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Ti(C,N) and (Ti,Al)N hard wear resistant coatings

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ABSTRACT

Purpose: Investigation the influence of kind of PVD coatings structure (homogenous or gradient) on properties of deposited tool materials: cemented carbides and cermets.

Design/methodology/approach: Analysis of the structure, analysis of the mechanical and functional properties: surface roughness, microhardness tests, scratch tests, cutting tests. The Ti(C,N) gradient coating was investigated by XPS method with multifunctional PHI 5700/660 spectrometer. The characteristic of surface region coating were determined from XPS depth profile. X-ray qualitative phase analysis and the grazing incidence X-ray diffraction method (GIXRD) was employed to collect the detailed information about phase composition of investigated material's surface layer. Microstructural of investigations substrates and coatings by transmission electron miocroscopy (TEM) were done.

Findings: Results of the investigation the influence of PVD coatings structure (homogenous or gradient) and kind on properties of coated tool materials: cemented carbides and cermets are given in the paper. Coatings are characterized by dense, compact structure, there have been identified no pores, fractures and discontinuities. The coatings were deposited uniformly onto the investigated substrate materials and show a characteristic columnar, fine-graded structure. The results of roughness, microhardness and cutting tests confirm the advantages of the PVD coatings. The coatings deposited onto the investigated substrates are characterised by good adhesion and causes increasing of wear resistance. The grazing incidence X-ray diffraction method (GIXRD) in the investigated coatings were used to describe the structure and gradient character of the coatings.

Practical implications: 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.

Originality/value: New techniques of gradient coatings deposition is one of the most spectacular aspect of the materials engineering development in the last years. The grazing incidence X-ray diffraction method (GIXRD) in the investigated coatings were used to describe the gradient character of the coatings.

Keywords: Tool materials; Gradient coatings; PVD

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

The technique of depositing of the hard and thin coatings is one of the most spectacular aspect of the materials engineering development in the last years. The physical vapour deposition (PVD) method of hard coating are widely used today for enhanced performance and have been evolved, because they can be deposited at temperatures much lower than those commonly needed for the chemical vapour deposition (CVD) of coating [7-8].

The coatings of high hardness, low friction coefficients, corrosion resistant and table in high temperature are produced at national research centres. Research projects are ongoing in the Department of Materials Processing Technology and Computer Techniques in Materials Science of the Institute of Engineering Materials and Biomaterials of the Silesian University of Technology focused on various aspects of coatings deposited in the PVD and CVD processes [1-6].

Coatings, which consist primarily of TiC, Ti(C,N), TiN, (Ti,Al)N, and their combinations, provide a considerable increase in tool life time of the coated tool materials, therefore have become popular as hard coatings for tools in recent years, in particular for higher speed cutting tools [1-7]. Gradient coatings are an innovative idea. The composition, microstructure and properties of gradient materials change continuously from the surface to the interior of the material. It is useful for increasing the adhesion strength between the coating and substrate material and provide expected functional properties of cutting tools, the investigated materials are used for. Moreover in case of continuous gradient coating problem of adhesion between particular layers of coating is eliminated in comparison with multilayer coatings [9-16].

The goal of the paper is the investigation of influence of PVD coatings structure (homogenous or gradient) and kind on properties of coated tool materials: cemented carbides and cermets.

2. Methodology of research

Both kinds of structure (homogenous and gradient) were achieved in case of Ti(C,N) and (Ti,Al)N coating. Each four combinations of coatings: homogenous (Ti,Al)N, gradient (Ti,Al)N, homogenous Ti(C,N) and gradient Ti(C,N) were deposited on cemented carbide as well as cermet substrates. Specification of the investigated materials has been presented in Table 1. Coatings deposition were carried out using the PVD method by the cathodic arc evaporation (CAE) process. Conditions of the process: substrate temperature: 500°C, pressure in the chamber: 0.04 Pa.

Observations of surfaces and structures of the deposited coatings were carried out on the transverse fractures in the scanning electron microscope SUPRA 35. To obtain the fracture images the Secondary Electrons (SE) detection method has been used with the accelerating voltage in the range of 15-20 kV and maximum magnification 30 000x.

The Ra 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 0.98 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 L_c (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.

The Ti(C,N) gradient coating was investigated by XPS method with use of multifunctional PHI 5700/660 spectrometer. The measurements were performed with use of monochromatized Al K_α X-ray source (hν = 1486.6 eV) for the XPS technique. All spectra were calibrated to binding energy for $Ag3d_{5/2}$, $Au4f_{7/2}$ and $Cu2p_{3/2}$ levels. The analysis were performed on "fresh" *ex situ* surfaces and after sputtering process by Ar^+ ions with energy 4 kV. The absolute sputter time was 90 minutes. The chemical states of titanium and carbon for vapour deposited coating were analysed from the shape of photoelectron core levels C1s and Ti2p. The characteristic of surface region coating were obtained from XPS depth profile.

Phase composition analyses of investigated samples were made on the PANalytical X'Pert PRO diffractometer, working in goniometer system by two methods:

- conventional Bragg-Brentano geometry (using the filtered X-ray Kα Co, step 0.05, time of counting 10 sec.) with use of proportional detector and parallel beam collimator at deflected beam, the lattice parameter was estimated at the voltage of 40 kV and tube current of 30 mA,
- the grazing incidence X-ray diffraction method (GIXRD) was employed to collect the detailed information about phase composition of investigated material's surface layer. Basing on reflections displacement measured by grazing incidence X-ray diffraction method (α = 1, 3, 5, 7), with use of proportional detector and parallel beam collimator at deflected beam, the lattice parameter was estimated and analyzed to confirm gradient character of investigated coatings.

Diffraction and thin film microstructure were made with use of the JEOL 3010 transmission electron microscope at the accelerating voltage 300 kV. The thin films were produced as a result of mechanical thinning and further ionic polishing using the Gatan apparatus. The electron diffractions from TEM were solved with use of Eldyf computer program.

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 hardness of about 250 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).

Table 1.
Characteristics of the investigated materials

Substrate	Coating	Coating thickness, μm	Roughness, R_a, μm	Microhardness, HV0.1	Critical Load, L_c, N	Tool life t, min
Cemented carbide*	uncoated	-	0.13	1755	-	2.5
	(Ti,Al)N	2.2	0.14	2750	47	20.0
	gradient (Ti,Al)N	2.6	0.14	3000	55.5	25.5
	Ti(C,N)	1.5	0.13	2600	44	5.0
	gradient Ti(C,N)	2.7	0.11	2850	64	5.0
Cermetal**	uncoated	-	0.06	1850	-	2.5
	(Ti,Al)N	1.5	0.13	2900	54	19.5
	gradient (Ti,Al)N	3.0	0.12	3150	63	22.0
	Ti(C,N)	1.5	0.12	2950	42	8.0
	gradient Ti(C,N)	2.6	0.11	2950	60	9.5

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

3. Results

It was found, basing on the metallographic examinations of fractures made on the scanning electron microscope (SEM) that the investigated materials are characteristic of the dense, compact structure, there have been identified no pores, fractures and discontinuities. The (Ti,Al)N and gradient Ti(C,N) coating were deposited uniformly onto the investigated substrate materials. They present a characteristic columnar, fine-graded structure, depending on the coating type employed. Investigated coatings adhere tightly to the substrate (Figs. 1-5).

Roughness of the substrate defined by R_a parameter is 0.13 μm. Depositing (Ti,Al)N coating onto the examined substrate causes increase of the roughness parameter to R_a=0.14 μm. In case of gradient Ti(C,N) coating deposited on investigation substrate the roughness parameter decreased in competition to uncoated substrate R_a = 0.11 μm (Table 1).

Depositing the wear resistant coatings onto cemented carbides, results in a significant increase of the surface layer microhardness, contributing in this way in machining to the decrease of the flank wear intensity of cutting tools' flanks (Table 1).

The coatings deposited onto the investigated substrate are characterised by good adhesion L_c = 47 N for the (Ti,Al)N coating and L_c=64 N for the gradient Ti(C,N) coating (Table 1, Figs. 7, 8).

The chemical composition of Ti(C,N) coating "free" from adsorbates is presented in Table 2. The presence of oxygen in chemical compound is very small. It may be connected with PVD process of obtaining coating or adsorbed oxygen atoms from residual gases of vacuum on roughness surface. The obtained ratio of C/N = 1.3 is characteristic for Ti(C,N) coating in surface region. The concentration of carbon atoms in the ratio to nitrogen atoms in the transition region between Ti(C,N) coating and substrate should be reversed. However, the XPS study was performed only for characterisation of coating. The distribution of atomic concentration for Ti, C, N in depend on sputter time is presented on Fig. 6. The level of impurities for oxygen is below 2%. The distribution of particular elements in surface region of investigation coating is stable. The binding energy determined for N1s (at 397 eV) corresponds to TiN [17].

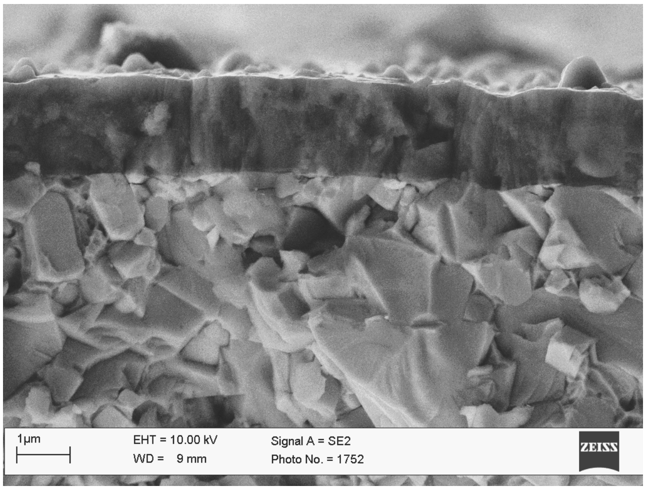

Fig. 1. Fracture surface of the (Ti,Al)N coating deposited onto the cemented carbides substrate

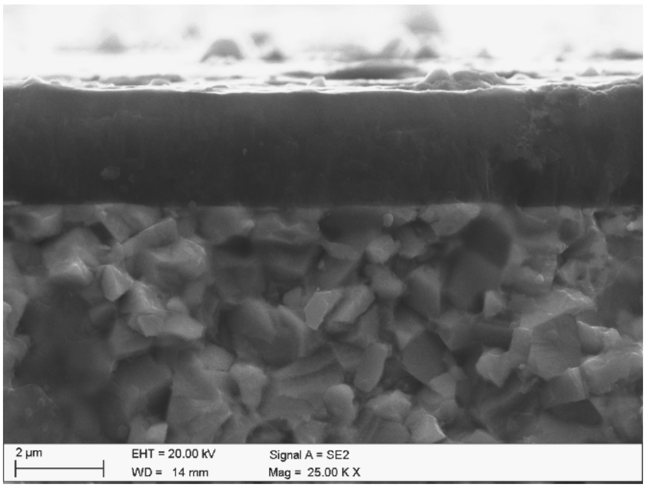

Fig. 2. Fracture surface of the gradient (Ti,Al)N coating deposited onto the cemented carbides substrate

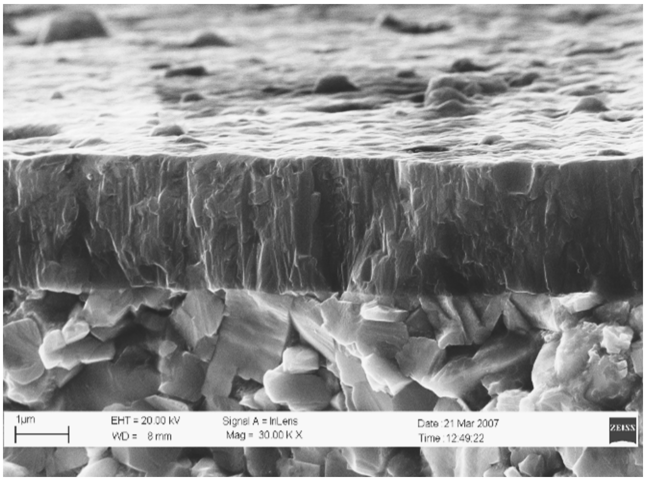

Fig. 3. Fracture surface of the (Ti,Al)N coating deposited onto the cermet substrate

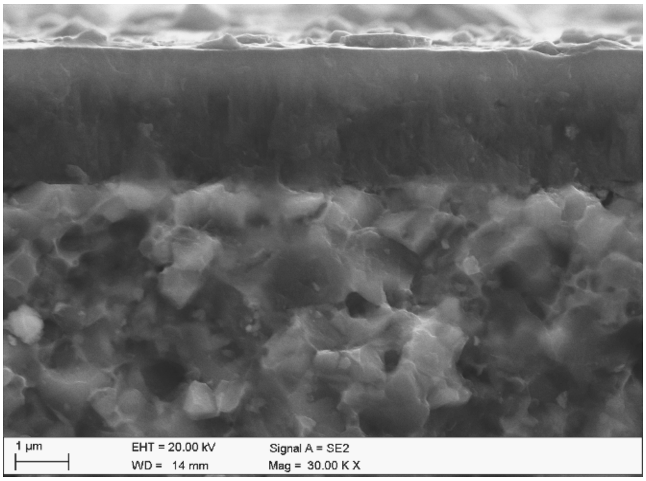

Fig. 4. Fracture surface of the gradient Ti(C, N) coating deposited onto the cermet substrate

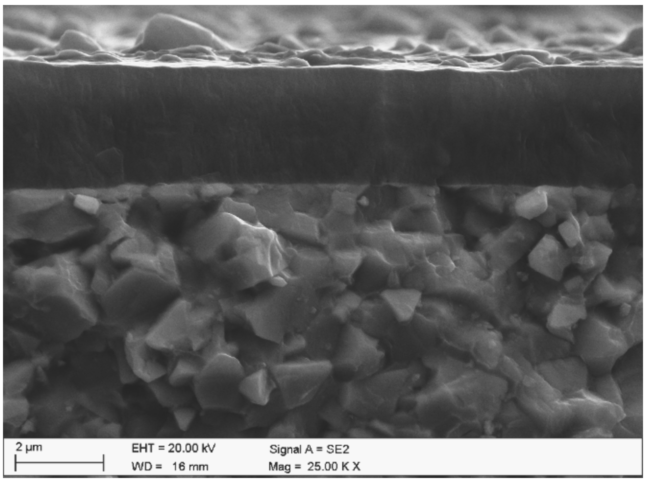

Fig. 5. Fracture surface of the gradient Ti(C, N) coating deposited onto the cemented carbides substrate

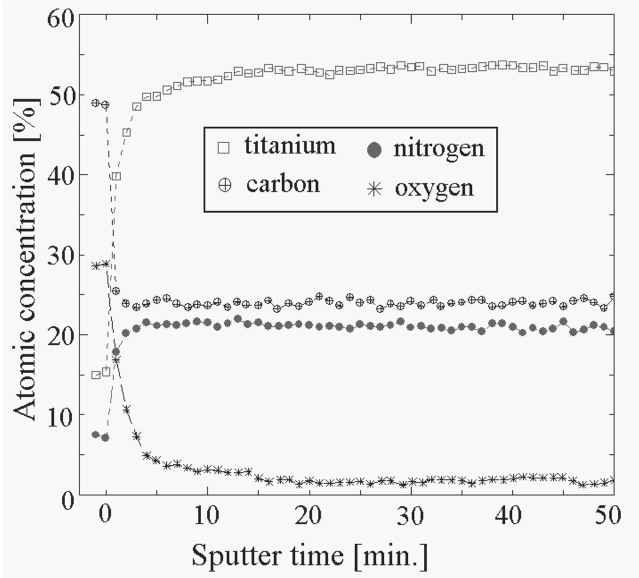

Fig. 6. The distribution of atomic concentration of elements in the surface region of Ti(C,N) coating onto cermet substrate obtained by XPS method

Table 2.
Chemical composition of investigated coating Ti(C,N) obtained by XPS method

Element	C	N	O	Ti
Atomic concentration, %	28	17	5	49

It was demonstrated using the X-ray qualitative phase analysis method that according to the initial assumptions coatings containing the (Ti,Al)N and gradient Ti(C,N) phases were deposited onto cemented carbides what is confirmed by crystallographic planes' reflections characteristic for (Ti,Al)N and Ti(C,N) phases (Figs. 9-11).

The grazing incidence X-ray diffraction method (GIXRD) was employed to collect the detailed information about phase composition of investigated material's surface layer. It was necessary because of the substrate's and coatings' reflections interference and their intensity making it difficult to analyze the results achieved with use of conventional Bragg-Brentano geometry (Fig. 12).

Basing on (200) reflection displacement of (Ti,Al)N coating and (111) reflection displacement of Ti(C,N) coating (Fig. 13), measured by grazing incidence X-ray diffraction method ($\alpha = 1$, 3, 5, 7), with use of proportional detector and parallel beam collimator at deflected beam, the lattice parameter was estimated.

Experimental results was approximated with use of basic functions' combination: linear function (matching of background level) and Voight's function (matching of analyzed (Ti,Al)N and Ti(C,N) reflections from (220) and (111) planes. The Levenberg-Marquardt's algorithm was used to determine the basic functions' parameters. The level of matching was characterized by $\chi 2$ function value. The $\chi 2$ function was determined as experimental and calculated results differences' sum of squares. The basic functions parameters appropriate for minimal value of $\chi 2$ function indicate the analyzed reflection position at diffraction pattern.

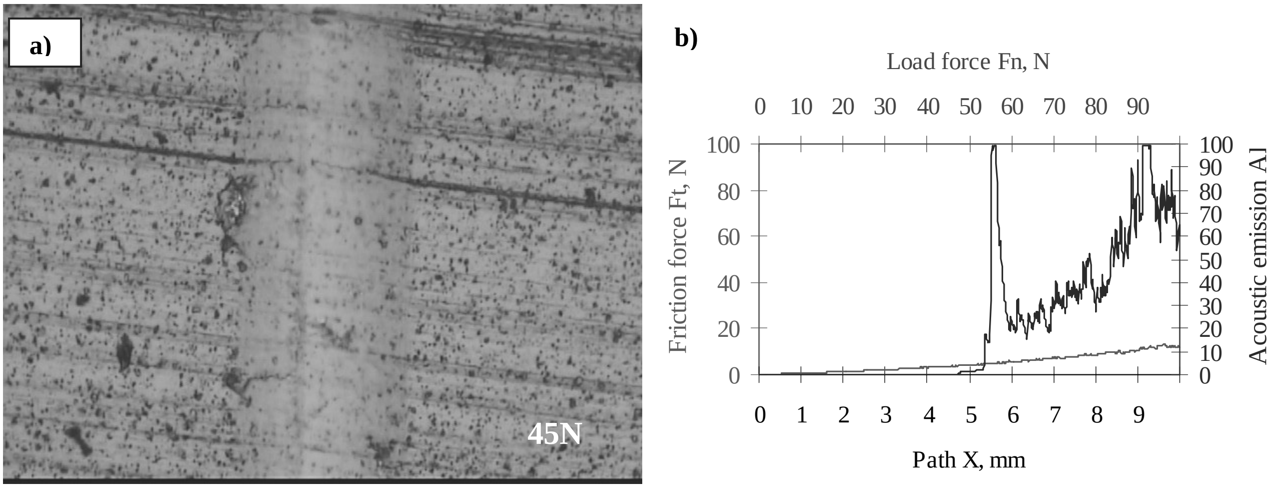

Fig. 7. a) Indenter trace with the optical L_c load, b) scratch test results of the (Ti,Al)N coating surface deposited on cemented carbides substrate

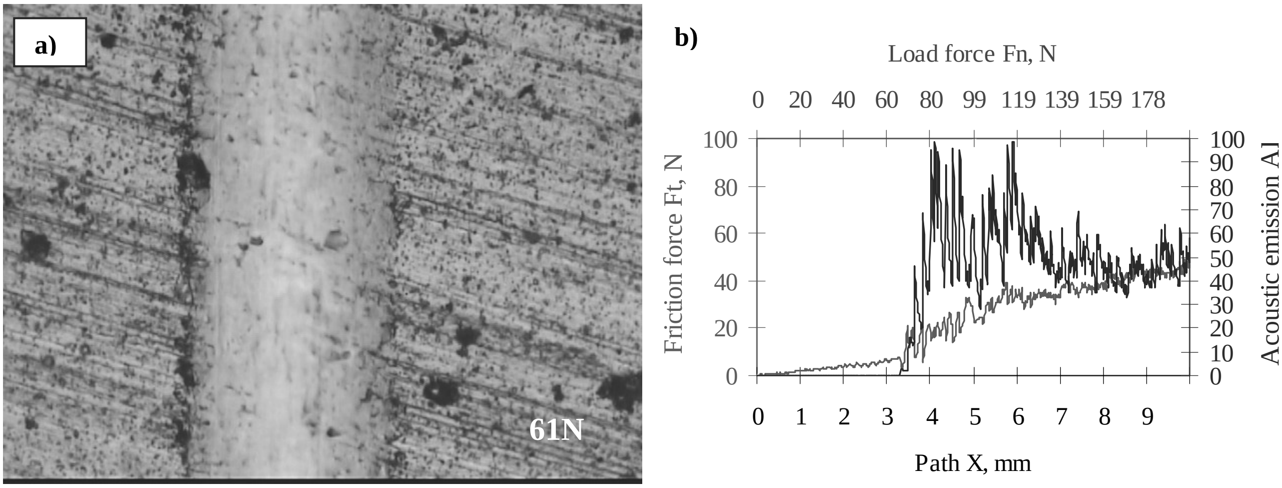

Fig. 8. a) Indenter trace with the optical L_c load, b) scratch test results of the gradient Ti(C,N) coating surface deposited on cemented carbides substrate

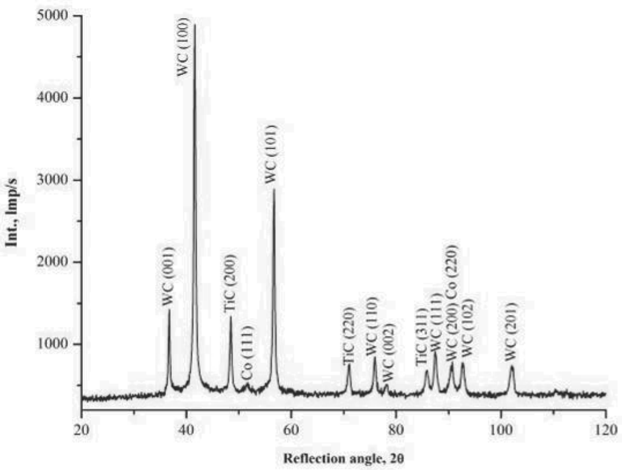

Fig. 9. X-ray phase analysis of the cemented carbides substrate (Bragg-Brentano geometry)

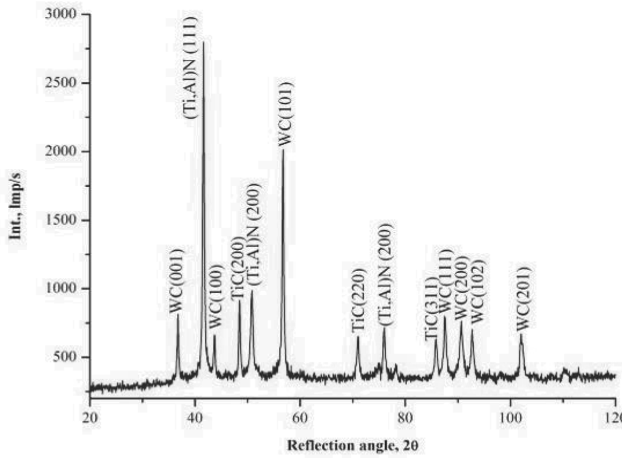

Fig. 10. X-ray phase analysis of the (Ti,Al)N coating (Bragg-Brentano geometry)

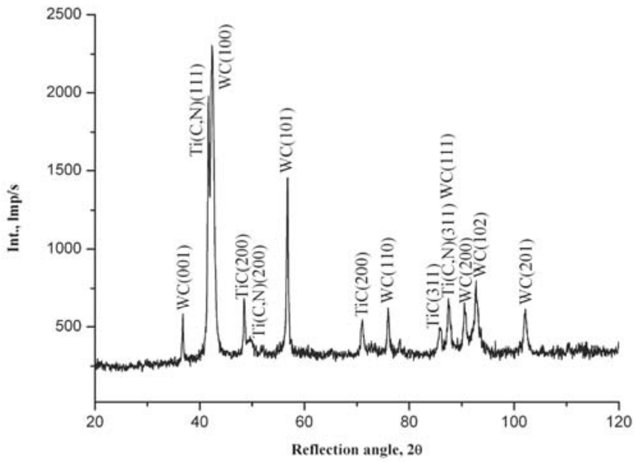

Fig. 11. X-ray phase analysis of the Ti(C,N) coating (Bragg-Brentano geometry)

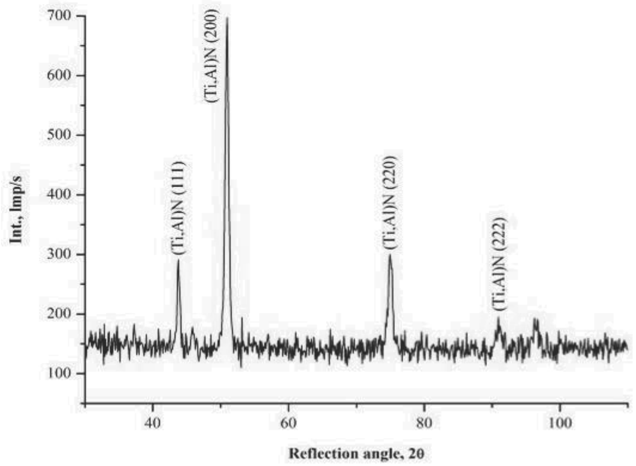

Fig. 12. X-ray phase analysis of the (Ti,Al)N coating (grazing incidence X-ray diffraction GIXRD method), α=1

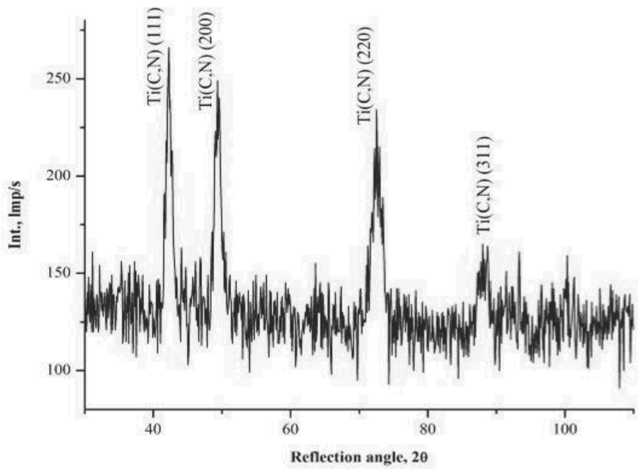

Fig. 13. X-ray phase analysis of the Ti(C,N) coating (grazing incidence X-ray diffraction GIXRD method), α=1

As a result of the research carried out it was found out, that in case of analyzed carbonitride coatings, lattice parameter estimated at 1μm depth is similar (in accordance with JCPDS (42-1489)) to the value characteristic for Ti(C,N) phase with high carbon fraction. When the grazing incidence of the primary beam grows (the volume of analyzed materials grows simultaneously), estimated lattice parameter is similar to the value characteristic for Ti(C,N) phase with high nitrogen fraction (in accordance with JCPDS (42-1488)). It can be interpreted as gradient character of coating confirmation. In case of (Ti,Al)N coating, the significant change of lattice parameter as a function of analyzes' depth wasn't stated (Fig. 14, 15). It can attest for inconsiderable diversification of chemical composition of the coating in investigated area. Figure 16 show the comparison of the change of lattice parameter estimated for Ti(C,N) and (Ti,Al)N coating.

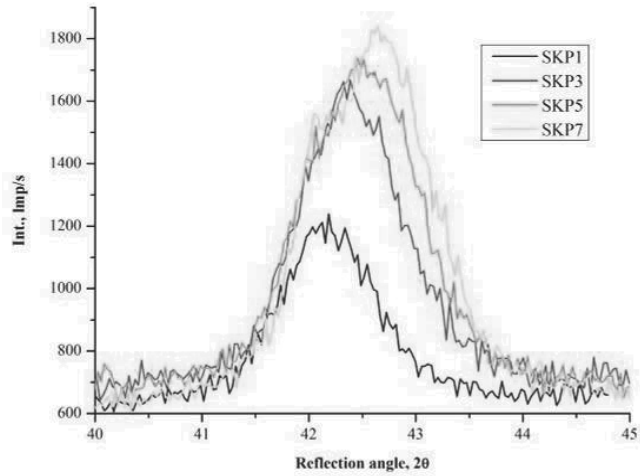

Fig. 14. Change of (111) reflection's position in relation to grazing incidence of the primary beam (Ti(C,N) coating)

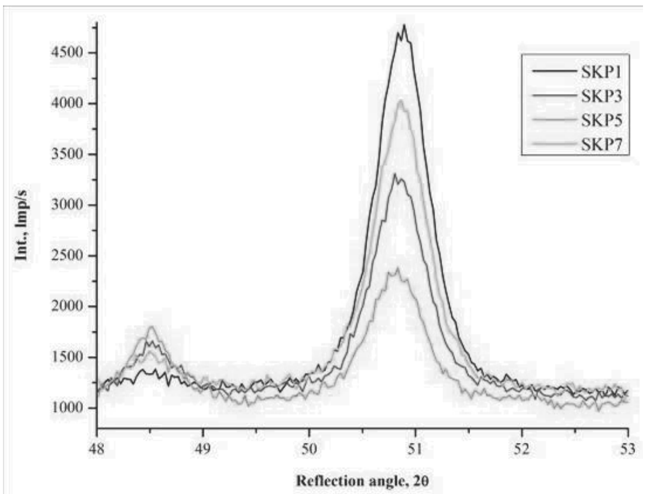

Fig. 15. Change of (200) reflection's position in relation to grazing incidence of the primary beam ((Ti,Al)N coating

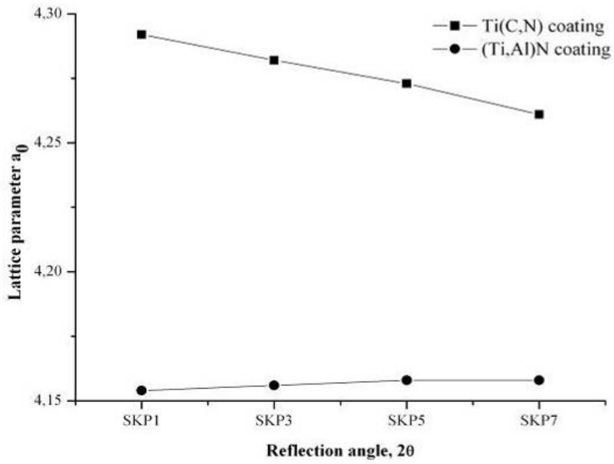

Fig. 16. Comparison of the change of lattice parameter estimated for Ti(C,N) and (Ti,Al)N coating

In case of uncoated materials tool life doesn't depend on kind of substrate and was 2.5 min. Depositing of investigated (Ti,Al)N coating onto all used sintered tool materials caused significant increase of tool life measured during cutting tests (Table 1). Comparison of the approximated values of the VB wear of all combinations of investigated materials depending on machining time is shown in Figs. 18-21.

In case of all deposited kinds of coatings, the increase of tool life was stated in comparison to uncoated substrates. Significantly better results was achieved in case of (Ti,Al)N (gradient, as well, as homogenous) coated tools than in case of Ti(C,N) kind of coatings. It can be connected with increased wear of Ti(C,N) coating over 400°C and relatively high wear resistance of (Ti,Al)N coatings at elevated temperature, which could appear at assumed test's conditions. It was also stated, that regardless of employed kind of substrate, the higher wear resistance was achieved in case of gradient coatings then in case of homogenous structure of coatings. This can be connected with reducing of internal stresses in zone between coating and substrate achieved due to gradient composition of coating [18].

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. 17).

Basing on the thin foils examinations of reinforced with hard carbide phases zone, in the transmission electron microscope, it was found out that the structure of the investigated cemented carbide is dispersed carbides, mostly of the WC type. Structure of the thin foil from cemented carbide substrate is presented in Fig. 23. Moreover, it was found out that the average diameter of the significant portion of tungsten carbide particles is smaller than 1.0-2.0 μm, which clearly classifies the investigated carbide as belonging to the fine-grained materials group. Examinations of thin foils from Ti(C,N) coatings confirm that, according to the original assumptions, coatings containing the TiN type phases were deposited onto the substrate. It is not feasible to differentiate these phases from the diffraction point of view, due to isomorphism of the TiN and Ti(C,N) phases. The average size of coatings crystallites is less then 100 nm, on deposited coatings can be classificated as nanostructural coatings. Structures of coatings deposited onto the substrates are presented in Fig. 24.

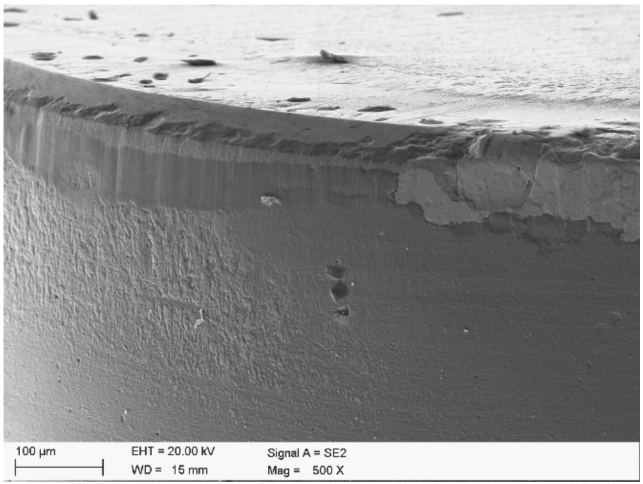

Fig. 17. Character of wear of cermet sample with (Ti,Al)N coating, investigated with SEM after cutting test

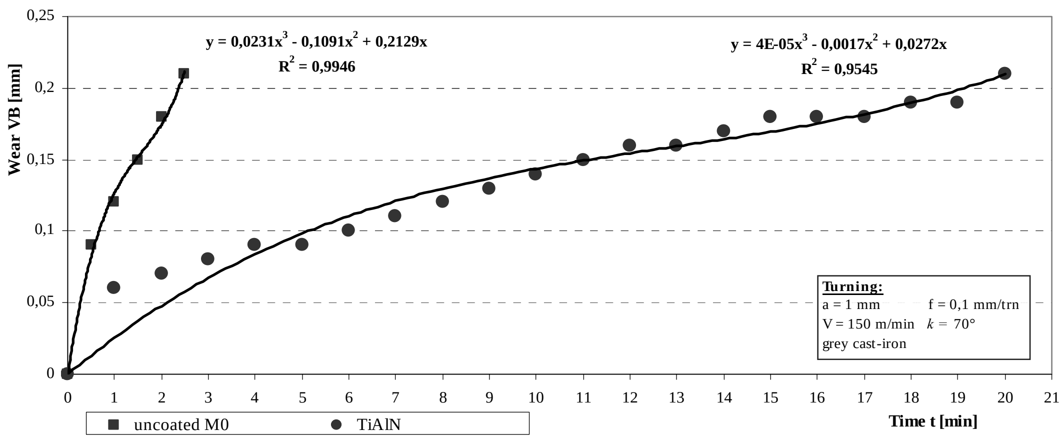

Fig. 18. Comparison of the approximated values of the VB wear of the cermetal sample: uncoated and coated with the (Ti,Al)N coating, depending on machining time

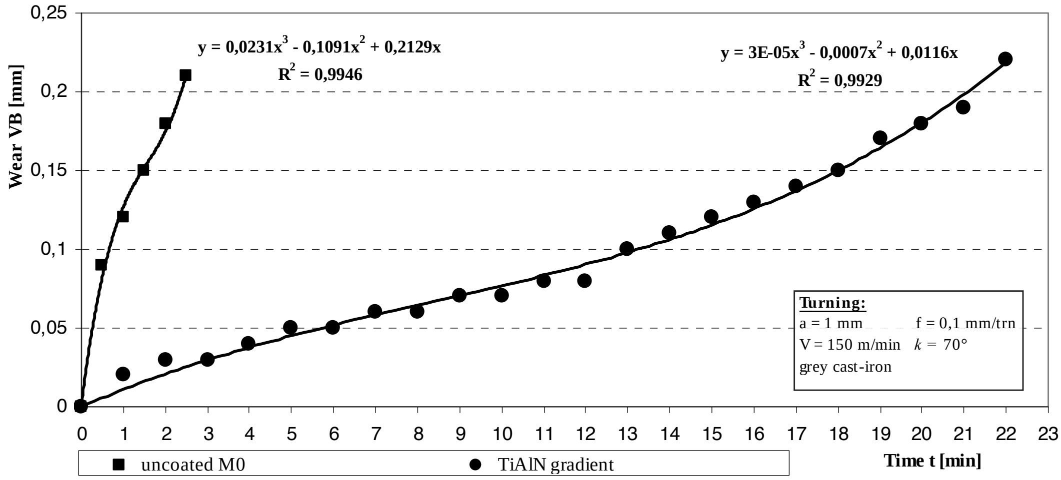

Fig. 19. Comparison of the approximated values of the VB wear of the cermets sample: uncoated and coated with the (Ti,Al)N gradient coating, depending on machining time

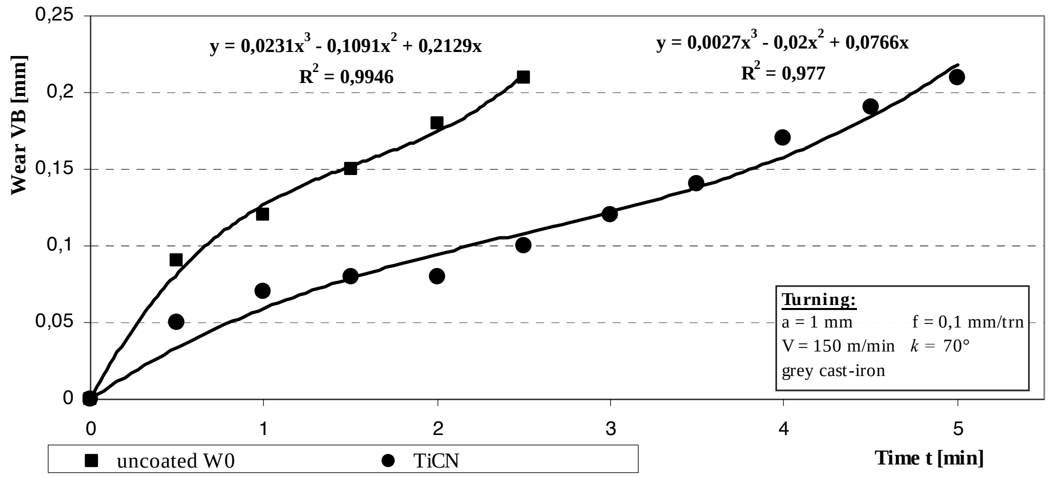

Fig. 20. Comparison of the approximated values of the VB wear of the cemented carbides sample: uncoated and coated with the Ti(C,N) coating, depending on machining time

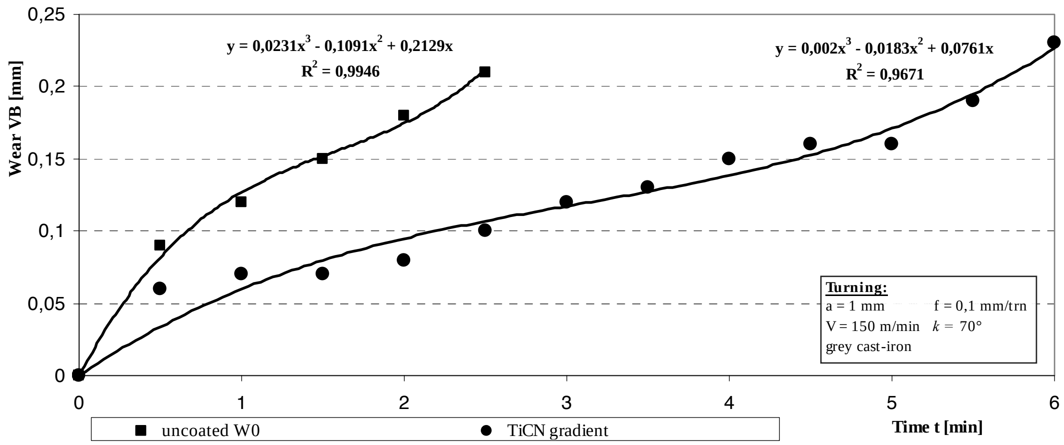

Fig. 21. Comparison of the approximated values of the VB wear of the cemented carbides sample: uncoated and coated with the Ti(C,N) gradient coating, depending on machining time

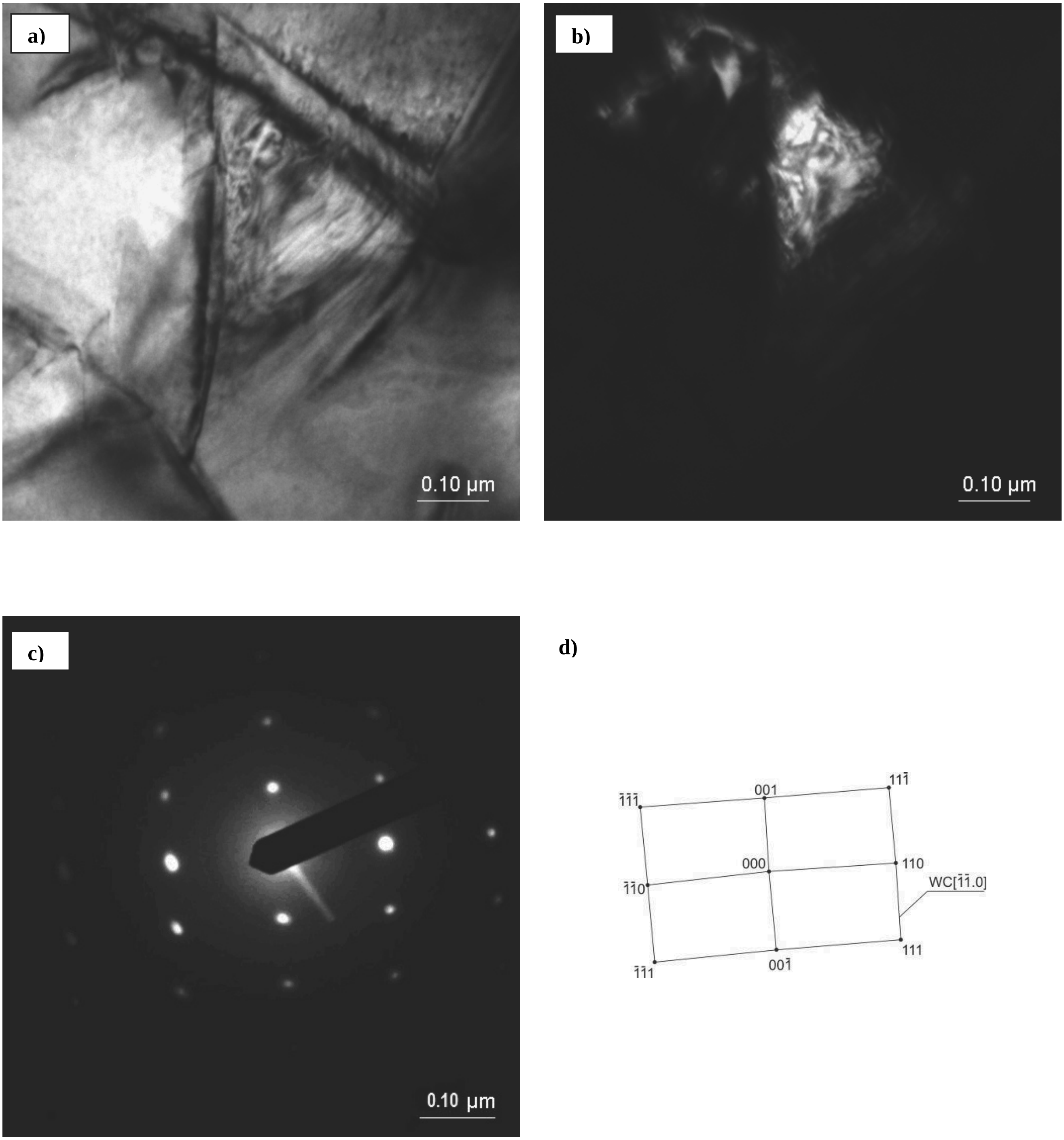

Fig. 22. a) Structure of the thin foil from the cemented carbide substrate, b) dark field, c) diffraction pattern for the area as from figure a, d) solution of the diffraction pattern from figure c, (TEM)

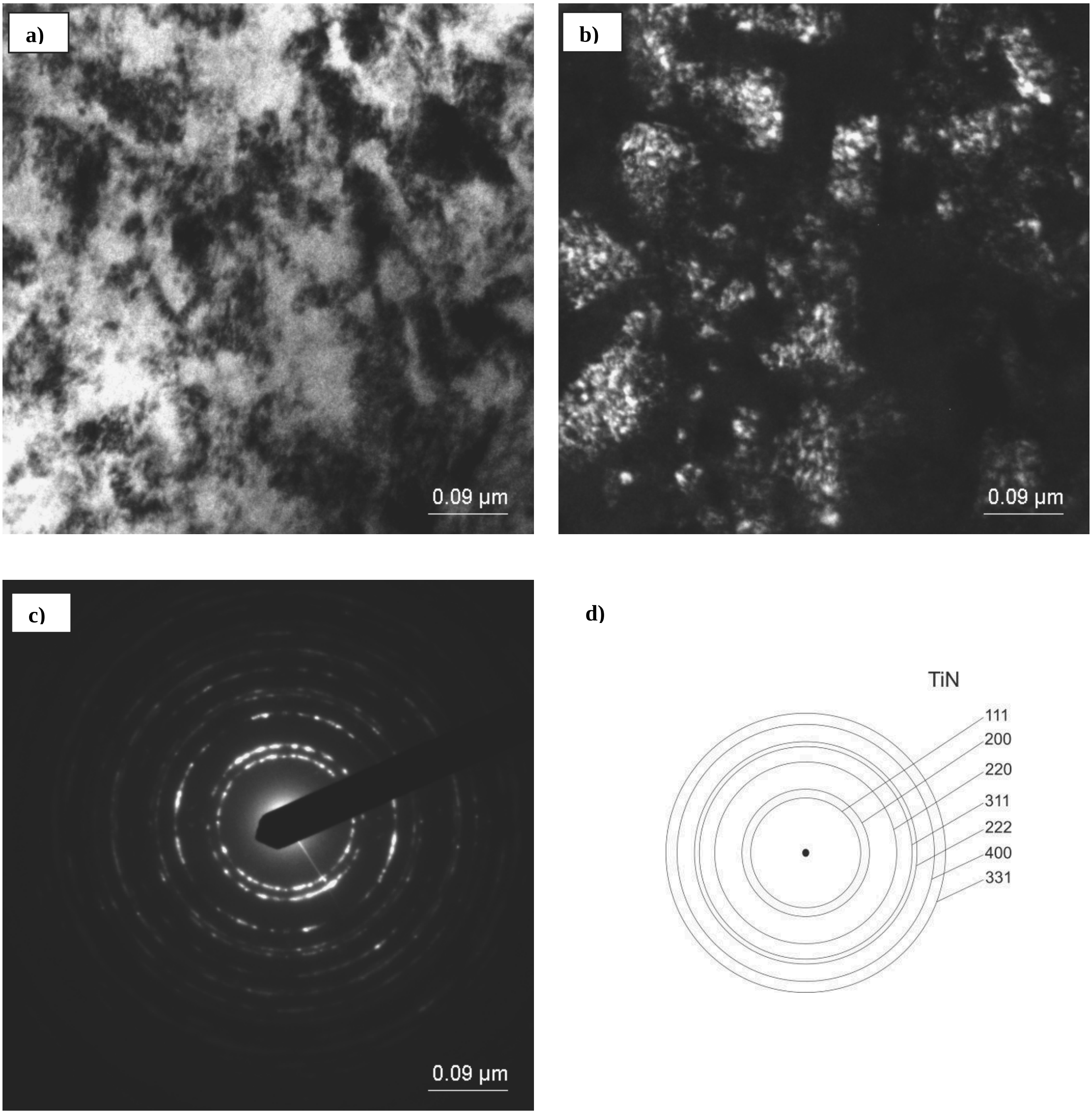

Fig. 23. a) Structure of the thin foil from the Ti(C,N) coating deposited on cermet substrate, b) dark field, c) diffraction pattern for the area as from figure a, d) solution of the diffraction pattern from figure c, (TEM)

4. Conclusions

The results of the investigations of influence of PVD coatings structure (homogenous or gradient) and kind on properties of deposited tool materials: cemented carbides and cermets are given in the paper. Coatings deposited onto cemented carbides and cermets have a dense, compact structure, there have been identified no pores, fractures and discontinuities. The coatings were deposited uniformly onto the investigated substrate materials and showed a characteristic columnar, fine-graded structure.

The grazing incidence X-ray diffraction method (GIXRD) in the investigated coatings were used to describe the structure and gradient character of the coating. As a result of the research carried out it was found out, that in case of analyzed carbonitride coatings, lattice parameter estimated at 1μm depth is similar to the value characteristic for Ti(C,N) phase with high carbon fraction. When the grazing incidence of the primary beam grows (the volume of analyzed materials grows simultaneously), estimated lattice parameter is similar to the value characteristic for Ti(C,N) phase with high nitrogen fraction It can be interpreted as gradient character of coating confirmation. In case of (Ti,Al)N coating, the significant change of lattice parameter as a function of analyzes' depth wasn't stated. It can attest for inconsiderable diversification of chemical composition of the coating in investigated area.

The results of roughness, microhardness and cutting tests confirm the advantages of PVD coatings deposited onto cemented carbides and cermets. Gradient and homogenous coatings deposited onto the investigated substrates are characterised by good adhesion, high microhardness, taking effect in increasing of wear resistance.

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INNOVATIVE ECONOMY
NATIONAL COHESION STRATEGY

FORSURF

EUROPEAN UNION
EUROPEAN REGIONAL
DEVELOPMENT FUND

References

[1] L.A. Dobrzański, S. Skrzypek, D. Pakuła, J. Mikuła, A. Křiž, Influence of the PVD and CVD technologies on the residual macro-stresses and functional properties of the coated tool ceramics, Journal of Achievements in Materials and Manufacturing Engineering 35/2 (2009) 162-168.

[2] L.A. Dobrzański, L.W. Żukowska, J. Mikuła, K. Gołombek, P. Podstawski, Functional properties of the sintered tool materials with (Ti,Al)N coating, Journal of Achievements in Materials and Manufacturing Engineering 36/2 (2009) 134-141.

[3] L.A. Dobrzański, L.W. Wosińska, J. Mikuła, K. Gołombek, Multicomponent and gradient PVD coatings deposited on the sintered tool materials, Material Engineering 3-4 (157-158) (2007) 627-630.

[4] L.A. Dobrzański, L. Wosińska, K. Gołombek, J. Mikuła, Structure of multicomponent and gradient PVD coatings deposited on sintered tool materials, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 99-102.

[5] L.A. Dobrzański, L.W. Wosińska, J. Mikuła, K. Gołombek, D. Pakuła, M. Pancielejko, Structure and mechanical properties of gradient PVD coatings, Journal of Materials Processing Technology 201(2008) 310-314.

[6] L.A. Dobrzański, K. Gołombek, J. Mikuła, D. Pakuła, Improvement of tool materials by deposition of gradient and multilayers coatings, Journal of Achievements in Materials and Manufacturing Engineering 19 (2006) 86-91.

[7] M. Cłapa, D. Batory, Improving adhesion and wear resistance of carbon coatings using Ti:C gradient layers, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 415-418.

[8] L.A. Dobrzański, Engineering materials and materials design. Fundamentals of materials science and physical metallurgy, WNT, Warsaw-Gliwice, 2006 (in Polish).

[9] Li Chen, S.Q. Wang, S.Z. Zhou, Jia Li, Y.Z. Zhang, Microstructure and mechanical properties of Ti(C,N) and TiN/Ti(C,N) multilayer PVD coatings, International Journal of Refractory Metals & Hard Materials 26 (2008) 456-460.

[10] M. Antonov, I. Hussainova, F. Sergejev, P. Kulu, A. Gregor, Assessment of gradient and nanogradient PVD coatings behaviour under erosive, abrasive and impact wear conditions, Wear 267 (2009) 898-906.

[11] Li Chen, S.Q. Wang, Yong Du, Jia Li, Microstructure and mechanical properties of gradient Ti(C, N) and TiN/Ti(C,N) multilayer PVD coatings, Materials Science and Engineering A 478 (2008) 336-339.

[12] W. Lengauer, K. Dreyer, Functionally graded hardmetals, Journal of Alloys and Compounds 338 (2002) 194-212.

[13] T. Liu, C. Dong, S. Wu, K. Tang, J. Wang, J. Jia, TiN, TiN gradient and Ti/TiN multi-layer protective coatings on Uranium, Surface and Coating Technology 201 (2007) 6737-6741.

[14] R. Manaila, A. Devenyi, D. Biro, L. David, P.B. Barna, A. Kovacs, Multilayer TiAlN coatings with composition gradient, Surface and Coatings Technology 151-152 (2002) 21-25.

[15] P. Panjan, I. Boncina, J. Bevk, M. Cekada, PVD hard coatings applied for wear protection of drawing dies, Surface and Coating Technology 200 (2005) 133-136.

[16] X. Qiao, Y. Hou, Y. Wu, J. Chen, Study on functionally gradient coatings of Ti-Al-N, Surface and Coating Technology 131 (2000) 462-464.

[17] J. Chastain, RC King, Jr, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, Inc.1995.

[18] A. Śliwa, J. Mikuła, K. Gołombek, L.A. Dobrzański, FEM modelling of internal stresses in PVD coated FGM, Journal of Achievements in Materials and Manufacturing Engineering 36/1 (2009) 71-78.