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Sintered tool materials with multi-component PVD gradient coatings

K. Gołombek, J. Mikuła, D. Pakuła, L.W. Żukowska, L.A. Dobrzański *
Division of Materials Processing Technology, Management and Computer Techniques in Materials Science, Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland
* Corresponding author: E-mail address: leszek.dobrzanski@polsl.pl

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Materials

ABSTRACT

Purpose: The main aim of researches was investigation of structure and properties of the (Ti,Al,Si)N gradient wear resistant coatings.

Design/methodology/approach: 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, glow-discharge optical emission spectroscope GDOES, auger electron spectroscope (AES) 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.

Findings: Deposition of the multicomponent gradient coatings with the PVD method, based on the Al and Si solid secondary solution in the TiN titanium nitride, isomorphous with the alternating pure titanium nitride TiN, on tools made from oxide, nitride ceramics and tool cermets, results in the increase of mechanical properties in comparison with uncoated tool materials, deciding thus the improvement of their working properties.

Practical implications: Deposition of (Ti,Al,Si)N nanocrystalline coatings by the use of PVD method causes the increase of cutting properties of tools made of cermets for ca. 300% and of Al_2O_3+ZrO_2 for ca. 100% comparing to adequately uncoated tools.

Originality/value: Comparison of the wide range of modern sintered tool materials with wide unique set of PVD coatings.

Keywords: Tool materials; Sintered materials, Gradient coatings; PVD

1. Introduction

Tools covered with coatings based on carbides, borides, nitrides, and oxides can work at higher service parameters (temperature and load). Moreover, the multilayer and multicomponent coatings make it possible to constitute freely properties of the entire coating as well as of its transition layer, ensuring good adhesion, compensation of the internal stresses, and transmission of the external loads. Tools with such coatings reveal a significant service life extension compared to the uncoated tools or coated with simple coatings based on mononitrides or carbonitrides, improvement of the tribological contact conditions in the tool-chip-machined material contact zone, and protection of the tool edge from oxidation and extensive overheating. Many aspects pertaining to forming of coatings, including also the process conditions effect on their properties, still remain inexplicable in spite of the enormous interest paid in them by many industrial centres and research laboratories. Moreover, each combination of the substrate material – coating type – deposition method calls for determining properties of the coated material and defining, based on them, the range of its possible applications. Research in this area is concentrated among

Table 1.
Chemical composition of the investigated materials

Substrate	Coating			Process type	Roughness, µm
	Type	Composition	Thickness, µm		
cemented carbide	uncoated				0.36
cermet					0.20
Al_2O_3+ZrO_2					0.21
Al_2O_3+TiC					0.07
Al_2O_3+$SiC_{(w)}$					0.26
Si_3N_4					0.06
cemented carbides	(Ti,Al,Si)N (1)		4.0	PVD	0.65
cermet			4.0		0.62
Al_2O_3+ZrO_2			2.0		0.43
Al_2O_3+TiC			1.8		0.37
Al_2O_3+$SiC_{(w)}$			2.5		0.37
Si_3N_4			2.0		0.45
cemented carbides	(Ti,Al,Si)N (2)		4.0		0.67
cermet			4.0		0.63
Al_2O_3+ZrO_2			2.3		0.37
Al_2O_3+TiC			1.5		0.27
Al_2O_3+$SiC_{(w)}$			2.8		0.33
Si_3N_4			4.0		0.40

other on searching the new composite gradient coatings, both multicomponent and multilayer ones, and adding new elements to coating combinations used since many years, like silicon or vanadium to TiAlN [1-15].

The paper presents the study of selected results of researches conducted by the authors and described in detail in works [1-8].

2. Materials and methodology

The investigations were carried out on the multi-point inserts made from the cemented carbides, cermets, Al_2O_3+ZrO_2, Al_2O_3+TiC and Al_2O_3+$SiC_{(w)}$ oxide ceramics and Si_3N_4 nitride ceramics coated using the PVD method in the CAE process, with the (Ti,Al,Si)N gradient wear resistant coatings obtained with two methods. (Ti,Al,Si)N (1) coating is characterized by continuous change of chemical composition while (Ti,Al,Si)N (2) was obtained with use of multilayer method. Specifications and chemical composition of the investigated materials are presented in Table 1.

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, glow-discharge optical emission spectroscope GDOES, auger electron spectroscope (AES) 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.

3. Discussion of results

3.1. Structure of substrates

Basing on the examinations of thin foils in the transmission electron microscope it was found out that the structure of the investigated cemented carbides is the γsolid solution of cobalt with dispersed carbides, mostly of the WC type. Structure of the thin foil from the cemented carbide is presented in Figure 1.

Moreover, it was found out that the average diameter of the significant portion of tungsten carbide particles is smaller than 0.5 µm, which clearly classifies the investigated carbide as belonging to the fine-grained materials group. Based on the examinations of thin foils from the cermet substrate it was found out that the structure consists of the γsolid solution of cobalt and nickel, filling the hard skeleton formed mostly from the Ti(C,N) particles. In case of the Ti(C,N) particles it was found out that their sizes are in the range from 0.5 µm to 1.0 µm. Crystalline structure defects were observed also in the characteristic shell-core structure.

The Al_2O_3+ZrO_2 oxide tool ceramics contains the aluminium oxide grains with the hexagonal lattice and the ZrO_2 ones with the monoclinic lattice occurring in the twinned lamellae form in case of the Al_2O_3+TiC oxide tool ceramics contains the aluminium oxide grains with the hexagonal lattice and the TiC ones with the hexagonal lattice.

The structure of the investigated Si_3N_4 nitride tool ceramics is the β-Si_3N_4 phase. Moreover, it was found out that the size of the significant portion of the β-Si_3N_4 phase particles is smaller than 0.5 µm, which unequivocally classifies the investigated ceramics to the fine-grained materials.

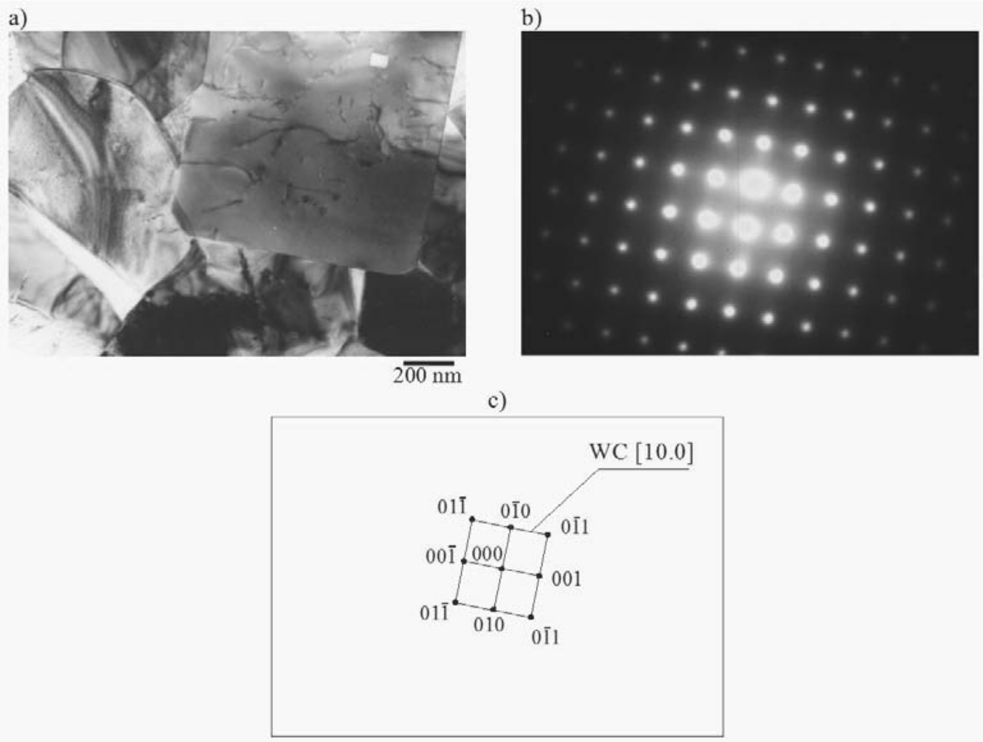

Fig. 1. Structure of cemented carbides substrate (TEM): a) bright field, b) diffraction pattern from the area as in figure a, c) solution of the diffraction patterns from figure b

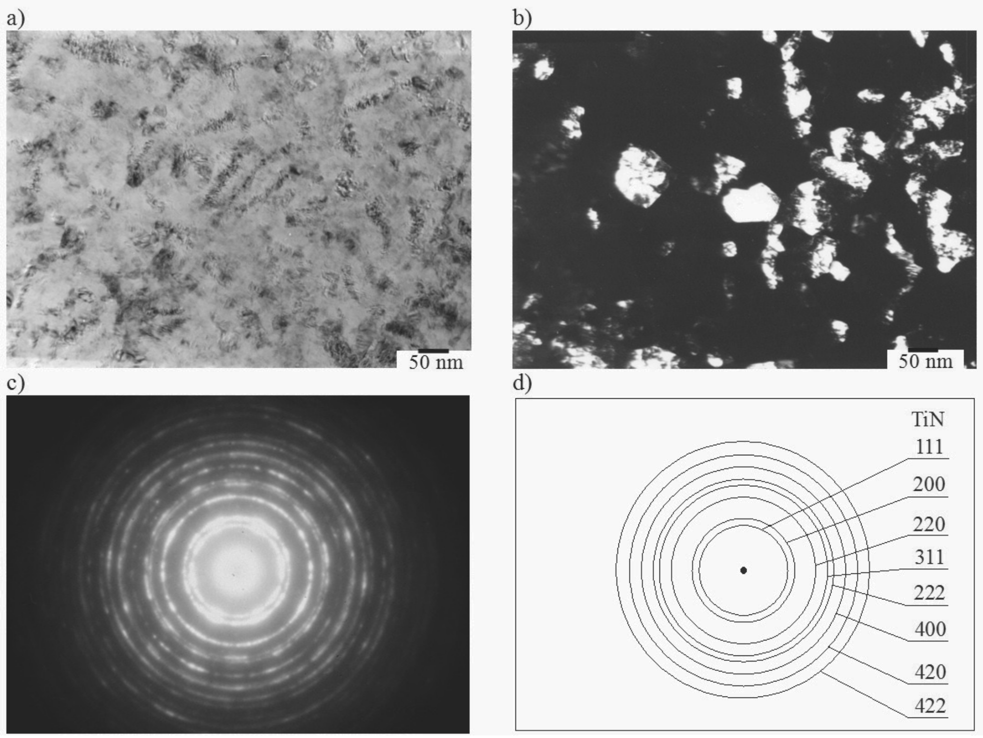

Fig. 2. a) Structure of the thin foil from the (Ti,Al,Si)N (2) coating deposited onto the cemented carbide, b) dark field from the (111) TiN reflection, c) diffraction pattern for the area as from figure a, d) solution of the diffraction pattern from figure c

3.2. Structure of deposited coatings

TEM examinations of coatings confirm that, according to the original assumptions, coatings containing the TiN type phases were deposited onto the cemented carbides and cermets substrates. It is not feasible to differentiate these phases from the diffraction point of view, due to isomorphism of the TiN and (Ti,Al,Si)N phases. Structure of (Ti,Al,Si)N (2) coating deposited onto the cemented carbide presented in Figure 2.

It was found out that the (Ti,Al,Si)N (1) coating deposited onto the Al_2O_3+ZrO_2 substrate is characteristic of the columnar structure, confirmed by texture examinations and in case of the other layers, even at the largest magnifications used, no grain boundaries were revealed, which may attest to their nanostructural character.

The fractographic examinations carried out give grounds to state that the coatings were deposited uniformly onto the investigated substrate materials and that they are characteristic of the depending on the coating type employed, and that the particular layers adhere tightly to themselves and to the substrate. Examinations of the chemical compositions of the coatings carried out using the X-ray energy dispersive spectrograph EDS confirm presence of the relevant elements in the deposited coatings and their layers (Fig. 3 a, b, d).

It was demonstrated, using the X-ray qualitative phase analysis methods, that – according to the initial assumptions – coatings containing the TiN type phases, and most probably the complex (Ti,Al,Si)N nitride one, were developed on surfaces of the investigated materials. Differentiation of the TiN and (Ti,Al,Si)N phases using the diffraction methods is impossible due to their isomorphous nature, as (Ti,Al,Si)N is – in fact – the secondary solid solution based on titanium nitride TiN (Fig. 3c).

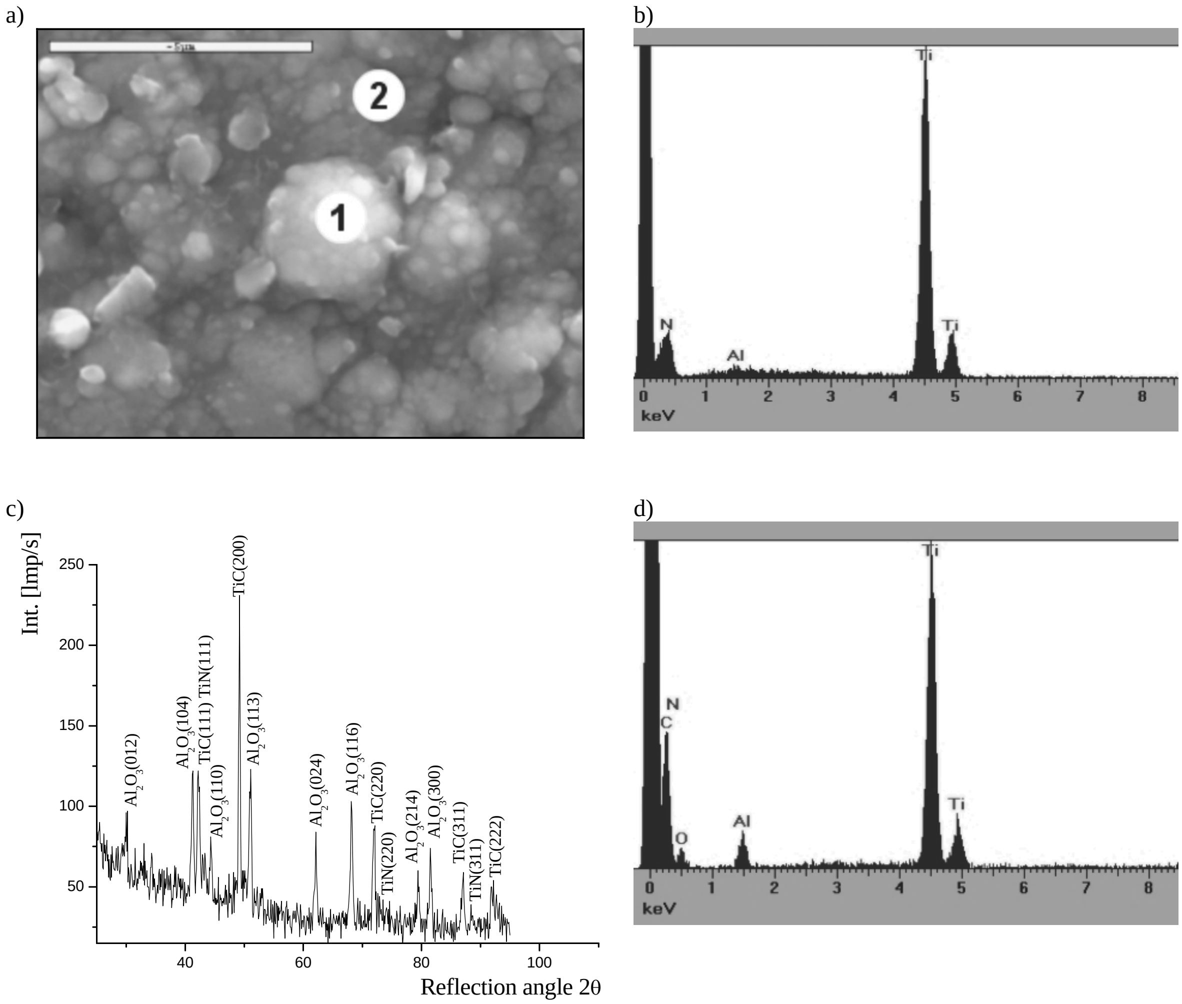

Fig. 3. (Ti,Al,Si)N (1) coating deposited on the Al_2O_3+TiC oxide ceramics: a) Topography of the coating surface, b) X-ray energy dispersive plot from the area 1 as in figure a, c) X-ray phase analysis, d) X-ray energy dispersive plot from the area 2 as in figure a

Table 2.
Comparison of obtained properties

Substrate	Coating	Microhardness, GPa	Critical load, N (max load)	Cutting conditions	Cutting quality, R_a, µm	Tool life, min
Cemented carbide	uncoated	18.0	-	a = 1 mm, f = 0.10 mm/trn, V = 400 m/min, k = 70°, C45E steel	2.4	1’00”
	(Ti,Al,Si)N (1)	31.0	57.2		1.9	20’00”
	(Ti,Al,Si)N (2)	32.0	59.5		1.2	27’00”
	uncoated	25.0	-		2.8	14’00”
	(Ti,Al,Si)N (1)	33.3	115 (200)		1.5	43’00”
	(Ti,Al,Si)N (2)	35.2	107 (200)		0.9	43’00”
Al_2O_3+ZrO_2	uncoated	18.5	-	a = 2 mm, f = 0.15 mm/trn, V = 200 m/min, k = 70°, grey cast iron	1.80	11’00”
	(Ti,Al,Si)N (1)	19.2	40		1.70	15’00”
	(Ti,Al,Si)N (2)	40.9	76		1.77	14’00”
Al_2O_3+TiC	uncoated	19.7	-		2.30	13’30”
	(Ti,Al,Si)N (1)	25.3	40		1.63	17’30”
	(Ti,Al,Si)N (2)	40.3	71		1.37	19’00”
Al_2O_3+$SiC_{(w)}$	uncoated	18.7	-	a = 2 mm, f = 0.2 mm/trn, V = 250 m/min, k = 70°, spheroidal cast iron	1.53	8’00”
	(Ti,Al,Si)N (1)	24.8	70		1.37	10’30”
	(Ti,Al,Si)N (2)	40.2	58		1.13	11’00”
Si_3N_4	uncoated	18.5	-	a = 2 mm, f = 0.15 mm/trn, V = 200 m/min, k = 70°, grey cast iron	5.60	8’00”
	(Ti,Al,Si)N (1)	23.3	22 (100)		5.10	8’00”
	(Ti,Al,Si)N (2)	35.2	23 (100)		4.10	8’00”

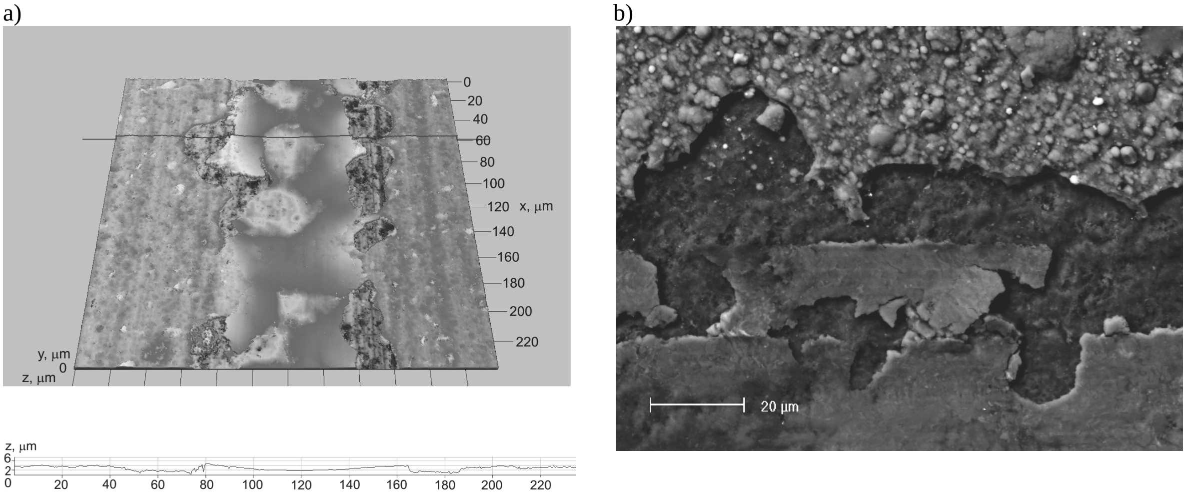
a)
b)

Fig. 4. Scratch test: Indenter trace of the (Ti,Al,Si)N (1) coating surface deposited onto the Si_3N_4 nitride ceramics substrate a) confocal microscope, b) SEM

3.3. Properties of investigated materials

The microhardness tests revealed that the uncoated cemented carbides, cermets, nitride and oxide ceramics has hardness equal to 18.0 to 25.0 GPa respectively. Deposition of the coatings onto the specimens causes the surface layer hardness increase reaching from 19.20 to 40.90 GPa, that is up to 100% more compared to the substrate hardness (Table 2).

The critical load values L_c (AE) were determined using the scratch method with the linearly increasing load („scratch test”), characterising adherence of the investigated coatings to the cermets and tool ceramics. The critical load was determined as the one corresponding to the acoustic emission increase signaling beginning of spalling of the coating. The coatings deposited onto the investigated substrates are characterised by good adherence (L_c = 40-137 N), only to the (Ti,Al,Si)N (1) gradient coating deposited onto the nitride ceramic substrate has a lower adherence equal L_c=22 N (Table 2).

Defects of the coatings, deposited onto the nitride ceramics are characterised by a significant number of the coating spalling defects on both scratch edges and by delamination within the scratch ending up at its final part with the local coating delamination at its contact with the scratch (Fig. 4).

In the case of coatings on Al_2O_3+ZrO_2 ceramic and cermet substrates the clear correlation between the improvement of wear resistance of multi-point inserts and the increase of surface layer microhardness and good adherence were stated. The very good adherence of PVD coatings to cermet substrate is a result of the fact that the source of the nitrogen for the developing coating is not only the working gas, but also nitrogen coming from the substrate alone, making diffusion mixing of elements in the interlayer easier. Therefore, not only the adhesion decides the adherence, but also the diffusion mixing of elements in the interlayer, between the substrate and the coating, with two simultaneously available sources of diffusion of elements constituting the coatings and titanium from the coating to the substrate, and also of nitrogen, and perhaps also titanium from the substrate to the coating, the more so, as the substrate temperature during the process is 550°C. However, the coatings deposited by the use of PVD methods on Si_3N_4 substrate do not cause the increase of cutting tool life as a result of weak substrate adherence in spite of the increase of microhardness. Undoubtedly, the influence on such significant differences in adherence of examined coatings has the fact that Si_3N_4 based nitride ceramic does not conduct current, which to a great degree makes the creation of PVD coatings on such substrate difficult.

The existence of interlayers between the substrates and coatings causes the increase of adherence and also the improvement of cutting ability of examined materials which was confirmed among others by research carried out with the GDOES and AES method (Figs. 5, 6).

The GDOES analyses show that in the interlayer the increase of concentration of elements being in the composition of the substrate from the coating surface appears at the concurrent decrease of elements creating coatings. It testifies the existence of the interlayer between substrate material and the coating with earlier described diffusion migration of the chemical elements, having the influence on the improvement of adherence of deposited coatings to the substrate. However, the results cannot be interpreted unequivocally because of the heterogeneous material evaporation from the sample surface during the analysis. The existence of the interlayer can be explained also by the action of ions having high energy and causing the migration of elements in the interlayer, the increase of desorption of substrate surface and the appearance of defects in the substrate in the conditions of coating deposition, especially in the PVD process.

Examinations in the glow discharge optical emission spectrometer GDOES make it possible only to evaluate the qualitative differences of the chemical compositions in the selected micro-area of each specimen. Based on these examinations, a certain regularity was found out of the distribution of elements included in both coatings and substrate. The analysis made using the glow discharge optical emission spectrometer GDOES indicates that in the analysed cases, in the joint zone, concentration of elements included in the substrate grows from the coating surface with the simultaneous decreasing concentration of elements constituting the coatings. This may attest to the existence of the interface between the substrate material and the coating, resulting in improvement of adherence between the deposited coatings to the substrate, albeit these results cannot be interpreted unequivocally because of the inhomogeneous vaporizing of the material from the specimens' surfaces during the analysis. The existence of the interface should be also connected with the increase of desorption of the substrate surface and development of defects in the substrate as well as with displacement of elements in the joint zone due to interaction of the high-energy ions (Fig. 5).

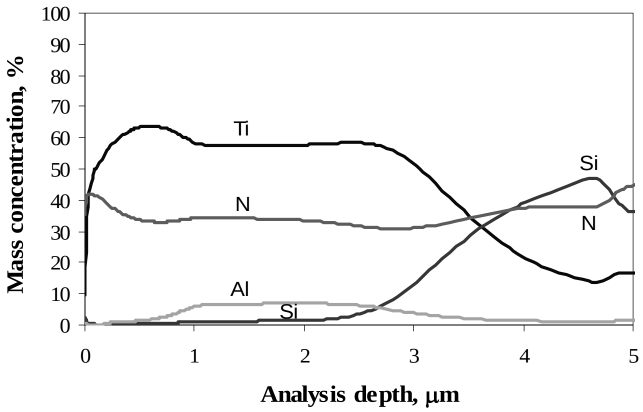

Fig. 5. Changes of concentrations of constituents of the (Ti,Al,Si)N (2) coating and of the substrate materials of Si_3N_4 ceramic nitride analysed in GDOS spectrometer

During the Auger Electron Spectroscopy (AES) investigations the depth profile finishing in the vicinity of substrate was reached after 3450 min of sputtering by Ar+ ions at the accelerating voltage of 2 kV. After the ion etching Auger survey spectrum of (Ti,Al,Si)N (1) gradient coating deposited on the Al_2O_3 oxide tool ceramic reinforced with SiC whiskers was carried out (Fig. 6). Unequivocal peak O1s of oxygen has identified on auger survey spectrum. Simultaneous occurrence of oxide and nitride at investigated area indicate, that the intermediate area between the coating and Al_2O_3+$SiC_{(w)}$ oxide ceramic substrate was reached. Simultaneous occurrence of titanium and nitride at investigated area can indicate the diffusion coating components into substrate material.

3.4. Cutting ability of tools reinforced with developed coatings

As a result of the research carried out it was found out that the deposition of (Ti,Al,Si)N coatings by the use of PVD method causes the increase of cutting properties of tools made of cemented carbides, cermets, Al_2O_3+ZrO_2, Al_2O_3+TiC, Al_2O_3+$SiC_{(w)}$ oxide ceramics and Si_3N_4 nitride ceramics comparing to adequately uncoated tools.

The detailed analysis were carried out of the relationships between the functional properties of the investigated tool materials and their structure, as well as their mechanical properties, taking into account the physical phenomena occurring during the coating deposition process.

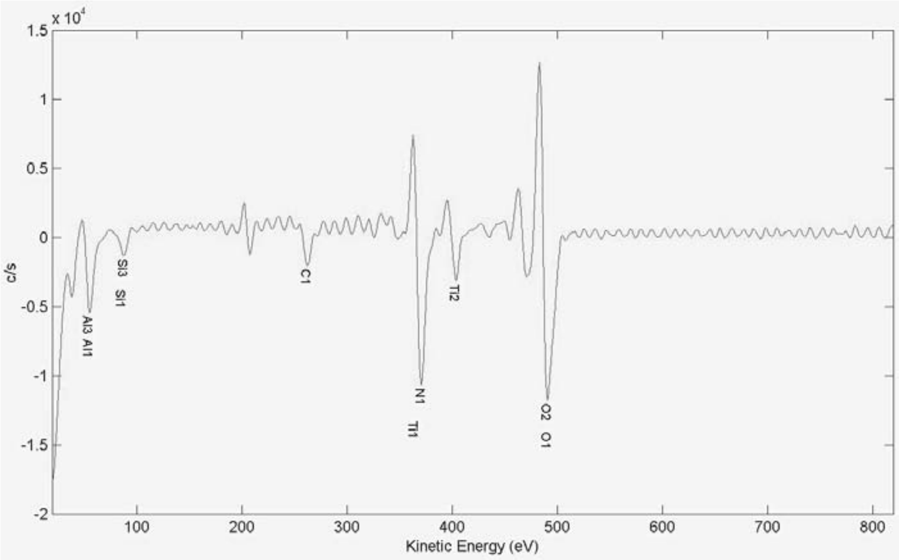

Fig. 6. Auger survey spectrum of (Ti,Al,Si)N (1) gradient coating deposited on the Al_2O_3 oxide tool ceramic reinforced with SiC whiskers after 3450 min ion etching

Comparison of experimental results of the VB wear of the cemented carbides, cermets, Al_2O_3+ZrO_2, Al_2O_3+TiC, Al_2O_3+$SiC_{(w)}$ oxide ceramics and Si_3N_4 nitride ceramics: uncoated and coated depending on machining time has been shown in Table 2.

4. Conclusions

Deposition of the multicomponent gradient and multilayer coatings with the PVD method in the cathode arc evaporation CAE process, whose basis is the Al and Si solid secondary solution in the TiN titanium nitride, isomorphous with the alternating pure titanium nitride TiN, on tools made from oxide, nitride ceramics and tool cermets, results in the increase of mechanical properties in comparison with uncoated tool materials, deciding thus the improvement of their working properties.

Coatings deposited onto the oxide, nitride ceramics and tool cermets are characterized by a structure without pores and discontinuities and by tight adherence to themselves and of the entire multilayer coating to the substrate. Basing on the examinations of thin foils in the transmission electron microscope it was found out that the structure of the substrates and coatings is fine-grained - phase particles is smaller than 500 nm.

The microhardness of investigated materials grows significantly after deposition of the coatings. Most coatings deposited onto the investigated substrates are characterised by good adherence. The very good adherence of PVD coatings to cermet substrate is a result of the fact that the source of the nitrogen for the developing coating is not only the working gas, but also nitrogen coming from the substrate alone, making diffusion mixing of elements in the interlayer easier. Therefore, not only the adhesion decides the adherence, but also the diffusion mixing of elements in the interlayer, between the substrate and the coating, with two simultaneously available sources of diffusion of elements constituting the coatings and titanium from the coating to the substrate, and also of nitrogen, and perhaps also titanium from the substrate to the coating, the more so, as the substrate temperature during the process is 550°C.

Deposition of (Ti,Al,Si)N nanocrystalline coatings by the use of PVD method causes the increase of cutting properties of tools made of cermets for ca. 300% and of Al_2O_3+ZrO_2 for ca. 100% comparing to adequately uncoated tools.

Employment of the hard wear resistant coatings deposited onto the sintered ceramic tool materials with the physical deposition from the gaseous phase (PVD) is reckoned as one of the most important achievements in the last years in the area of improvement of the service properties of ceramic cutting tools. Depositing the wear resistant coatings of the gradient and multi (Ti,Al,Si)N types onto the investigated ceramic tool materials makes it possible to achieve the clear improvement of their tool life and also of the quality of the machined surfaces, reduction of machining costs and elimination of cutting fluids used in machining. The widespread use in machining of oxide and nitride ceramics, as well as of cermets with the complex nanocrystaline coatings deposited in the PVD processes contributes to the increased interest in the contemporary "Near-Net-Shape" technology, i.e., manufacturing semi-products with the shape and dimensions as close as possible to those of the finished products.

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References

[1] L.A. Dobrzański, K. Gołombek, J. Mikuła, D. Pakuła, Multilayer and gradient PVD coatings on the sintered tool materials, Proceedings of the 11th International Research Conference "Trends in the Development of Machinery and Associated Technology" TMT 2007, Hammamet, Tunisia, 2007, 5-33.

[2] L.A. Dobrzański, L.W. Żukowska, 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.

[3] L.A. Dobrzański, L.W. Wosińska, J. Mikuła, K. Gołombek, Multicomponent and gradient PVD coatings deposited on the sintered tool materials, Materials Engineering 3-4/157-158 (2007) 627-631.

[4] K. Gołombek, L.A. Dobrzański, Hard and wear resistant coatings for cutting tools, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 107-110.

[5] L.A. Dobrzański, D. Pakuła, J. Mikuła, K. Gołombek, Investigation of the structure and properties of coatings deposited on ceramic tool materials, International Journal of Surface Science and Engineering 1 (2007) 111-124.

[6] L.A. Dobrzański, J. Mikuła, K. Gołombek, Structural characteristic of the modern sintered tool materials, Materials Science Forum 530-531 (2006) 499-504.

[7] J. Mikuła, L.A. Dobrzański, PVD and CVD coating systems on oxide tool ceramics, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 75-78.

[8] L.A. Dobrzański, L. Wosińska, J. Mikuła, K. Gołombek, T. Gawarecki, Investigation of hard gradient PVD (Ti,Al,Si)N coating, Journal of Achievements in Materials and Manufacturing Engineering 24/2 (2007) 59-62.

[9] M. Rosso, Properties of coatings on sintered iron alloys, Worldwide Journal of Achievements in Materials and Manufacturing Engineering 19/1 (2006) 35-41.

[10] L. Cunha, A.C. Fernandes, F. Vaz, N.M.G. Parreira, Ph. Goudeau, E. Le Bourhis, J.P. Riviere, D. Munteanu, F. Borza, Characterisation of TiC_xO_y thin films produced by PVD techniques, Journal of Achievements in Materials and Manufacturing Engineering 21/1 (2007) 35-38.

[11] 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.

[12] W. Grzesik, Z. Zalisz, S. Król, Tribological behaviour of TiAlN coated carbides in dry sliding tests, Journal of Achievements in Materials and Manufacturing Engineering 17 (2006) 279-282.

[13] 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.

[14] P.H. Mayrhofer, Ch. Mitterer, L. Hultman, H. Clemens, Microstructural design of hard coatings, Progress in Materials Science 51 (2006) 1032-1114.

[15] B.A. Movchan, Functionally graded EB PVD coatings, Surface and Coatings Technology 149 (2002) 252-262.