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Comparison of the PVD coatings

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ABSTRACT

Purpose: of the paper was comparison of the structure, adhesion and wear resistance of the monolayers CrN and TiN PVD coatings deposited onto plasma nitrited X37CrMoV5-1 type hot work tool steel.

Design/methodology/approach: Diffraction and thin film structue were tested with the use of the transmision electron microscopy. The surfaces' thopography and the structure of the PVD coatings were observed on the scanning electron microscopy.The evaluation of the adhesion of coatings to the substrate was made using the scratch test. The wear and friction tests were performed on a pin-on-disc device at the room temperature and at the temperature of 500°C.

Findings: The best wear resistance in both conditions (20°C, 500°C temperature) demonstrate the TiN coating. These test results correspond with the very good adhesion of the coating to the substrate material and its high hardness. The critical load L_{c5} (coating total delamination) lies within the range 86-92 N, depending on the coating type. It was revealed that the coating damage mechanism in the scrtch test commences in all cases with the widespread coating at the edge of the scratch being made and next develops depending on the coating type and location of the originated defects.

Practical implications: The good properties of the plasma nitriding and the PVD coatings make them suitable in various engineering and industrial applications.

Originality/value: The duplex surfaces treatment of the hot work tool steel for tools made for work at the elevated temperature improves their abrasion wear resistance significantly, compared to coatings developed with the PVD process.

Keywords: Thin&thick coatings; Plasma nitriding; Mechanical properties; Wear resistance

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

The recent advances in modern manufacturing technologies demand coating with high wear resitance, mehanical toughness, and tailored coefficent of friction. Speaking, the role of tool surface characteristics on the performance of precission manufacturing processes is well recognized [1-3].

Wear of extrusion dies is an important topic for the aluminum hot work industry. The difficult operating conditions inolve the achievement of the elevated temperatures, elevated pressures, oxidative atmospheres and existence of hard particulates. There have been continuos developments in the area of surface engineering in order to increase the durability of the tools while maintaining their mechanical properties, dimensional tolerance and surface finish of the product. Due the high temperature involved the extrusion dies are generally fabricated from hot work tool steels. The most popular amongst them being the X37CrMoV5-1 steel type, due to its high tougness and resistance to softening [4-6]. Their good toughness and reasonable hardness obtained as a consequence of the tempering treatment at higher temperature. These steel need to be surface treated in order to improve their mechanical and tribological properties, as well as their resistance to thermal crack initiation [7-9].

It is largely accepted that the performance of tools and components in a tribological, corrosive or mechanical loaded environment is mainly determined by the properties ot the near surface coating. It has been documented in the literature that PVD hard coatings provide surfaces with low friction and high wear resistance, in the field of extrusion dies this techniques has some disadvantages. The main point is the large difference in hardness between coating and substrate which reslts in coating failure [10-12]. TiN and CrN coatings have been successfully employed as wear resistance coatings in many fields for their high hardness, low wear coefficient and other good properties. Chromium nitride is one of the most commonly used coating materials for casting, machining and forming applications, due to its excellent wear, hardness and corrosion resistance properties [13,14].

The plasma nitriding is carried out in the broad temperature range (400-590ºC), which makes it possible to obtain varying growth of the surface layers, depending on the process conditions, and also on the chemical composition of the substrate. Deposition of hard wear resistant coatings in the PVD processes features the intensively developed research area in the field of improvement of the service properties of tools made from the hot-work tool steels, like employment of the duplex surface treatment - consisting mostly in combining the plasma nitriding and the PVD processes used successfully for the hot work tool steels [15-19].

The paper present the results of the project focused on the investigation of the structure, mechanical and tribological propertis of CrN and TiN PVD coatings deposited onto plasma nitrited hot work tool steel X37CrMoV5-1 type. Several analitycal methods will provide usefull information to understanding and applying of PVD coatings and plasma nitriding for the improvement of wear resistance of tools made from hot work steels.

2. Materials and research methodology

The monolayers CrN and TiN coating was prepared in BALZERS BAI 730 deposition system by ion plating PVD process at 450˚C and deposited onto X37CrMoV5-1 type hot work steel substrate. The samples were quenched at 1020°C and tempered at 550°C to hardness 55 HRC. After the heat treatment, the samples were ground and polished and the PVD coating was deposited. After the heat treatment the samples were nitrided, the following plasma nitriding (PN) conditions were applied:

- gas composition - 90%N_2+10%H_2,
- surface temperature - 550°C,
- treatment time – 3 h.

After nitiriding the samples were polished to a roughness R_a = 0.08 μm, then the CrN and TiN coatings were deposited.

Diffraction and thin film structure were tested with the use of the JOEL 3010CX transmision electron microscope, at 300 kV bias voltage. The thin films were produced as a result of mechnical thining and further ionic polishing using Gatan apparatus. The surfaces' topography of the investigated PVD coatings was observed on the scaning electron microscope (SEM) ZEISS. The specimens with the notch cut were cooled in liquid nitrogen before breaking in order to observe their structure on transverse fractures on the ZEISS SEM. Detection of secondary electron was used for generation of fracture images with 20 kV bias voltage and 20.000x maximum magnification. The phase composition of the coatings was determined using the X'Pert Philphs diffractometer, using the X-ray radiation with the Cu anode. The measurements were made in the 2Θ angle ranging from 10 to 110°. The distribuation of the concentrations of the elements along the thickness of the coating was determined using the GDOS method – glow discharge optical emission spectrometry, employing a SDP 750A spectrometer made by LECO. The spputering parameters were: cathode voltage 700 V, ion current 25 mA. The evaluation of the adhesion of coatings to the substrate was made using the scratch test with the linearly increasing load, the test were made by the CSEM REVETEST scratch tester. The critical forces at which coating failures appear, called the critical load L_c, were determined basing on the acoustic emission AE registered during the test and microscope observations for five critical forces: L_{c3} – flaking on the scratch edge, L_{c4} – coating partial delamination, L_{c5} – coating total delamination and $L_c(F_t)$ – sudden increase of the scratching force. Obsevation of the demage developed in the scratch test on a scaning electron microscope Opton DSM 940. Wear resistance tests with the pin-on-disc method were carried out on the CSEM THT (High Temperature Tribometer) device at the room temperature and at the temperature of 500˚C. The Al_2O_3 - corundum ball of the 6 mm diameter was used as counter specimen. During the pin-on-disc test carried out at the room temperature and at 500°C the stationary ball was pressed with the load of 7.0 N to the disc rotating in a horizontal plane. The rotational speed of the disc with the specimen was 50 cm/s. The friction coefficient between the ball and disc was measured during the test. The friction radius and number of rotation were changed like:

- 1000 revolutions – 20°C – friction radius –10 mm
- 7500 revolutions – 20°C – friction radius – 13 mm
- 1000 revolutions – 500°C – friction radius – 16 mm
- 7500 revolutions – 500°C – friction radius – 17.5 mm

Examinations of wear traces developed during the pin-on-disc test were made on the scaning microscope. Wear trace profiles were measured on the Taylor – Hobson Form Talysurf 120L laser profilometer in eight directions (every 45°). Hardness tests of the investigated PVD coatings were made using Vickers micro-hardness testing method. The thickness of coatings was determined using the "kalotest" method, measuring the characteristic of the spherical cap crater developed on the surface of the coated specimen tested.

3. Results and discussion

The investigated PVD coatings deposited onto plasma nitrited steel X37CrMoV5-1 type are characterised by a uniform thickness. The TiN coating show a compacted, columnar structure while the CrN coating has a compacted submicrocrystalline structure (Figs. 1, 2). The morphology of the CrN and TiN PVD coatings deposited onto plasma nitrided hot work steel

X37CrMoV5-1 type is characterised by a significant inhomogeneity connected with the occurrence of multiple drop-shaped micro-particles on their surface and also with pits developed by falling out by some of these drops. The presence of these defects was observed in the largest scale in case of CrN coating when the presence in TiN coating was the smallest one (Figs. 3, 4). The results of this investigation correspond with the results of the friction coefficient.

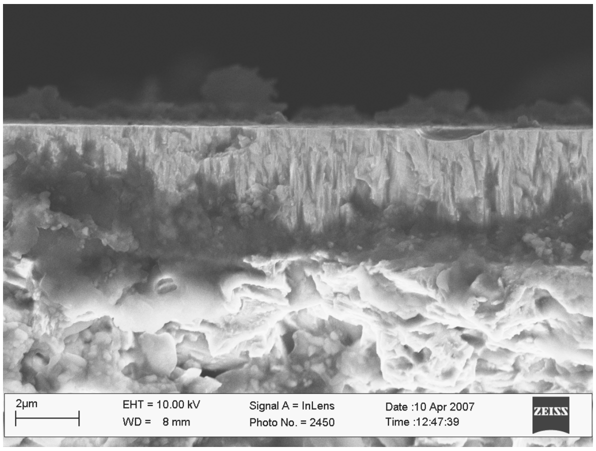

Fig. 1. Fracture of the TiN coating deposited onto plasma nitrited hot work steel X37CrMoV5-1 type

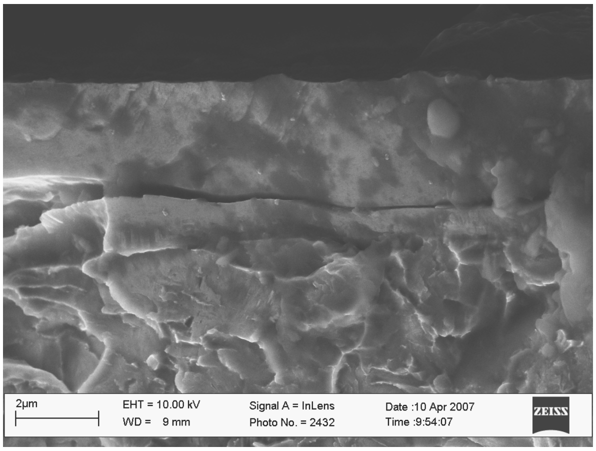

Fig. 2. Fracture of the CrN coating deposited onto plasma nitrited hot work steel X37CrMoV5-1 type

The CrN and TiN monolayers coatings observations in the TEM indicate that such coatings consist of fine crystalites (Fig.5 a-c). Generally, there are no foundations to confirm the epitaxial growth of the investigated coatings.

On the X-ray diffraction patterns for all the investigatd coatings as well as the nitride coating , the appearance of the reflex coming fom substrate material tempered martensite, has been ascertained (Figs.6,7). It develops from a little thickness of the deposited coatings, smaller than the X-rays penetration depth into the material. The CrN and TiN coatings show a privileged crystallographic orientation. In case of PVD coated steel, the indetified reflex come from the nitride coating Fe_3N and Fe_4N.

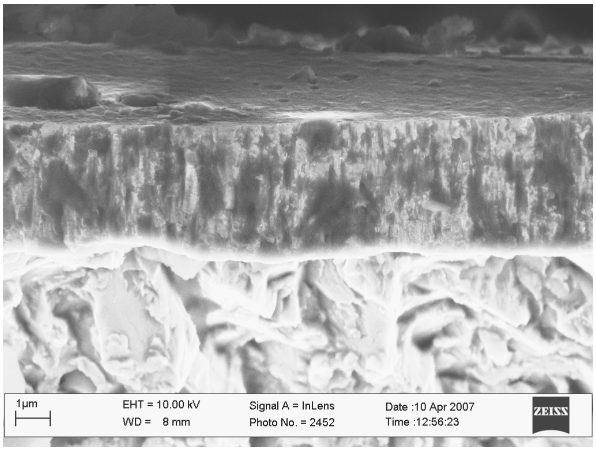

Fig. 3. Fracture and topography of the TiN coating deposited onto plasma nitrited hot work steel X37CrMoV5-1 type

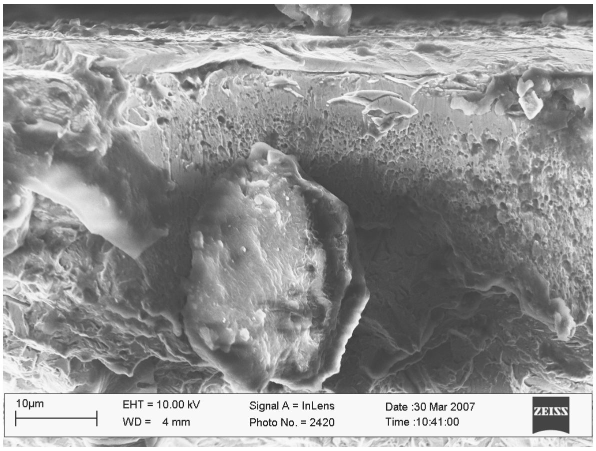

Fig. 4. Topography of the CrN coating deposited onto plasma nitrited hot work steel X37CrMoV5-1 type

The changes of the chemical concentration of the coating constituens and substrate material upon tests carried out on the glow-discharge optical emission spectroscope are present on the Figures 8, 9. These test also indicate the existence of the transistion zone between substrate material and coating, improving adhesion of the deposited coatings to the substrate. In the transistion zone the concentration of elements included in the substrate grows, while the concentration of elements constituting the coatings decreases rapidly. Its dvelopment may also be connected with high-energy ions causing transfer of the elements in the joint zone, increase of desorption of the substrate surface and development of defects in the substrate. Result of the GDOS test correspond with the qualitative linear microanalyze EDS from the cross-section of the investigated coatings (Figs. 10 a-c, 11 a-c).

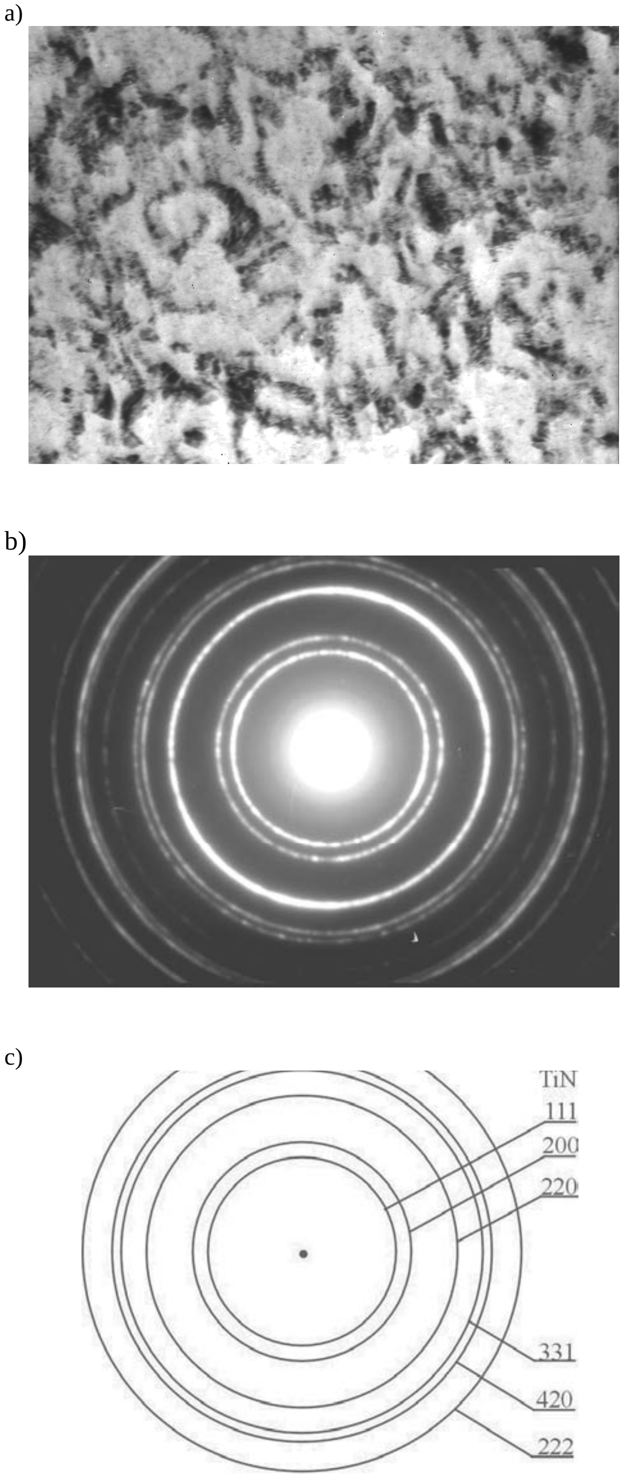

Fig. 5. a) Structure of the thin foil from the TiN coating deposited onto plasma nitrited hot work tool steel X37CrMoV5-1, b) diffraction pattern from the area as in Figure a, c) solution of the diffraction pattern

The microhardness tests of the PVD coatings were carried out at 10 mN load, which ensures the limited indenter penetration depth to eliminate the substrate influence. The highest microhardness of 2927 $HV_{0.001}$ is characteristic of the TiN coating, and the lowest of 2443 $HV_{0.001}$ of the CrN coating.

The critical load values L_c, were determined using the scratch method with the linearly increasing load, characterising adhesion of the investigated PVD coatings to the substrate from the nitrited hot work tool steel (Table 1).

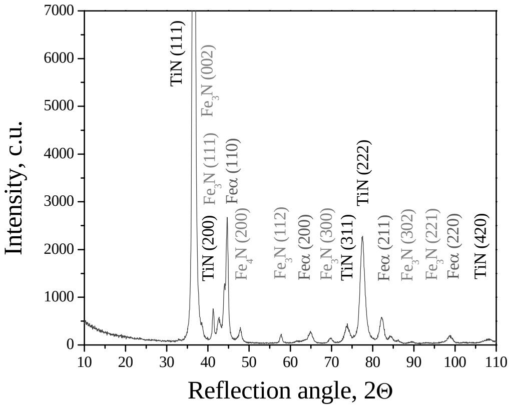

Fig. 6. The X-ray diffraction pattern of the TiN coating deposited onto plasma nitrited X37CrMoV5-1 steel type

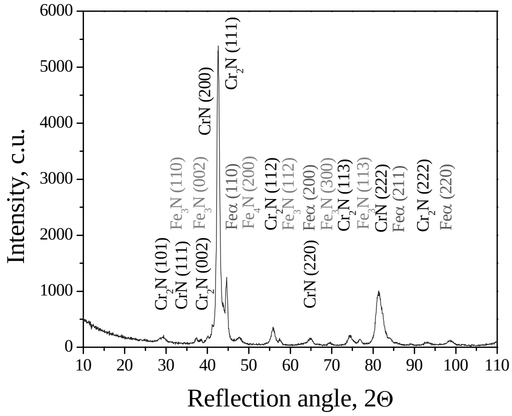

Fig. 7. The X-ray diffraction pattern of the CrN coating deposited onto plasma nitrited X37CrMoV5-1 steel type

Table 1.
Critical loads for TiN and CrN coatings deposited onto plasma nitrited X37CrMoV5-1 type hot work tool steel

Substrate material/coating type	Type of defect/Force [N]				
	L_c(AE)	L_{c3}	L_{c4}	L_{c5}	$L_c(F_t)$
X37CrMoV5-1+PN+CrN	37.00	51.00	70.00	86.00	83.00
X37CrMoV5-1+PN+TiN	44.00	58.00	73.00	92.00	91.00

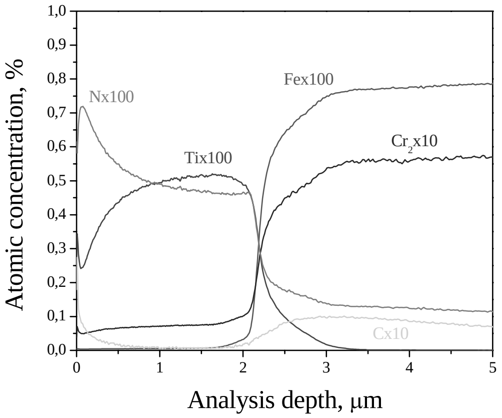

Fig. 8. Concentration changes of components of the TiN coating and its X37CrMoV5-1 substrates

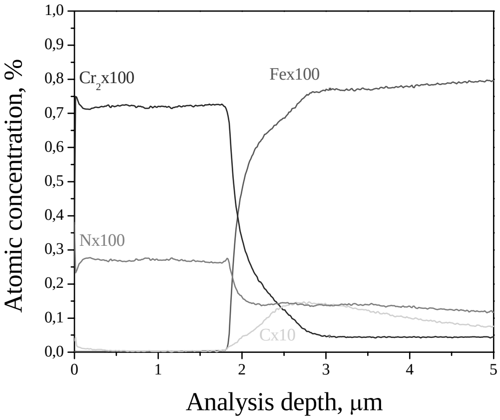

Fig. 9. Concentration changes of components of the CrN coating and its X37CrMoV5-1 substrates

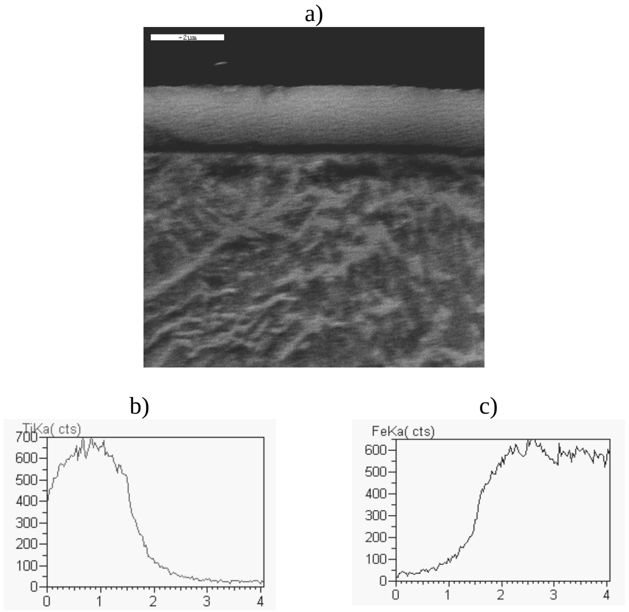

Fig. 10. a) The cross-section of the TiN coating deposited onto plasma nitrited X37CrMoV5-1 steel; linear distribution of elements – b) Ti from coating, c) Fe from substrate material

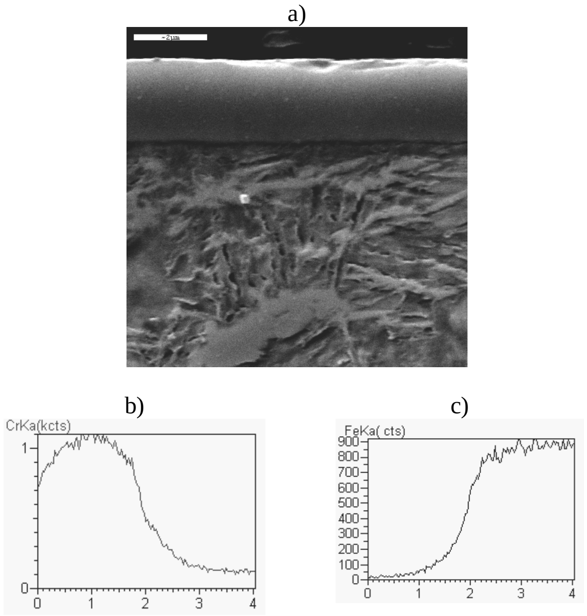

Fig. 11. a) The cross-section of the CrN coating deposited onto plasma nitrited X37CrMoV5-1 steel; linear distribution of elements – b) Cr from coating, c) Fe from substrate material

It has been found out, on the basis of on the determined Lc (AE) values and on the developed failures metallographic examinations that monolayer TiN coating have very good adhesion to the substrate from the nitrided hot work tools steels, whereas the CrN coatings adhesion reaches the lowest value. The damage of the coatings commences in all cases with the widespread coating spallation on both edges of the originating scratch. The difference consists in the location of these spalling defects. In case of the TiN coating, the damage begins (58N) from numerous double-sided chips on the edges of the scratch combined with stretching on its bottom. Next there are flakes and conformal cracks connected with delamination (Fig. 12a). In case of the CrN coating (Fig. 13a) the spalling defects begin at the load value of about 51 N. Next, cracks and coating stretches, develop on the scratch bottom, and finally the total coating delamination on the scratch bottom takes place. In all case L_{c3} corresponds to the first small jump on the accoustic emission signal, as well as on the friction force curve (Figs. 14, 15). The critical load L_{c5} is the point at which complete delamination of the coatings start, after this point all the acoustic emission and friction force signals become noisier (Figs. 14, 15). The employment of the EDS analyser on the scanning microscope will provide usefull information for better understanding of coatings damage mechanism during scratch test (Figs. 12b-c, 13b-c). Results of the investigated PVD coatings adhesion to the substrate from the nitrided hot work tool steel correspond with the results of the wear test.

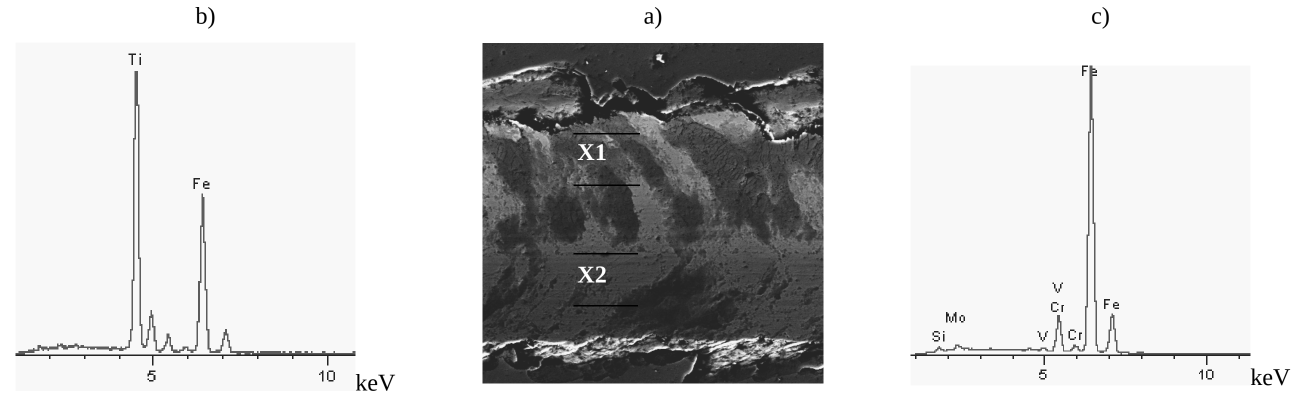

Fig. 12. Scratches with critical load: a) L_{c4} – partial delamination of TiN coating; EDS spectra – b) X1 from areas with coating, c) X2 from areas without coating

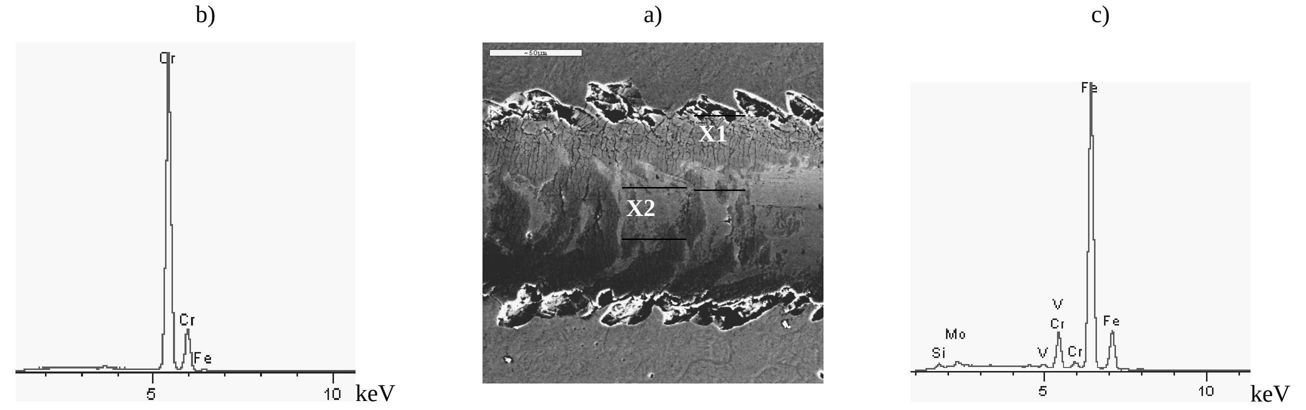

Fig. 13. Scratches with critical load: a) L_{c4} – partial delamination of CrN coating; EDS spectra – b) X1 from areas with coating, c) X2 from areas without coating

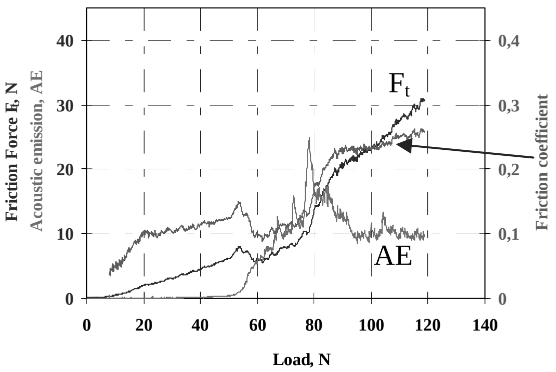

Fig. 14. Diagram of the dependence of the acoustic emission, friction force and friction coefficient on the load for the TiN coating

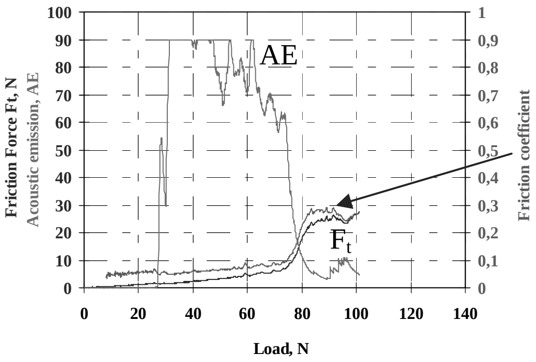

Fig. 15. Diagram of the dependence of the acoustic emission, friction force and friction coefficient on the load for the CrN coating

The investigated coatings were subjected to the pin-on-disc tribological test carried out at room temperature (20˚C) and at the temperature elevated to 500˚C to determine their wear resistance. Changes of the friction coefficient values between the corundum ball and the examined test piece were recorded during the tests at room temperature and at the temperature of 500˚C. The more abrasions that decide about the growth of the value of friction coefficient. The analysis of the friction coefficient value changes of the investigated test pieces makes it possible to state that at the assumed experiment conditions the friction coefficient changes to about 0.4 for the TiN coating and to about 0.6 for the CrN after 1000 test piece revolutions at the room temperature. The friction coefficient values for the coated test pieces are 0.5 for the TiN coating and 0.7 for the CrN one at the same conditions of the test carried out at the temperature of 500˚C. The increase of the test piece number of revolutions to 7500 at room temperature results in the change of values of the friction coefficients. However, one can state that they are close to the values obtained after 1000 revolutions at room temperature and are nearly the same – about 0.85 - for all examined PVD coatings. The friction coefficient changes to 0.5 for the TiN coating and to about 0.65 for the CrN one at the temperature of 500˚C after 7500 revolutions. Only the TiN coating changes slightly its friction coefficient during the entire test period. The low values of the friction coefficient and their stable run are related to the adhesive character of the wear. The coating after the wear test at temperature of 20°C and 1000 and 7500 revolutions has had very little traces of wear. This tendency has also been observed after the test at the 500°C temperature. The arisen in such conditions strips and wear grooves are very shallow. The jumping character of changes of the friction coefficient in case of some coatings may be related to the stripping of the coating as the result of the friction, what next contributes to the fact that the globule starts to rub against the substrate material in these places. This causes the sudden increase of the coefficient of friction which is similar to the value of the substrate material friction coefficient. The quantitative evaluation of the examined test pieces surface wear due to friction was carried out basing on the measurements of the scratch trace profiles on the CrN, TiN coatings put down onto the substrate from the plasma nitrided X37CrMoV5-1 hot work steel in eight directions every 45˚. The measured profiles' data were collected and the average profiles of the scratch trace for each of the examined coatings were determined. The width and depth of the wear were measured for the average profile determined in this way. Moreover, the widths of the wear traces developed during the pin-on-disk test on the examined coatings were measured on the scanning electron microscope (Figs. 16, 17). At the known wear trace width, the average volume of the material removed due to friction of the corundum ball against the test piece surface can be calculated according to the following formula:

$$V = (\pi R D^3)/(6 r) \qquad [mm^3] \qquad (1)$$

where:
V – volume of the material worn out due to friction, R – wear track radius [mm], D – wear track width [mm], r – ball radius [mm]

One can state, basing on the completed wear measurement results of the PVD coatings on the X37CrMoV5-1 nitrided hot work steel (Tables 2, 3), that during the tests at the temperature of 20˚C and 500°C for both 1000 and 7500 revolutions the highest wear resistance was characteristic of the TiN coating.

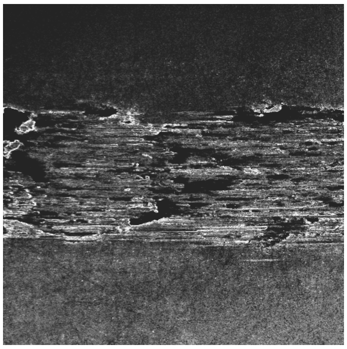

Fig. 16. Wear track on the TiN coating (20˚C, 1000 revolutions)

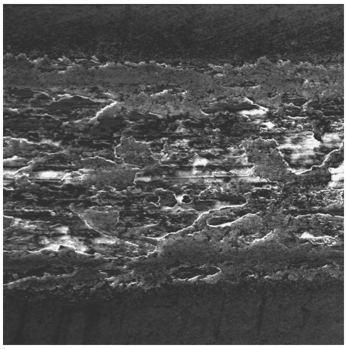

Fig. 17. Wear track on the CrN coating (500˚C, 7500 revolutions)

Table 2.
Comparison of widhts of the wear traces during tribological wear for 1000 and 7500 revolutions

Substrate material/Coating type	Width of the wear traces, [mm]			
	1000 revolutions		7500 revolutions	
	20˚C	500˚C	20˚C	500˚C
X37CrMoV5-1 +PN+CrN	0.24681	0.40848	0.30677	0.62388
X37CrMoV5-1 +PN+TiN	0.17763	0.40079	0.24364	0.59709

Table 3.
Comparison of volume of materials removed during tribological wear for 1000 and 7500 revolutions

Substrate material/Coating type	Volume of materials removed, V [mm^3]			
	1000 revolutions		7500 revolutions	
	20˚C	500˚C	20˚C	500˚C
X37CrMoV5-1 PN+CrN	0.026	0.190	0.065	0.741
X37CrMoV5-1 +PN+TiN	0.009	0.179	0.032	0.649

4. Conclusions

The compacted columnar structure of the TiN coating and the compacted submicrocrystalline structure of the CrN was observed in the scaning electron microscope. Upon examination of the thin foil obtained from TiN and CrN coatings, it was found out that the coatings were composed of fine crystallites.

The scratch test on coating adhesion reveal the cohesive and adhesive properties of teh coatings deposited onto plasma nitrited hot work steel X37CrMoV5-1 type. On the basis of the above exminations, it was founf that the critical load L_{c5} is between 86 and 92N. The highest value of the critical load was obtained for the TiN coating. A very good adhesion of the TiN coating to the plasma nitride steel substrate and its high hardness are connected with the good results of the pin-on-disc tribological test for this coating. The type of the damages of the coating and the substrate, arisen during the scratch test, is similar to the damages and the character of wear during the tribological test. During this test the coatings are worn in the adhesion-abrasive way, and the damage, in most cases, reaches the material substrate. It has been stated that the biggest resistance to the wear resistance at 20 and 500°C temperatures is characterized by the TiN coating, while the smallest resistance shows the CrN coating.

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