whereas the steel without coating corroded actively.

5. Conclusions

In the article, basing on an analysis of the wear mechanism of disc cutters for cutting rubber during service, a recommendation is made for the application of the modern hybrid technology known in surface engineering, in order to improve the durability of these cutters.

The subject of the study were hybrid coatings of the Cr/CrN type on the X210Cr12 tool steel, obtained by deposition o a thin chromium coating (of a thickness below 1 μm) on its surface, prior to the deposition of chromium nitride, by the Arc PVD method.

The thickness of the Cr/CrN hybrid coating, containing two separate sub-zones (the outer sub-zone containing the CrN nitride and thin inner sub-zone containing the chromium, adheres to steel substrate) was about 4 μm (see Fig. 6). X-ray phase analysis of the surface of steel sample with the Cr/CrN coating, in conjunction with an analysis of the chemical composition of the coating in selected micro-areas (see Figs. 3 and 6 and Table 2), conducted with the aid of the scanning electron microscope (SEM+BSE+EDS modes), showed that it is composed mainly of chromium nitride and a small quantity of chromium.

The hardness of the Cr/CrN coating and its Young's modulus, evaluated with the aid of the Nano-Hardness Tester amounted to, accordingly $H = 2475$ HV and $E = 309$ GPa (Table 3). Similar results were reported in other papers [3,4,20,29,30], pertaining to this type of hybrid coatings.

Adhesion of the Cr/CrN coatings to the steel substrate, measured by the scratch test, was very good. Total decohesion of the coating was observed only under a load of Fc3 = 102 N (Table 4). A direct positive effect on the good adhesion of the Cr/CrN hybrid coatings to the steel substrate is exerted by the thin chromium coating deposited on its surface, prior to the deposition of chromium nitride [18,28].

Resistance to abrasive wear of samples made from tool steel with Cr/CrN hybrid coatings, evaluated by the ball-on-disc method, turned out to be ten times better than that of steel samples without the hybrid coating. This was indicated by the wear index which for the samples with Cr/CrN hybrid coatings, $W = 1.30\times10^{-8}$ mm^3/N×km, turned out to be smaller by an order of magnitude, than those for the steel without the hybrid coatings, which amounted to W = 1.29×10^{-7} mm^3/N×km (Table 5). This speaks of very good tribological properties of hybrid coatings. Similar results were obtained in other papers [22,27-29].

Electrochemical corrosion tests revealed that the Cr/CrN hybrid coatings applied on tool steel surface could offer an effective protection against corrosion in 0.5 M NaCl. The steel samples with hybrid coatings exhibited spontaneous passivation and remained passive in a wide range of potentials, whereas the steel without a coating corroded actively (Fig. 10).

The hybrid coatings of the Cr/CrN type can therefore be used to improve the durability of steel tools exposed during service to abrasive wear and corrosion in aggressive environments, containing chlorine ions.

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