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Comparison of the PVD coatings deposited onto plasma nitrited steel

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ABSTRACT

Purpose: The paper presents the structure, mechanical and tribological properties investigation results of the CrN, TiN and TiN/(Ti,Al)N anti-wear PVD coatings deposited onto substrates from the plasma nitrided hot work steel X37CrMoV5-1 type.

Design/methodology/approach: Tests of the coatings' adhesion to the substrate material were made using the scratch test. The surfaces' topography and the structure of the PVD coatings were observed on the scanning electron microscopy. The microhardness tests were made on the dynamic ultra-microhardness tester. Wear resistance tests with the pin-on-disc method were carried out on the CSEM THT (High Temperature Tribometer).

Findings: The duplex coatings demonstrate high hardness and very good adhesion. It was found out that the duplex TiN/(Ti,Al)N coating show the best adhesion to the substrate material.

Practical implications: This investigation is to determine the usefulness of CrN and TiN, TiN/(Ti,Al)N PVD coatings deposition in order to improve the mechanical and tribological properties of hot work steels, particularly X37CrMoV5-1 type one.

Originality/value: The investigation results will provide useful information to applying the duplex and nanostructure PVD coatings for the improvement of mechanical properties of the hot work tool steels. The very hard and antiwear PVD coatings deposited onto hot work tool steel substrate are needed.

Keywords: Thin&thick Coatings; PVD coatings, Duplex coatings; Mechanical properties

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1. Introduction

Metalworking industry has shown interest in improving tools used in hot working process: metal die casting, hot extrusion, hot forging and rolling [1,2,3]. Service life of tools made from hot work steels (among others forging tools, moulds for light metals pressure die casting, rolls for copper hot rolling, mandrels, tools for hot cutting) for the sake their prices is an extremely essential thing in the context of production costs lowering and optimization. One of the most frequently applied method of tool life improvement is PVD technique [4,5,6]. Thin hard PVD coatings are today employed in vast number of applications for reducing friction and wear of tools and mechanical components. PVD coatings have also been used for selected hot-working processes [7,8]. PVD TiN/(Ti,Al)N, CrN and TiN coatings have become important for several industrial applications at elevated temperature. It has been documented in the literature that TiN, CrN and TiN(Ti,Al)N PVD coatings can reduce friction in tribological contacts and increase the abrasive wear resistance. The TiN(Ti,Al)N coating can also provide wear and oxidation resistance, especially at high temperature. However, application of PVD hard coatings to the relatively soft substrate cannot guarantee the optimal tribological performance. The best results in protection of tools made of hot work steel were obtained with duplex treatment procedure. Duplex treatment is combined thermo-chemical treatment of the tool followed by PVD hard coatings deposition. Surface layers obtained in this way display properties characteristic of both types of treatment, ensuring simultaneously the quasi-gradient changes of structure and properties of the surface layers of the hot-work tools [9,10,11]. The thermo-chemical treatment like plasma nitriding provides better mechanical support to the hard and mainly brittle coating. Duplex treatment has proven successful in improving wear, fatigue and corrosion resistance and the load carrying capability of hot work steel substrates [12-15].

The paper presents the results of the project focused on the investigation of the structure, mechanical and tribological properties of CrN, TiN and TiN/(Ti,Al)N PVD coatings deposited onto plasma nitrided hot work steel X37CrMoV5-1 type. Several analytical methods such as an X-ray diffraction (XRD), surface profilometry, scratch test, pin-on-disc test performed in the room and at 500˚C temperatures will be described. The investigation results including SEM and LM as well as mechanical characteristics will provide useful information to understanding and applying of these PVD coatings for the improvement of wear resistance of tools made from hot work steels.

2. Investigation methodology

All coatings were deposited onto X37CrMoV5-1 type hot work steel substrate. The samples in the form of disc (diameter 55mm and thickness 4mm) were quenched at 1020˚C and tempered at 550˚C to hardness 55 HRC. After the thermal treatment, the samples were grounded and polished, another these samples were nitrided, the following plasma nitriding conditions were applied: gas composition - 90%N_2+10%H_2, surface temperature - 550˚C, treatment time - 3h, after nitiriding the samples were polished to a roughness R_a = 0.08 μm, than the PVD coatings were deposited. CrN and TiN coatings were prepared in BALZERS BAI 730 deposition system by ion plating PVD process at 450˚C temperature, while TiN/(Ti,Al)N multilayer coating was deposited by magnetron sputtering in CemeCon apparatus at the temperature 450˚C. The thickness of the investigated coatings measured using the kalotest method are presented in Table 1.

Table 1.
Thickness of investigated coatings

Coating type	Thickness [μm]	Number of layers
CrN	2.23	1
TiN	1.91	1
(TiN/(Ti,Al)N)	1.83	40

The surface roughness of the polished specimens and roughness of the PVD coatings were measured on the Taylor-Hobson Form Talysurf Series 2 profilometer. The parameter R_a was assumed as a quantity describing the surface roughness. Hardness test of the investigated specimens from hot work steel in the heat treated state has been made using Rockwell method. The distribution of microhardness in the nitriding layer was measured using Vickers micro-hardness testing method using a load of 0.981 N. Hardness tests of the investigated PVD coatings were made using Vickers micro-hardness testing method with a load of 10mN which ensures the limited indenter penetration depth to eliminate the substrate influence. The tests were carried out on the Fischerscope micro - hardness tester. The examinations of the microstructure of the nitrided layer were made in the scanning electron microscope (DSM 940 Opton) on the etched crosssections. The surfaces' topography of the investigated PVD coatings was observed on the scaning electron microscope (SEM) Opton DSM 940. The specimens with the notch cut were cooled in liquid nitrogen before breaking in order to observe their structure on transverse fractures on the Opton DSM 940 SEM. The phase composition of the plasma nitrided hot work steel and coatings was determined using the Dron 2.0 diffractometer, using the X-ray radiation with the Co anode. The measurements were made in the 2Θ angle ranging from 10 to 110˚. 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 crytical forces at which coating failures appear, called the critical load L_c, was 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. The character of the defects was determined basing on observation performed on the scanning 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 LEICA MEF4A light microscope at 100x magnification. Wear traces profiles were measured on the Taylor - Hobson Form Talysurf 120L laser profilometer in eight directions (every 45˚).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. Discussion of results

The maximal hardness of the 3h long plasma nitride coating onto the hot work tool steel X37CrMoV5-1 is 1478 $HV_{0.1}$ with the increase of the distance from the surface, microhardness of the investigated nitride coating goes down to 612 $HV_{0.1}$ specific for the core. It has been stated, on the basis of the observation of microstructure of the nitride coating on the scanning microscope, that it is characterized by a homogenous, compact and zonal structure. The results of research done with the method of X-ray phase analysis confirm the occurrence of nitride phases in the structure of surface coating, obtained through plasma nitriding.

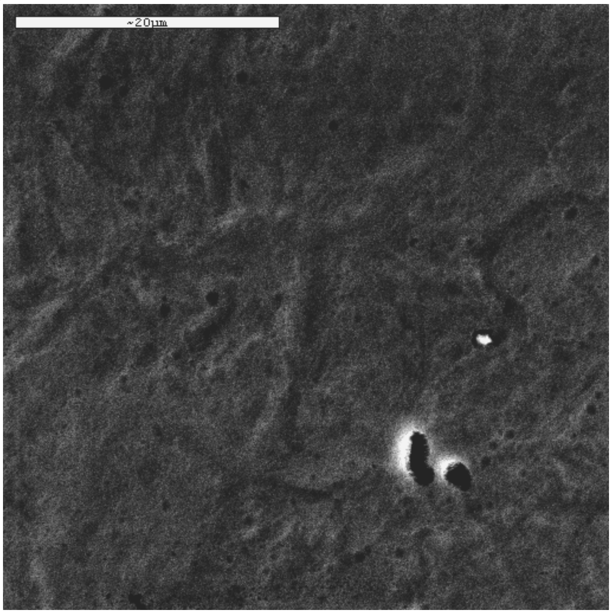
As a result of the metallographic examinations made on the SEM it has been found out that the morphology of the investigated PVD coatings deposited onto plasma nitrided hot work steel X37CrMoV5-1 type is characterised by a significant inhomogeneity connected with the occurrence of multiple drop-shaped 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 TiN and CrN monolayer coatings when the presence in TiN/TiAlN multilayer coating was the smallest one. Most probably the limited presence of defects in case of multilayer TiN/TiAlN coating results from their deposition process conditions. Periodically changing of metallic vapor sources in the PVD process of coatings deposition do not allow to build up micro droplets deposited in the early stage of deposition of each layer as well as hide the pits after their falling out (Fig. 1).

The results of this investigation correspond with the results of roughness and value of the friction coeffiction. Metallographic examinations of coatings fractures show that TiN, TiN/(Ti,Al)N coatings have compacted, columnar structure while the CrN coating has a compacted submicrocrystalline structure. Examinations of the fracture surface of the TiN/(Ti,Al)N coatings indicate their laminar structure. It has been found out that the investigated PVD coatings deposited onto plasma nitrided hot work steel X37CrMoV5-1 type are characterized by a uniform thickness (Fig. 2).

The X-ray phase analysis confirms the occurrence of nitride coating and the TiN, CrN and TiN/(Ti,Al)N coatings onto the examined hot work tool steel. The nitride coatings consist of nitride phases of iron ε-Fe_3N and γ-Fe_4N type (Fig. 3a). On the X-ray diffraction patterns for all the investigated coatings as well as the nitride coating, the appearance of the reflexes coming from substrate material martensite, has been ascertained. It develops from a little thickness of the deposited coating, smaller than the X-rays penetration depth into the material. The single-layer TiN, CrN coating and TiN/(Ti,Al)N multilayers show a privileged crystallographic orientation. In case of PVD coated steels: CrN, TiN and TiN/(Ti,Al)N (Fig. 3b), the identified reflexes come from the nitride coating Fe_3N and Fe_4N.

The roughness of the investigated PVD coatings ranges from 0.101 to 0.319 μm. The results of these measurements correspond with the metallographic examinations made on the SEM. The topography of the coatings influences the roughness, which is characterized by heterogeneity in the forms of cavities and elementary particles as well as a little smoothness of the surfaces of the investigated PVD coatings. The microhardness of the PVD coatings was made using a load 10 mN, making it possible to eliminate, to the greatest extent, the influence of the substrate on the obtained results.

a)



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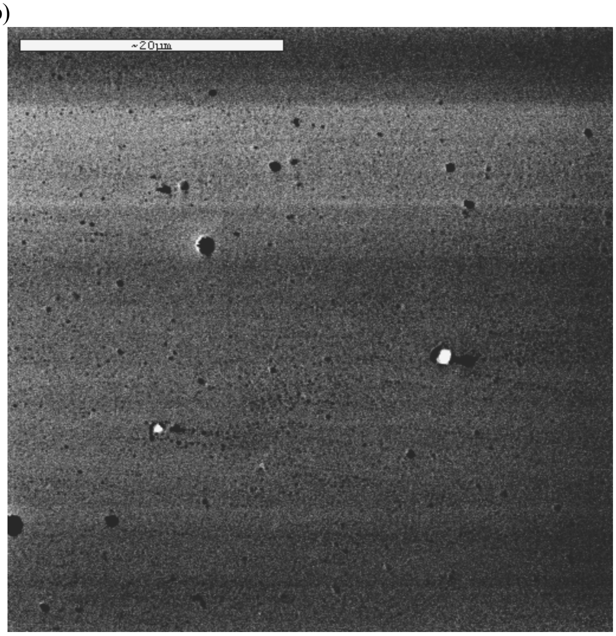
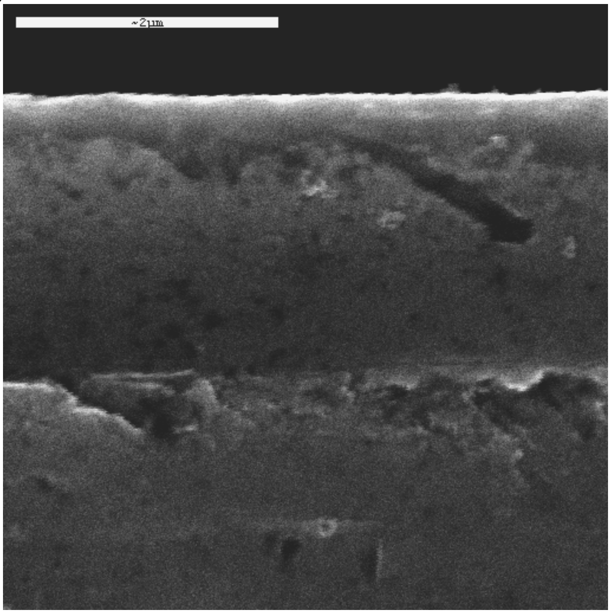


Fig. 1. Topography of the PVD coatings deposited onto plasma nitrided hot work steel X37CrMoV5-1 type: a) CrN coating, b) TiN/(Ti,Al)N coating

a)



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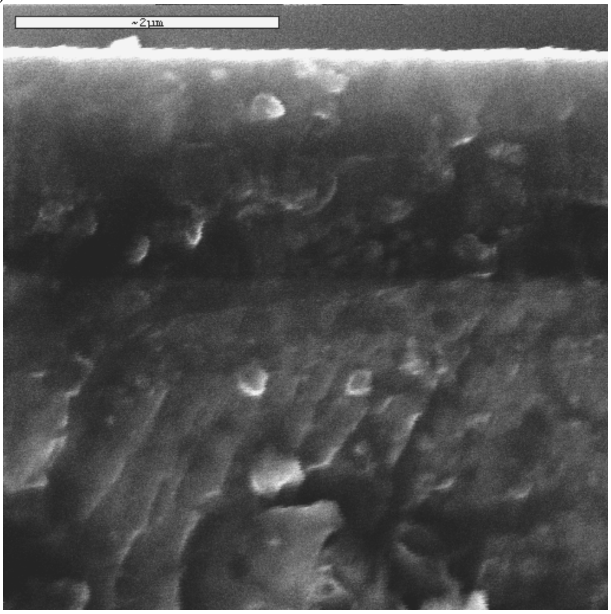
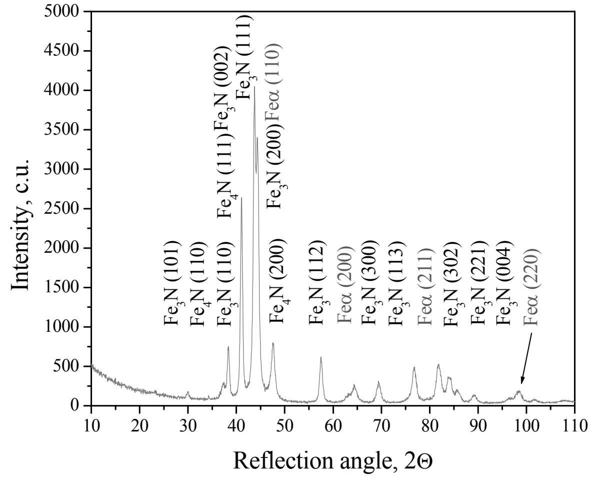


Fig. 2. Fracture of the investigated PVD coatings deposited onto plasma nitrided hot work steel X37CrMoV5-1 type: a) CrN coating, b) TiN/(Ti,Al)N coating

The microhardness ranges from 2443 to 2927HV$_{0.001}$. The results of this investigation can be indicated the correlation between hardness and adhesion of the PVD coatings to the substrate material. The results of the microhardness tests and of the measurements of roughness are presented in Table 2.

The critical load values L_c, that are characterized by the adherence of the investigated PVD coatings to the substrate from the nitrided hot work steel are presented in Table 3.

a)



b)

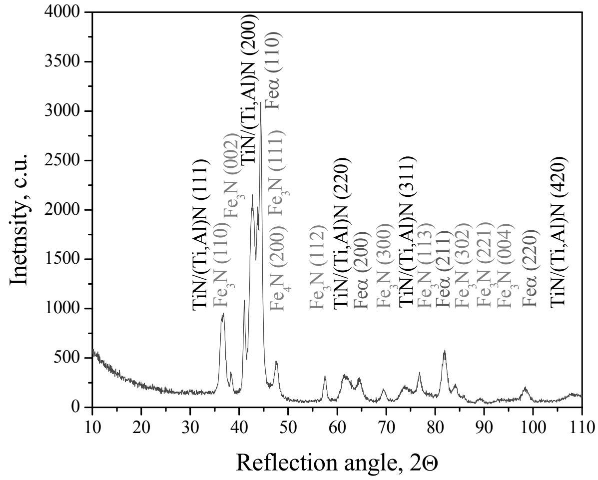


Fig. 3. The X-ray diffraction pattern of the: a) plasma nitrided hot work steel X37CrMoV5-1 type, b) TiN/(Ti,Al)N coatings deposited onto plasma nitirded hot work steel X37CrMoV5-1 type

Table 2.
Summary of the roughness parameter R_a and microhardness of the investigated PVD coatings

Coating type	Roughness, R_a [µm]	Microhardness $HV_{0.001}$
CrN	0.175	2443
TiN	0.319	2927
TiN/(Ti,Al)N	0.101	3354

Table 3.
Critical loads for investigated coatings

Coating type	Type of defect/Force [N]				
	L_c (AE)	L_{c3}	L_{c4}	L_{c5}	L_c (F_t)
CrN	37	51	70	86	83
TiN	44	58	73	92	91
TiN/(Ti,Al)N	56	62	85	110	100

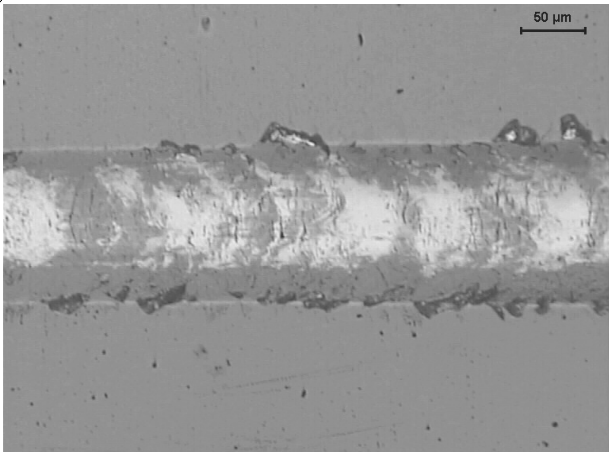
It has been found out, on the basis of on the determined L_c(AE) values and on the developed failures metallographic examinations that multilayer TiN/(Ti,Al)N coatings have very good adhesion to the substrate from the nitrided hot work tools steels, whereas the CrN coatings adhesion reaches the lowest 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/(Ti,Al)N coating (Fig. 4a) the spalling defects begin at the load value of about 62 N. Next, cracks and coating stretches, develop on the scratch bottom, and finally the total coating delamination on the scratch bottom takes place. The employment of the EDS analyser on the scanning microscope has let it to reveal, that in case of the TiN/(Ti,Al)N coating delamination occurs from the initially deposited titanium sublayer. In case of the TiN coating, the damage begins 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. 4b).

The analysis of the test results makes it possible to state that in case of the single-layer CrN coating the numerous spalling defects of the scratch edges begin at load of 51 N (Fig. 4c). Spalling defect at the edge gets deeper and next coating delamination occurs. A weak adhesion of the CrN coating to the substrate may result from its relatively low hardness. As a result of the pressure of the indenter, the plastic deformation of the coating may take place as the softer and more elastic CrN coating undergoes a bigger deformation than the hard, multilayer TiN/(Ti,Al)N coating. Test 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.

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. It has been stated that the friction coefficient of the plasma nitride steel is about 0.5 for 1000 revolutions. The wear has an adhesive character at the temperature of 20°C for 1000 revolutions. At the temperature of 500°C the friction coefficient grows at the beginning, and on the surface there are craters arisen after the removed coating as a result of friction of the ball against the sample surface.

a)



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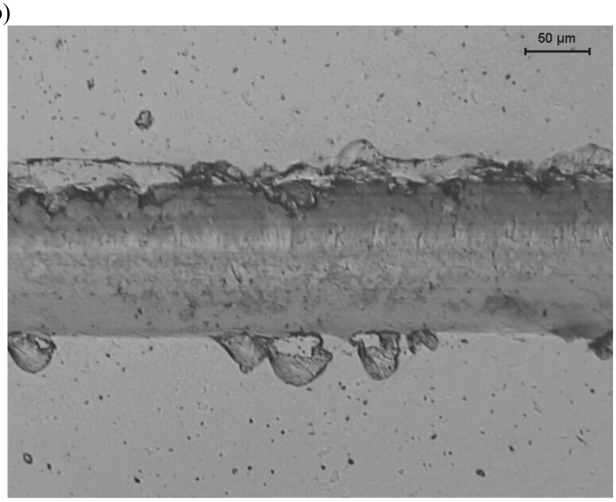

c)

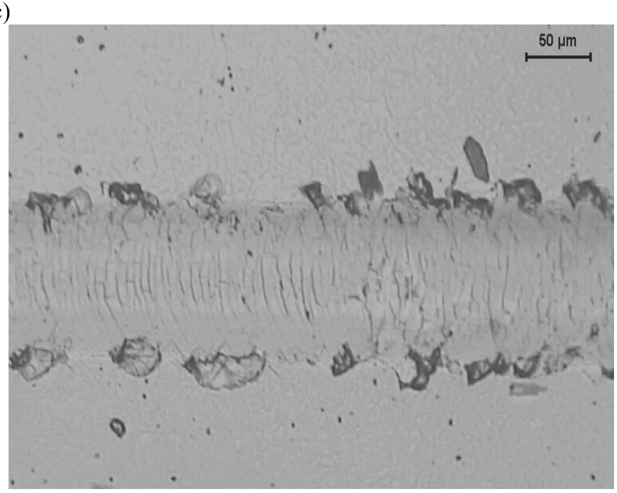

Fig. 4. Scratches with critical load L_{c4} - partial delamination: a) TiN/(Ti,Al)N coating, b) CrN coating,

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. 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:

$V = \pi * R * D^3 / 6 * r$ [mm^3]

where:

V - average volume of the material worn out due to friction,

R - friction radius [mm],

D - wear trace width [mm],

r - ball radius [mm].

It has been noted, on the basis of research done, that the plasma nitrided at 20°C and 500°C temperatures steel underwent the biggest wear. The deposition of the coating significantly increases the wear resistance. One can state, basing on the completed wear measurement results of the PVD coatings on the X37CrMoV5-1 nitrided hot work steel (Tables 4, 5), that during the tests at the temperature of 20˚C for both 1000 and 7500 revolutions the highest wear resistance was characteristic of the TiN/(Ti,Al)N coating. The TiN/(Ti,Al)N coating proved to perform well in the test conditions for 1000 and 7500 revolutions. Therefore, one can state that both at the room and elevated temperatures the multilayer TiN/(Ti,Al)N coating is characteristic of the best wear resistance, with the single layer CrN coating taking the second place. In case of the TiN/(Ti,Al)N coating deposited onto the X37CrMoV5-1 nitrided hot work steel the very good adherence was revealed to the substrate material compared to the CrN coating. On the basis of the research done one can state that the temperature has been a decisive coefficient in the carried out test. There is the biggest material wear at the temperature of 500°C.

Table 4.
Comparsion of volume of materials removed during tribological wear for 1000 revolutions

Substrate material/Coating type	Volume of materials removed V [mm^3]	
	20˚C	500˚C
Plasma nitrided hot work steel X37CrMoV5-1 type	0.26375	0.41216
CrN	0.24681	0.40848
TiN	0.17763	0.40079
TiN/(Ti,Al)N	0.14358	0.30250

Table 5.
Comparsion of volume of materials removed during tribological wear for 7500 revolutions

Substrate material/Coating type	Volume of materials removed V [mm^3]	
	20˚C	500˚C
Plasma nitrided hot work steel X37CrMoV5-1 type	0.31025	0.69655
CrN	0.30677	0.62388
TiN	0.24364	0.59709
TiN/(Ti,Al)N	0.22303	0.47413

The deposition of PVD coatings onto the nitride tool steel, however, considerably improves its anti-wear properties. The nitride coating improves the adhesion of the examined coatings and consequently their anti-wear properties through the decreasing of the friction coefficient. The evaluation results of the volume of material removed during the pin-on-disc test correspond with the wear trace width measurements made by observations carried out on the scanning electron microscope. The wear trace width values measured on the scanning electron microscope grow with the test temperature, regardless of the number of revolutions made by the test piece (Figs. 5, 6, 7).

a) b)

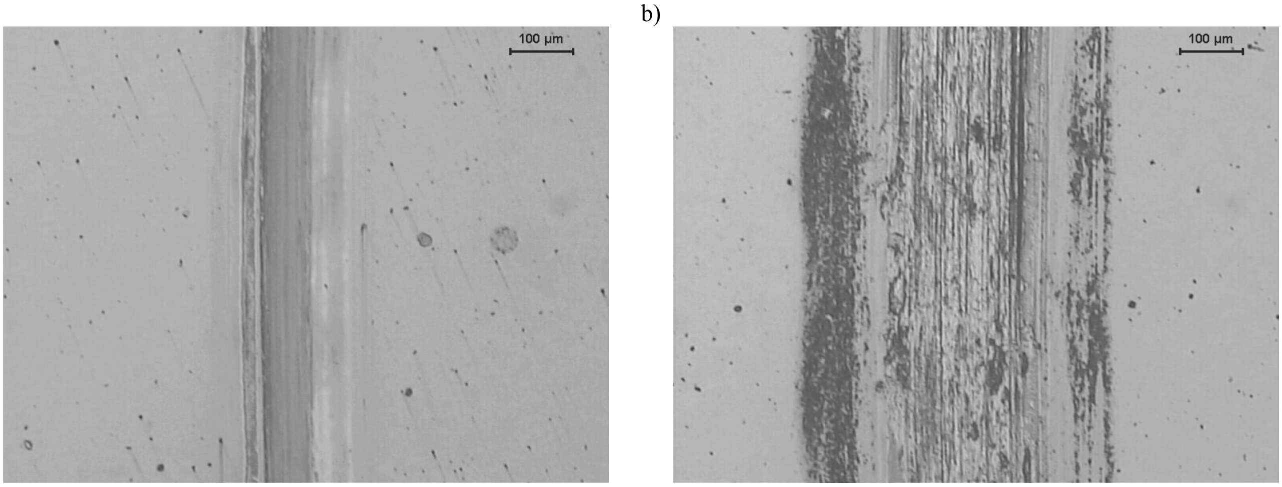

Fig. 5. Microphotography of wear track on the surface of investigated samples for TiN/(Ti,Al)N coating: a) 20°C, b) 500°C; 7500 revolutions

a) b)

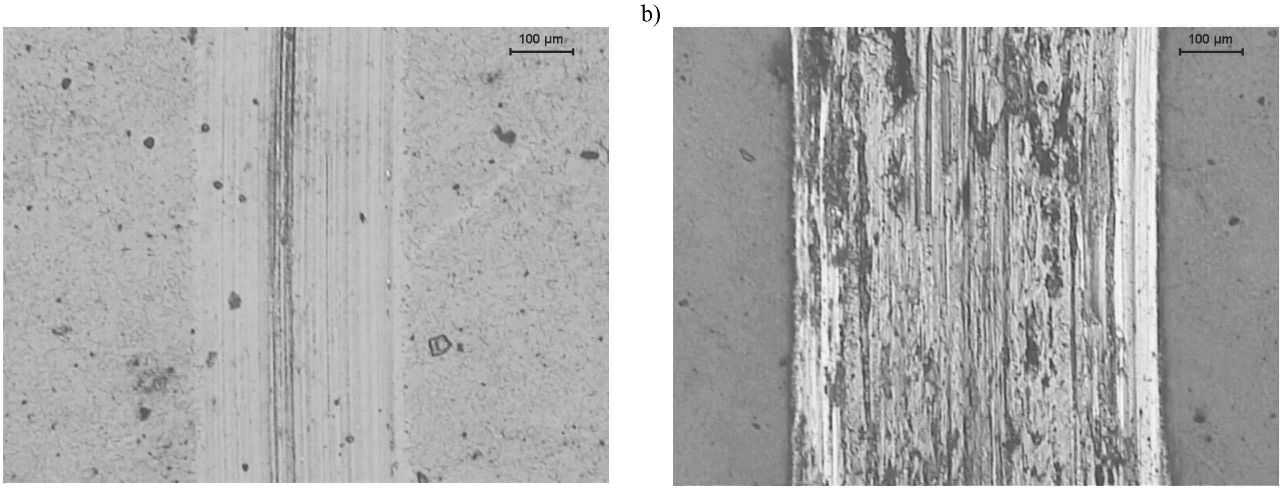

Fig. 6. Microphotography of wear track on the surface of investigated samples for CrN coating: a) 20°C, b) 500°C; 7500 revolutions

a) b)

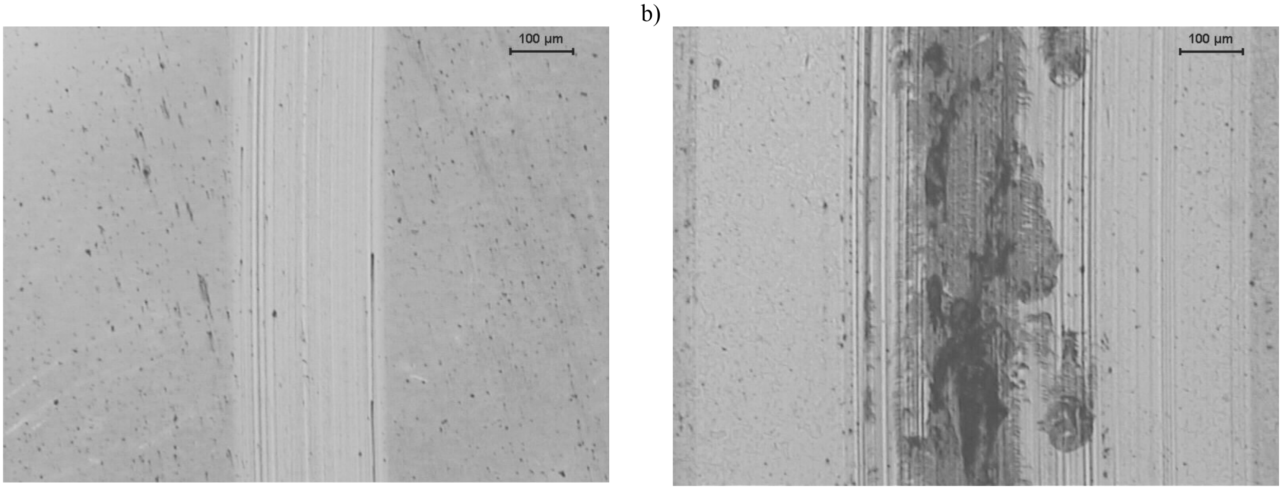

Fig. 7. Microphotography of wear track on the surface of investigated samples for TiN coating: a) 20°C, b) 500°C; 7500 revolutions

4. Conclusions

The deposited PVD coatings onto the plasma nitrided X37CrMoV5-1 steel substrate are characterized by an identical thickness as well as a tight adhesion to the substrate material and a close construction without noticeable discontinuities in the form of delaminations or pores. The structure of TiN and TiN/(Ti,Al)N coatings is columnar while of the CrN coating – fine-crystalline. What decides about the roughness of the PVD coatings deposited onto plasma nitride steel is also the topography of the coatings with heterogeneous surfaces. The roughness of the investigated coatings is between R_a= 0.101-0.31 9 µm for the TiN/(Ti,Al)N and TiN coatings adequately. The TiN coating also shows the biggest heterogeneity of the surface. There is the friction coefficient connected with the roughness which, in turn, influences the resistance wear of the examined coatings. The smaller roughness, the smaller friction coefficient what leads to the increase of resistance wear of the examined coatings. In case of some coatings the friction coefficient is characterized by the jumping course of changes. In case of the plasma nitride coatings the friction coefficient is influenced by the hardness and adhesion of the coatings. With the increase of the hardness of the PVD coatings there is the increase of the wear resistance as well. The hardness of the investigated coatings is between 2443 $HV_{0.001}$ for the CrN coatings and 3354 $HV_{0.001}$ for the TiN/(Ti,Al)N coatings. The hardness of the examined PVD coating correlates with their adhesion to the substrate material. The PVD coatings deposited onto plasma nitride steel show the adhesion (L_c=51-62 N) of the CrN and TiN to the substrate respectively. As regards all the examined PVD coatings the failures begin with the double-sided chippings on the scratch edges and flakes on their bottoms.

These damages appear at different loadings depending on the type of the coating. The increased hardness and resistance of the substrate in the plasma nitride layer contributes to the limitation of the fragmentation of coatings as a result of plastic deformation of the substrate, its conformal cracking, stratification, crumbling and delamination, what finally causes the increase of the adhesion parameters as a consequence of the scratch test. A very good adhesion of the TiN/(Ti,Al)N 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/(Ti,Al)N coating, while the smallest resistance shows the CrN coating.

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Additional information

Selected issues related to this paper are planned to be presented at the 16th International Scientific Conference on Contemporary Achievements in Mechanics, Manufacturing and Materials Science CAM3S'2010 celebrating 65 years of the tradition of Materials Engineering in Silesia, Poland and the 13th International Symposium Materials IMSP'2010, Denizli, Turkey.

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