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STRUCTURE AND PROPERTIES OF PVD COATINGS DEPOSITED ON CERMETS

STRUKTURA I WŁASNOŚCI POWŁOK PVD NANIESIONYCH NA PODŁOŻE Z CERMETALI

The main aim of the research is the investigation of the structure and properties of single-layer and gradient coatings of the type (Ti,Al)N and Ti(C,N) deposited by physical vapour deposition technology (PVD) on the cermets substrate.

The structural investigations include the metallographic analysis on the transmission and scanning electron microscope. Examinations of the chemical compositions of the deposited coatings were carried out using the X-ray energy dispersive spectrograph EDS, and using the X-ray diffractometer. The investigations include also analysis of the mechanical and functional properties of the materials: substrate hardness tests and microhardness tests of the deposited coatings, surface roughness tests, evaluation of the adhesion of the deposited coatings as well as cutting properties.

The results of the investigations carried out confirm the advantages of PVD coatings deposited onto cermets substrate especially in case of (Ti,Al)N. Coatings deposited onto the investigated substrates are characterised by good adhesion, high microhardness, taking effect in very high increasing of wear resistance.

Deposition of hard, thin, gradient coatings on materials surface by PVD method features one of the most intensely developed directions of improvement of the working properties of materials. Equally important is the development of tool materials with respect to the fabrication of thin coatings resistant to wear in PVD process. It is of considerable importance, since through the selection of appropriate components, we can obtain a tool material of better properties. This area of tool material development is a priority nowadays, since it is the main route leading to the acquisition of machining tools of suitable properties.

The results of the investigation provide useful information on microstructure, adhesion characterized in a scratch test, wear resistant properties of the gradient and single-layer coatings deposited onto cermet.

Keywords: Tool materials, Gradient coating, Cermets, PVD

Celem artykułu było zbadanie struktury i właściwości jednowarstwowych i gradientowych powłok typu (Ti,Al)N oraz Ti(C,N) naniesionych metodą fizycznego osadzania z fazy gazowej (PVD) na podłożu z cermetali narzędziowych.

Badania strukturalne obejmują transmisyjną i skaningową mikroskopię elektronową. Analizę składu chemicznego i fazowego badanych powłok wykonano metodą spektroskopii energii rozproszonego promieniowania rentgenowskiego (EDS) oraz metodą dyfrakcji rentgenowskiej za pomocą dyfraktometru rentgenowskiego. Badania obejmują również analizę właściwości mechanicznych i funkcjonalnych badanych materiałów: badanie twardości podłoża z cermetalu i testy mikrotwardości naniesionych powłok, badania chropowatości powierzchni, ocena przyczepności naniesionych powłok, jak również właściwości skrawne.

Wyniki przeprowadzonych badań potwierdzają zalety powłok PVD osadzanych na podłożu z cermetalu, zwłaszcza w przypadku powłok typu (Ti,Al)N. Powłoki osadzone na badanych podłożach charakteryzują się dobrą przyczepnością, wykazują wysoką mikrotwardość, co wpływa na wzrost odporności ściernej.

Istoty jest rozwój materiałów narzędziowych w zakresie wytwarzania cienkich powłok odpornych na zużycie w procesie PVD. Ma to duże znaczenie, ponieważ wykorzystując cechy odpowiednio dobranych składników można uzyskać materiał narzędziowy o lepszych własnościach. Ta dziedzina rozwoju materiałów narzędziowych stanowi w obecnych czasach priorytet, ponieważ jest główną drogą, wiodącą do uzyskania narzędzi skrawających o odpowiednich własnościach.

Wyniki przeprowadzonych badań dostarczają przydatnych informacji na temat mikrostruktury oraz adhezji, odpornych na zużycie gradientowych i jednowarstwowych powłok naniesionych na podłoże z cermetalu.

1. Introduction

Cermets, similarly to sintered carbides, are produced by powder metallurgy methods. These materials are a separate group of tool materials. Cermets are formed from a combination of ceramic particles based on titanium carbide TiC, titanium nitride TiN and elements Ni, Co, Mo, forming a binding phase. Besides the fundamental carbides and nitrides also

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can be applied composite of carbides and nitrides: (Ti,Ta) N, (Ti,Mo) C, (Ti,W) C and (Ti, Ta, W) C [1, 2, 14,16]. Cermets differ from sintered carbides, that in the occurrence of carbides WC, TiC, TiN they also contain nitrides TiN. The concentration of tungsten carbide WC is sometimes comparable with the content of titanium nitride TiN [1,2,17]. In comparison to tungsten carbide, cermets are characterized by a lower density, which is 6-7.5 g/cm^3. Compounds responsible for the hardness of the cermets are mainly titanium carbonitrides with a high concentration of N, as well as titanium carbide TiC and molybdenum carbide Mo_2C. Titanium carbide TiC except increasing the hardness, increases also wear resistance and together with its increment decreases ductility of cermets. The elements of nickel and cobalt used in the binding phase favor a suitable wetting of carbides, providing stable binding of the grains and and adequate ductility. However the concentration of cobalt cannot be too large, because favor increased abrasive wear [1,2,11]. The application of PVD for the acquisition of gradient coatings of high wear resistance, also in high temperatures, enables to improve the properties of these materials in machining conditions, among others by the reduction of friction factor, increase of microhardness, improvement of tribological contact conditions in the contact area tool-machined item it makes it also possible to protect these materials against adhesive or diffusive wear and against oxidation [3-5,7, 10-16]. At the present time, coatings obtained by PVD process are widely used in the sintered tool materials industry. Coatings based on (Ti,Al)N as well as Ti(C,N) were developed to provide better performance over titanium nitride since the incorporation of aluminum or carbon atoms into TiN is conducive to greater hardness and smaller coefficient of friction of the coatings [3-9]. The goal of this work is to investigate and compare the structure and properties of single-layer and gradient coatings of the type (Ti,Al)N and Ti(C,N) deposited by physical vapour deposition technology on the cermets substrates.

2. Methodology of research

The tests were made on specimens of the cermet substrates deposited with single-layer and gradient (Ti,Al)N and Ti(C,N) coatings, using the cathodic arc evaporation method (CAE). The characteristics of the investigated materials are presented in Table 1.

The PVD deposition process of single-layer and gradient (Ti,Al)N and Ti(C,N) coatings was carried out in the Institute of Engineering Materials and Biomaterials of the Silesian University of Technology at Gliwice, on the apparatus DREVA ARC400 of the German Company VTD Vakuumtechnik. The apparatus is equipped with three independent sources of metal vapours. For the deposition of coatings, shields of the diameter of 65 mm cooled with water were applied. The shields contained pure Ti and the alloy TiA1 of 50:50 at. %. The vacuum of 10^{-4} Pa was created in the operating chamber. The coatings were deposited in the atmosphere of inert gas Ar and reactive gases N_2 in order to obtain nitrides, and the mixture of N_2 and C_2H_2 to obtain carbonitride coatings. The gradient concentration change of the chemical composition along the cross-section of the coatings was obtained by changing the dosage proportion of the reactive gases or by changing the intensity of evaporation current of the shield on arc sources. The deposition conditions are summarized in Table 2.

TABLE 1

Characteristics of the investigated materials

Substrate	Coating	Coating thickness, μm	Roughness, R_a, μm	Microhardness, HV	Critical Load, L_c, N	Tool life t, min
Cermet**	uncoated	-	0.06	1850	-	2.5
	(Ti,Al)N	1.5	0.13	2900	54	19.5
	Ti(C,N)	1.5	0.12	2950	42	8.0
	(Ti,Al)N gradient	3.0	0.12	3150	63	22
	Ti(C,N) gradient	2.6	0.11	2950	60	9.5

** phase composition: TiCN, WC, TiC, TaC, Co, Ni

TABLE 2

Coating types and their deposition parameter

Coating type	Arc current source, A	Substrate bias voltage, V	Gas flow rate, cm^3/min			Temperature, °C
			Ar	N_2	C_2H_2	
(Ti,Al)N	TiAl – 80	-150	250	500	-	~300
(Ti,Al)N gradient	TiAl – 80	-150	250	0→250	-	
Ti(C,N)	Ti – 60	-200	80	150	100	
Ti(C,N) gradient	Ti – 60	-200	100	250→0	0→200	

The surface topography and the structure of the deposited coatings was investigated at transverse fractures in the scanning electron microscope SUPRA 35 of Zeiss Company, with the accelerating voltage of 10-20 kV and maximum magnification of 60000x. To obtain the images of the structure, the detection of secondary electrons (SE) and back scattered electrons (BSE) was applied. To obtain a brittle fracture of the investigated specimens, notches were cut into their surface with a diamond shield, and then they were broken up after cooling in liquid nitrogen. To improve the conductivity of the investigated material, the specimens were coated with carbon using the apparatus JEOL JEE 4B.

The qualitative and quantitative analyses of the chemical composition of the investigated coatings were carried out using the X-ray energy dispersive spectroscopy (EDS), with the application of the spectrometer EDS LINK ISIS of Oxford Company, being a component of the scanning electron microscope Zeiss Supra 35. The research studies were carried out with the accelerating voltage of 20 kV.

The diffraction studies and the observations of thin foil structure were carried out in the transmission electron microscope JEM 3010 UHL of JEOL Company, with the accelerating voltage of 300kV and maximum magnification of 300000x. The diffraction patterns from the transmission electron microscope were being solved using the computer program "ElDyf". Thin foils were made in the longitudinal section, cutting out inserts about 0.5 mm thick from the solid specimens, from which discs of the diameter of 3 mm were cut out, using an ultrasonic erosion machine. Then, such discs were subjected to mechanical rubbing down to the thickness of about 90 μm, and a notch of the depth of around 80 μm was then ground down in the discs. Ultimately, the specimens were subjected to ionic thinning out in the apparatus of Gatan Company.

The analysis of phase composition of the substrates and coatings was carried out using the X-ray diffraction method on the X-ray apparatus X'Pert Pro of Panalytical Company, in the Bragg-Brentano system, applying the filtered radiation of cobalt tube at the voltage of 40 kV and filament current of 30 mA. We accepted the step of 0.05° and calculation time of impulses of 10 seconds.

The R_a surface roughness parameter measurements and observations of surfaces topography of the developed coatings were made on LSM 5 PASCAL confocal microscope.

The Vickers microhardness was measured using the Hanemann tester. The tests were made with the load of 0.1 N, making it possible to minimalize the influence of the substrate material on the measurement results. Adhesion evaluation of the coatings on the investigated inserts was made using the scratch test on the CSEM REVETEST device, by moving the diamond penetrator along the examined specimen's surface with the gradually increasing load. The critical load values Lc (AE) were determined using the scratch method with the linearly increasing load ("scratch test"), characterising adhesion of the investigated PVD coatings onto the substrate. The critical load was determined as the one corresponding to the acoustic emission increase signalling beginning of spalling of the coating.

Cutting ability of the investigated materials was determined basing on the technological continuous cutting tests of the EN-GJL-250 grey cast iron with the minimal strength R_m of 250 MPa and hardness of about 210 HB. The VB=0.20 mm width of the wear band on the surface of the tool used for machining was the criterion of the cutting edge consumption evaluation. The following parameters were used in the machining capability experiments: feed rate f=0.1 mm/trn, depth of cut a_p =1 mm, cutting speed v_c =150 m/min. The character of the developed failure was evaluated basing on observations on the light microscope and on the scanning electron microscope and analysis of the chemical composition of the tool wear using the X-ray energy dispersive spectrograph (EDS).

3. Results

The deposited coatings, both single-layer and gradient ones, have a continuous structure. In the case of gradient coatings, the lines separating particular zones of the coating of the chemical composition different from one another were not determined.

It was demonstrated that the coatings are uniformly deposited and are characterized by close adhesion to the substrate, without pores, cracks and discontinuities (Fig. 1).

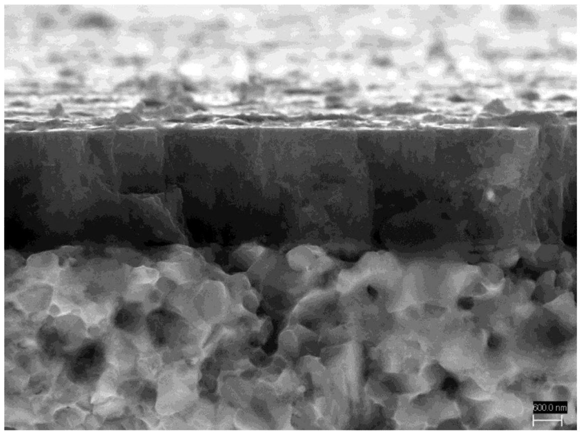

Fig. 1. Fracture surface of the gradient (Ti,Al)N coating deposited onto the cermet substrate

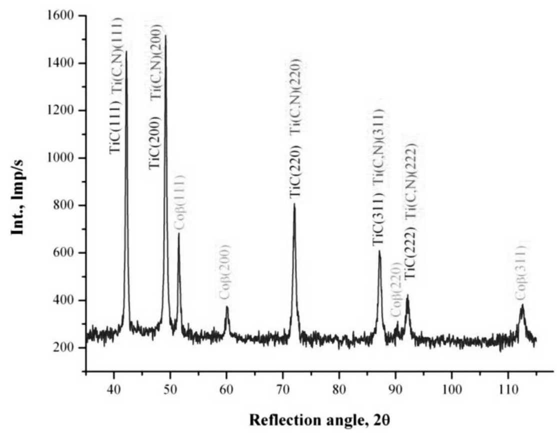

Fig. 2. X-ray phase analysis of the Ti(C,N) coating (Bragg-Brentano geometry)

Through the application of the X-ray qualitative phase analysis, we can confirm that on the substrate from cermets the coatings containing the phases (Ti,Al)N, Ti(C,N) were produced in compliance with the assumptions (Fig. 2). On the X-ray diffractograms obtained with the use of Bragg-Brentano technique, we also determined the presence of the reflexes from the cermet substrate.

The investigated sintered tool materials which is cermet is characterized by a well condensed compact structure without pores (Fig. 3).

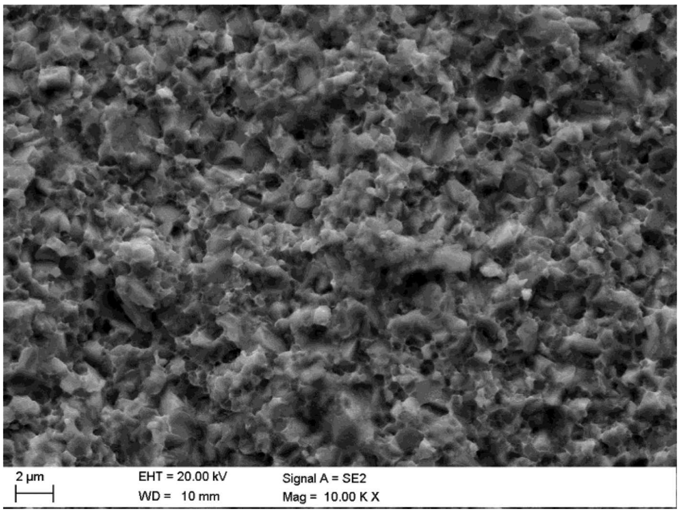

Fig. 3. Structure from the cermet substrate

It was demonstrated, using the X-ray qualitative phase analysis methods, that the cermets substrate occurrences of the Ti(C, N) carbonitride, TiC and WC carbides, and cobalt-nickel matrix were revealed (Fig. 5). It was confirmed, by observations on the scanning electron microscope and analysis of the chemical composition of the substrate fracture surface using the X-ray energy dispersive spectrograph EDS (Figs. 3, 4).

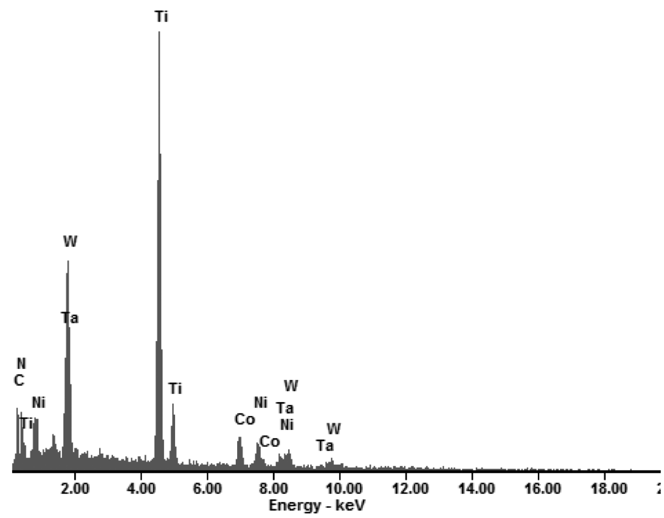

Fig. 4. Plot of the X-ray dispersive energy spectrometer measurement from cermet substrate

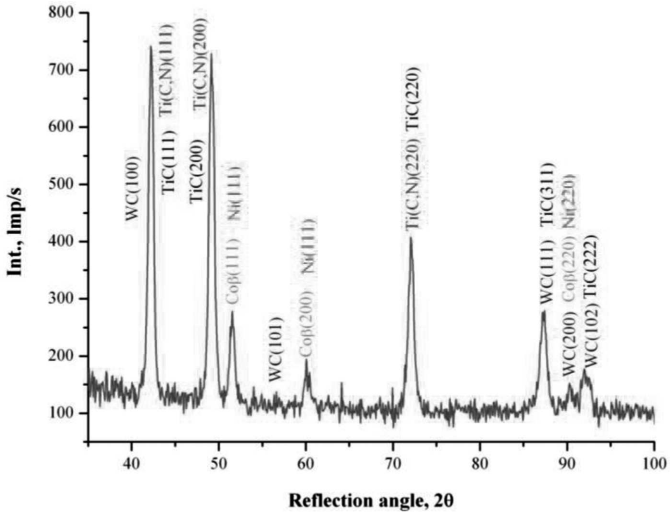

Fig. 5. X-ray phase analysis of the cermets substrate (Bragg-Brentano geometry)

Basing on the diffraction tests and on the studies involving the structure of thin foils carried out in the transmission electron microscope it was demonstrated that in the investigated substrate materials from cermet was identified grains of titanium carbide TiC with regular lattice and tungsten carbide WC (Fig. 6), and between the carbide grains there are areas with crystal structure corresponding to the variation of the allotropic structure of cobalt Coβ with regular lattice (Fig. 7), isomorphic to the crystal lattice of nickel , also present in the matrix cermet. Inside the grains of carbides WC and TiC, there are many defects of the crystalline structure, including dislocations and stacking faults. Some dislocation creates low-angle boundaries separating areas of the carbide grain on the subgrains with small angle disorientation (Figs. 6,7).

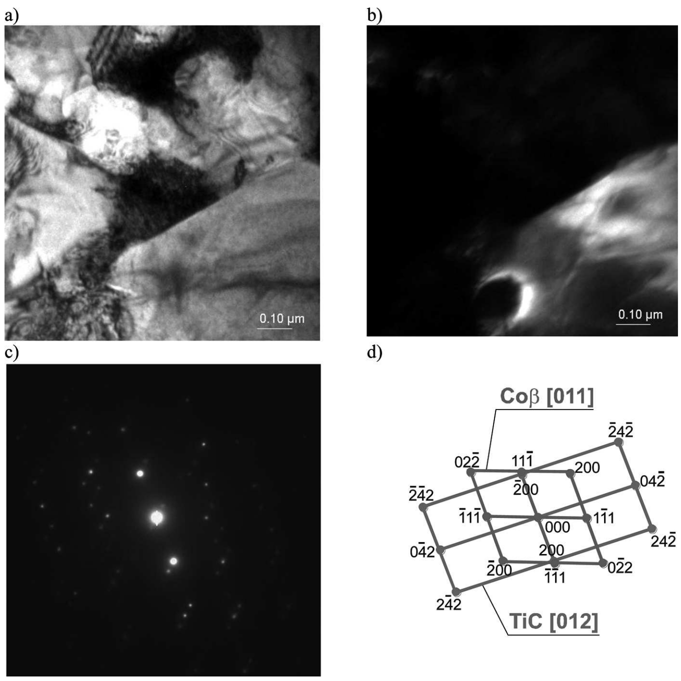

Fig. 6. Structure of cermets substrate: a) bright field; b) dark field from ($\bar{2}00$) TiC and ($11\bar{1}$) Co reflex; c) diffraction pattern from area b and d) solution of the diffraction pattern

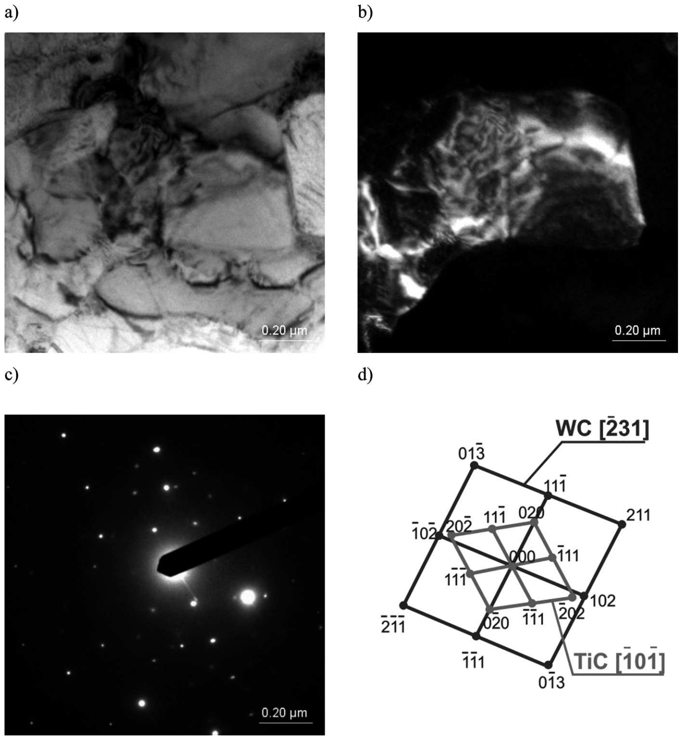

Fig. 7. Structure of cermets substrate: a) bright field; b) dark field from (102) WC and ($\bar{2}$02) TiC reflex; c) diffraction pattern from area b and d) solution of the diffraction pattern

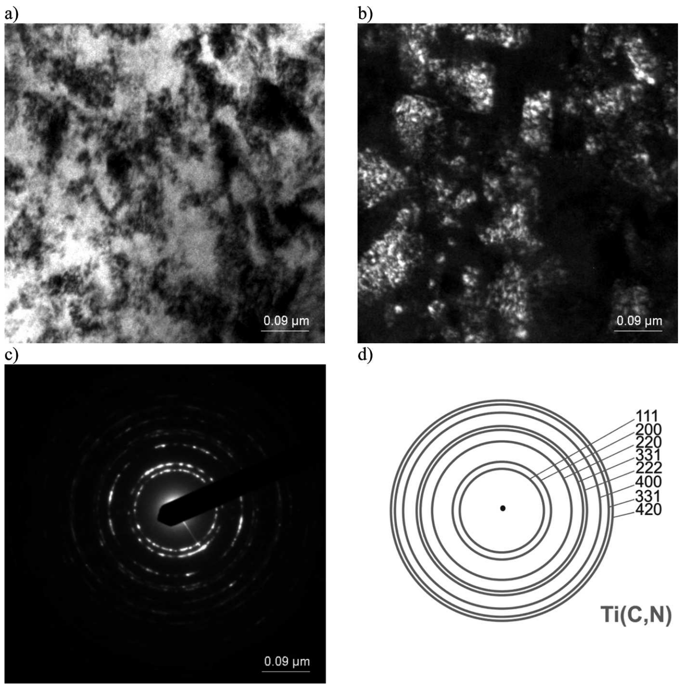

Fig. 8. Structure of gradient Ti(C,N) coating deposited onto the cermet substrates: a) bright field; b) dark field from {111}Ti(C,N) reflex; c) diffraction pattern from area b and d) solution of the diffraction pattern

The results of diffraction tests involving thin foils from the Ti(C,N) coating confirm the occurrence of a phase of the regular crystalline network, in compliance with TiN and Ti(C,N). Due to the isomorphism of phases TiN and Ti(C,N) and the similar value of network parameter, it is not possible to differentiate these phases with the electrons diffraction method. It was also demonstrated, basing on the tests involving thin foils from the (Ti,Al)N coating that this coating contains principally very fine grains of the crystalline structure corresponding to the phase AlN of the regular network (Fig. 8), and also very few grains of the structure and parameters of AlN phase of the hexagonal network. The grains of carbonitrides and of nitrides forming the coating have a very high dislocation density and are very fine – the average grain diameter in the coatings from carbonitrides Ti(C,N) and nitrides (Ti,Al)N does not exceed 0.1 μm (Fig. 8).

Roughness of the cermets substrate defined by R_a parameter is 0.06 μm. Depositing single-layer and gradient coatings of the type (Ti,Al)N and Ti(C,N) onto the examined substrate causes increase of the roughness parameter to R_a =0.13 μm (Table 1).

The hardness of the cermet substrate material is 1850 HV for (Table 1). The deposition of the coatings (Ti,Al)N and Ti(C,N) on the investigated sintered tool materials results in a considerable increase of microhardness in the area around the surface within the range of 2900-3150 HV (Table 1).

Hardness depends on the values of intermetallic bonds, so the hardest materials have covalence bonds, and the increase of the share of ionic character of the bond is associated with the drop of hardness [1]. Basing on the carried out research it was demonstrated that the hardness of Ti(C,N) coatings, in which the metallic phases TiN and TiC occur, demonstrates lower hardness than (Ti,Al)N coatings in which there are both metallic bonds TiN and covalence bonds AlN. The deposition of the wear resistant coatings on the investigated substrates results in a considerable increase of microhardness of the surface layer, which contributes to lower wear intensity of the cutting edge of machining tools from cermets during the machining process.

The coatings deposited onto the investigated substrates are characterised by good adhesion to the substrate within the critical load range L_c = 42-64N (Table 1, Figs. 9). In general, the deposition of wear resistant gradient (Ti,Al)N and Ti(C,N) coatings on the investigated sintered tool materials results in a considerable increase of microhardness in surface area, which, combined with the good adhesion of the coating to the substrate obtained in effect of the application of gradient structure of the coating, yields good functionality properties of these materials, confirmed during machining tests (Table 1). Thickness of the employed coatings differ in terms of thickness, but the thickness achieved in all cases is enough to ensure wear resistance and not so large to encourage the cracks formation.

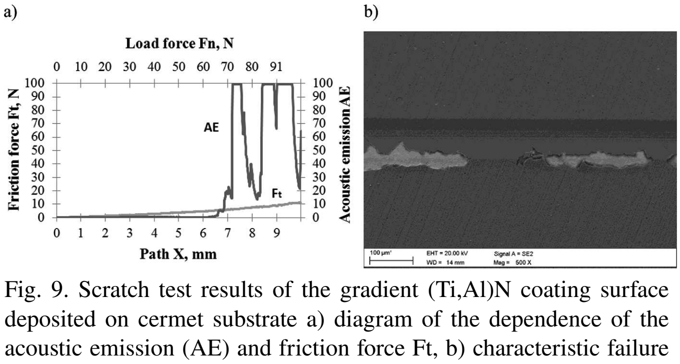

Fig. 9. Scratch test results of the gradient (Ti,Al)N coating surface deposited on cermet substrate a) diagram of the dependence of the acoustic emission (AE) and friction force Ft, b) characteristic failure around L_C zone(SEM)

Depositing of investigated coatings onto cermet tool materials caused significant increase of tool life measured during cutting tests (Table 1). Much lower results was achieved in case of Ti(C,N) kind of coatings. It can be connected with increased wear of Ti(C,N) coating over 400°C (especially chemical wear) and relatively high wear resistance of (Ti,Al)N coatings at elevated temperature, which could appear at assumed test's conditions [1,7]. Comparison of the approximated values of the VB wear of the cermets sample: uncoated and coated with the PVD coatings, depending on machining time show in Figure 10. As a result of metallographic observations it was stated that linear and uniform character of wear was achieved in case of all deposited samples (Fig. 11).

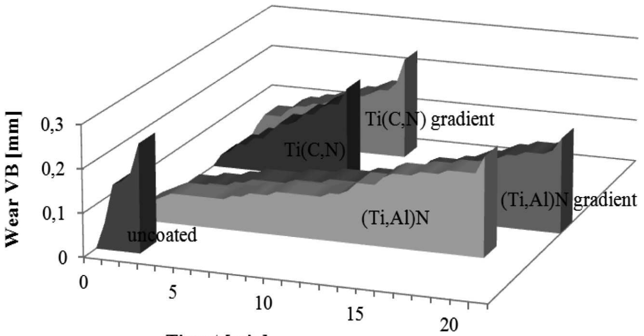

Fig. 10. Comparison of the approximated values of the VB wear of the cermets sample: uncoated and coated with the PVD coatings, depending on machining time

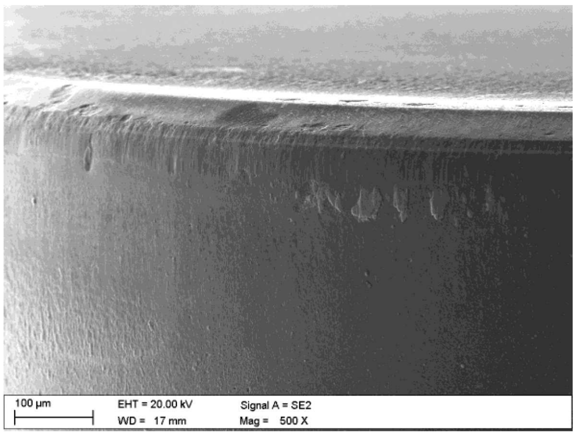

Fig. 11. Character of wear of the cermets sample with (Ti,Al)N coating, investigated with SEM after cutting test

4. Conclusions

The hard PVD coatings (both single-layer and gradient ones) deposited by the cathodic arc evaporation method (CAE) have a continuous structure. It was demonstrated that the coatings are uniformly deposited and are characterized by close adhesion to the substrate, without pores, cracks and discontinuities. Basing on the tests involving thin foils from the Ti(C,N) coating confirm the occurrence of a phase of the regular crystalline network, in compliance with TiN and Ti(C,N). In case of the (Ti,Al)N coating contains principally very fine grains of the crystalline structure corresponding to the phase AlN of the regular network, and also very few grains of the structure and parameters of AlN phase of the hexagonal network.

The wear resistant gradient coatings of the type (Ti,A1)N and Ti(C,N) deposited on the cermets yield a considerable rise of microhardness in the area around the surface, which, combined with good adhesion of the coating to the substrate obtained in effect of the application of gradient structure of the coating, has the influence on the applicability properties of these materials during machining tests, since the deposition of both single-layer and gradient coatings of the (Ti,Al)N type results in the rise of cutting edge durability as compared to the tools deposited with Ti(C,N) coatings. It is connected with high resistance to wear of the (Ti,Al)N coating in raised temperature. It was also demonstrated that the higher resistance to wear is exhibited by the materials deposited with gradient coatings as compared to the materials deposited with single-layer coatings.

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