Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 34
ISSUE 1
May
2009

Study on steel matrix composites with (Ti,Al)N gradient PVD coatings

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Received 12.02.2009; published in revised form 01.05.2009

Manufacturing and processing

ABSTRACT

Purpose: The paper presents investigation results of structure and properties of steel matrix composites (SMC) uncoated and coated with hard (Ti,Al)N gradient coatings with use of physical vapour deposition process.
Design/methodology/approach: Powder Metallurgy, PVD, TEM, SEM, XRD, GDOES, Microhardness tests, Scratch test.
Findings: Depositing of gradient (Ti,Al)N coatings onto SMC materials meets the requirements connected with hybrid technology of production, joining powder metallurgy and physical vapour deposition techniques, in area of producing modern composite gradient tool materials. Sintered steel matrix composites reinforced with hard carbide phases and deposited with gradient PVD coatings can be widely employed in industry for tools, especially for machining and plastic forming processes.
Practical implications: Tool materials used especially for tools employed especially in machining and plastic forming processes.
Originality/value: Modern methods of powders' forming application make possible to achieve gradient structure of tool, which is very advantageous in respect of mechanical properties. Employed compositions of technologies joining powder metallurgy and physical vapour deposition techniques give the possibility to achieve high properties characteristic of cemented carbides with the high ductility characteristic of steels.
Keywords: Sintering; PVD; Tool materials; Composite materials; FGM

Reference to this paper should be given in the following way:
G. Matula, Study on steel matrix composites with (Ti,Al)N gradient PVD coatings, Journal of Achievements in Materials and Manufacturing Engineering 34/1 (2009) 79-86.

1. Introduction

Permanent development of existing manufacturing processes and introducing of new solutions in processing technologies is connected with increasing of products properties, increasing of tool properties and decreasing of production costs, with taking in to account ecology aspects of manufacturing processes.

Up-to-date manufacturing techniques in area of sintered tool materials aim at maximal utilization of raw material and at achieving as much as possible close to final shape of tools after sintering process. Expensive plastic forming and machining can be eliminated in this way. Especially powder injection molding (PIM) and pressureless forming (PLF) seems to be very hopeful in that aspect. PIM method originate from injection moulding of polymers, widely used in production of thermoplastics. Advantages of injection moulding can be used for processing of metals, ceramics and cermets making it possible to develop of „near-net-shape" technologies.

Employment of powder metallurgy, especially of the contemporary methods of forming the powders improves the service properties of the high-speed steels. However, application potential of this material is still limited. This can be changed forming the tool surface with the relevant technology, which significantly extends their life and resistance to their degradation processes. New generation of the composite gradient tool materials with the high-speed steel core, reinforced with the WC and TiC type hard carbide phases providing of high properties characteristic of cemented carbides with the high ductility characteristic of steel. Properties can be also changed by putting down the durable coating material on the surface [1-11].

Hard, wear-resistant PVD coatings like (Ti,Al)N differ in structure and properties from much less hard and more ductile substrates (e.g. steels). This is a reason of stress accumulation at coating/substrate connection zone occurring during plastic strain process. Such accumulation of internal stresses can be a reason of cracking and delamination of coating. The abrupt change of properties can be reduced with use of FGM idea in coatings development. Gradient character of (Ti,Al)N coating can be achieved by changing of substrate's bias voltage, by change of magnetron working parameters or by changing the pressure of gas influencing the nitrogen fraction. Such character of coatings structure can be reason of significant improving of coatings adhesion [12-15].

The paper presents investigation results of structure and properties of steel matrix composites (SMC) uncoated and coated with hard (Ti,Al)N gradient coatings with use of physical vapour deposition process.

2. Experimental procedure

Contemporary methods of powders forming and sintering , as well as the PVD coatings deposition technique were merged to develop a new generation of abrasion wear resistant tool materials with the properties and structure gradient. Employment of the state-of-the-art powder metallurgy methods for developing a tool and coating it in the process of physical deposition from the gaseous phase makes it possible obtaining the tool material with the layered or gradient structure, depending on the method and fabrication conditions used.

The tool, with the relatively ductile core with the structure of composite and of the high-speed- or constructional steel turning into the composite structure in its surface layer, was coated with the hard, abrasion wear resistant coatings in the PVD process. Two powder forming techniques were used to fabricate the substrate material, i.e., injection moulding and pressureless forming. Both these methods require using a large amount of binder in the form of polymer which makes it possible to form the fabricated element's shape, next the binder has to be removed by thermal or solvent degradation and finally the porous green compact has to be sintered. In case of injection moulding the Arburg type commercial injection moulding machine does not make it possible to obtain the compact with the gradient or layered structure. Therefore, the substrate material is a kind of composite with the uniform structure and only its the PVD coating deposited after sintering and heat treatment has the gradient character.

The fabrication process of composite based on the HS6-5-2 high-speed steel substrate with the addition of carbides powders was described in detail in the previous work [8]. The composite hardness in the heat treated state, before deposition with the PVD coatings is about 1100 HV. The type of the deposited coatings on the substrate material fabricated in this way, designated as PIM HSSMC, is presented in Table 1. In case of tool material obtained by the pressureless forming two substrate types were picked out, coated with the PVD coatings, presented in Table 1 and designated as HS6-5-2/PLF HSSMC and 41Cr4/PLF SMC. This material was fabricated by putting down the surface layer with the pressureless forming method on the high-speed- or constructional steel substrate. These steels were selected to retain the relatively high core ductility. The coating formed with the pressureless method, like the injection moulded materials requires carrying out binder degradation and finally sintering. Fabrication process of these materials was described in detail in paper [8]. Structure of the newly developed tool materials, fabricated by injection moulding and pressureless forming of coatings on the commercially available steels is presented in Figures 1, 2.

Table 1.
Type of manufactured materials

Type of materials	PIM HSSMC	HS6-5-2/PLF HSSMC	41Cr4/PLF SMC
Substrate	High Speed Steel Matrix Composite	High Speed Steel Matrix Composite type of FGM with HS6-5-2 core	Steel Matrix Composite type of FGM with 41Cr4 core
Manufacturing method	Powder Injection Moulding	Pressureless Forming of layer on the commercial steel	Pressureless Forming of layer on the commercial steel
Type of PVD coating	(Ti,Al)N	(Ti,Al)N	(Ti,Al)N

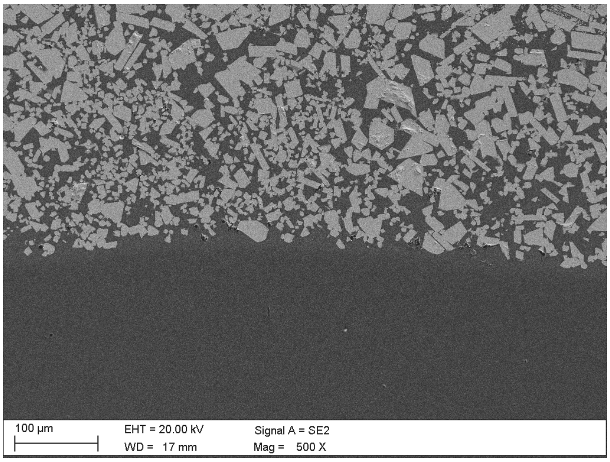


Fig. 1. Microstructure of 41Cr4/PLF SMC sintered at 1240°C

Injection moulded materials (PIM HSSMC) were quenched directly from sintering point (1260ºC) in oil, then triple tempered at temperature of 600ºC. Such heat treating process allowed to achieve maximal hardness of 1100 HV. In case of HS6-5-2/PLF HSSMC and 41Cr4/PLF SMC, samples were austenitized at temperature of 1240ºC, quenched and triple tempered at temperature of 570ºC.

The investigations were carried out on the steel matrix composite uncoated and coated using the PVD method, with the (Ti,Al)N gradient coatings (Table 1).

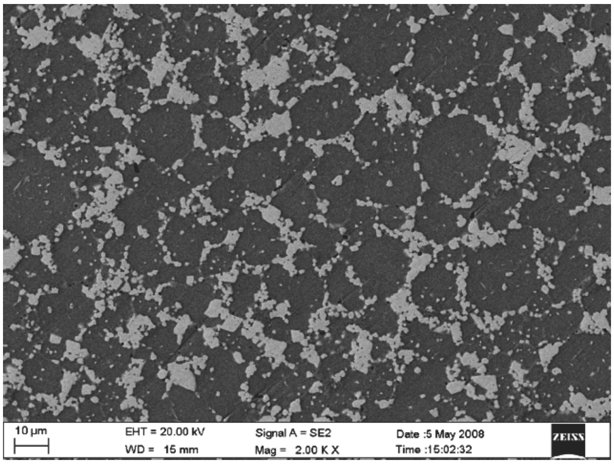


Fig. 2. Microstructure of HSSMC (HS6-5-2 reinforced by WC) sintered at 1260°C with PIM method

Such prepared substrates was coated using the PVD method with (Ti,Al)N gradient coating. Following parameters were used in coating deposition: substrate polarisation -200 V, substrate temperature 500°C, pressure in the chamber 0.2 Pa.

Structure examination, qualitative and quantitative X-ray microanalyses were made on ZEISS SUPRA 35 scanning microscope. To obtain the fracture images the Secondary Electrons (SE) detection method was used with the accelerating voltage in the range of 20 kV and maximum magnification 50000 x.

The diffraction examinations and examinations of thin foils were made on the JEM-3010 JEOL transmission electron microscope at the accelerating voltage of 300 kV and maximum magnifications 250 000x.

Evaluation of the phase composition of the investigated coatings and substrates was made using the Panalytical X'Pert X-ray diffractometer, using the filtered cobalt lamp rays with the voltage of 40 kV and heater current of 20 mA.

The microhardness tests using the Vickers method were made on the FUTURE-TECH FM-700ARS tester and SHIMADZU DUH 202.

Changes of the chemical concentrations of the coating constituents in the direction perpendicular to its surface and of concentrations in the interlayer between the coating and the substrate material were evaluated basing on examinations made in the LECO Instruments glow-discharge optical emission spectroscope GDOES-750A. The following spectrometer Grimm lamp working conditions were set during the examinations: lamp internal diameter – 4 mm; lamp power supply voltage – 700 V; lamp current – 20 mA; working pressure – 100 Pa. The continuous concurrent spectrometer in the Paschen-Runge configuration was used in the device, with the focal length of 750 mm, with the holographic mesh of 2400 lines per millimeter. The maximum depth of the chemical composition analysis is a dozen or so µm.

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 tests were made with the following parameters: load range 0-200 N, load increase rate (dL/dt) 100 N/min, penetrator's travel speed (dx/dt) 10 mm/min, acoustic emission detector's sensitivity AE 1.

3. Discussion of results

Basing on SEM and light microscope examinations it was found, that as a result of employing hybrid manufacturing processes (HS6-5-2/PLF HSSMC and 41Cr4/PLF SMC) completed with PVD process, composite gradient structure of tool materials was achieved. Developed materials are characterized by growing fraction of hard carbide phases in 1-2 mm thick surface layer of substrate (Figs. 1, 2) and are coated with up to 2 µm thick PVD gradient coatings (Fig. 3). Developed functional graded materials are characterized of the dense, compact structure and low porosity, without fractures and discontinuities (Figs. 1, 2). Moreover, in case of HSSMC substrate, manufactured with use of PIM process, concentration of reinforcing carbide phases at the grain boundaries was observed (Fig. 2). Porosity tests of investigated PIM HSSMC, HS6-5-2/PLF HSSMC and 41Cr4/PLF SMC materials gave the basis to state, that all developed composite, gradient structured tool materials are characterized by low porosity up to 1.03 % in case of HS6-5-2/PLF. HSSMC manufactured with use of PIM process is characterized by the lowest porosity of 0.65%.

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 SMCs is dispersed carbides, mostly of the WC type. Structure of the thin foil from 41Cr4/PLF SMC is presented in Figure 4. 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.

It was found out during the observations on the SEM that (Ti,Al)N gradient coatings developed in the PVD process were put down evenly on the substrates: PIM HSSMC, HS6-5-2/PLF HSSMC and 41Cr4/PLF SMC. The coatings are compact without any pores and cracks and adhere tightly to their substrates (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, that the substrate is characterized by the evenly distributed high-melting carbides in the steel matrix. Structure of the investigated substrates is characterized by the fine grains of the remanding in respect of chemical composition M_6C and MC carbides (Figs. 3, 5). It was found out, basing on the analysis of chemical composition of the substrate fracture surface with the EDS method, that in the substrate elements suitable for HS6-5-2 high speed steel occur respectively, and also W, Ti, and C respectively and also N from carbides or nitrides.

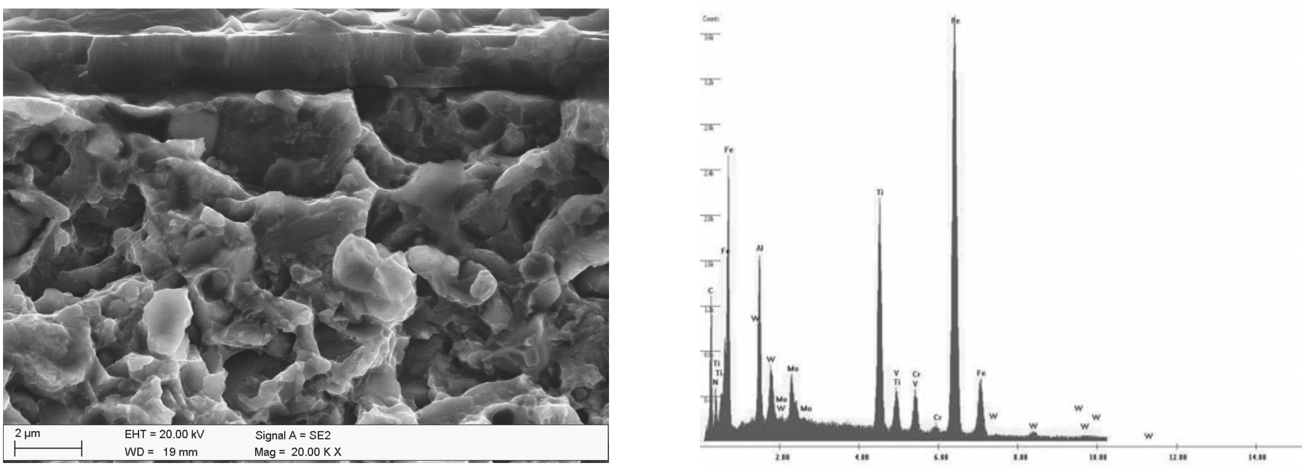
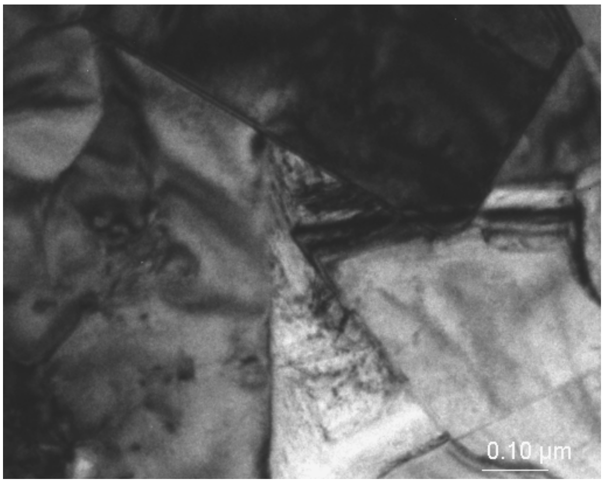
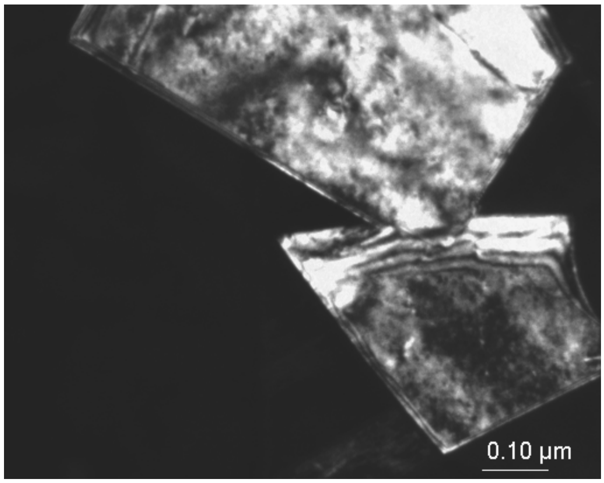


Fig. 3. Fracture surface of the PIM HSSCM substrate with (Ti,Al)N coating and X-ray energy dispersive plot

a)



b)



c)

d)

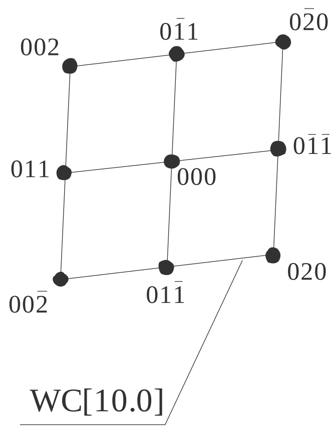


Fig. 4. a) Structure of the thin foil from the HS6-5-2/PLF HSSMC substrate, b) dark field, c) diffraction pattern for the area as from figure a, d) solution of the diffraction pattern from figure c, (TEM)

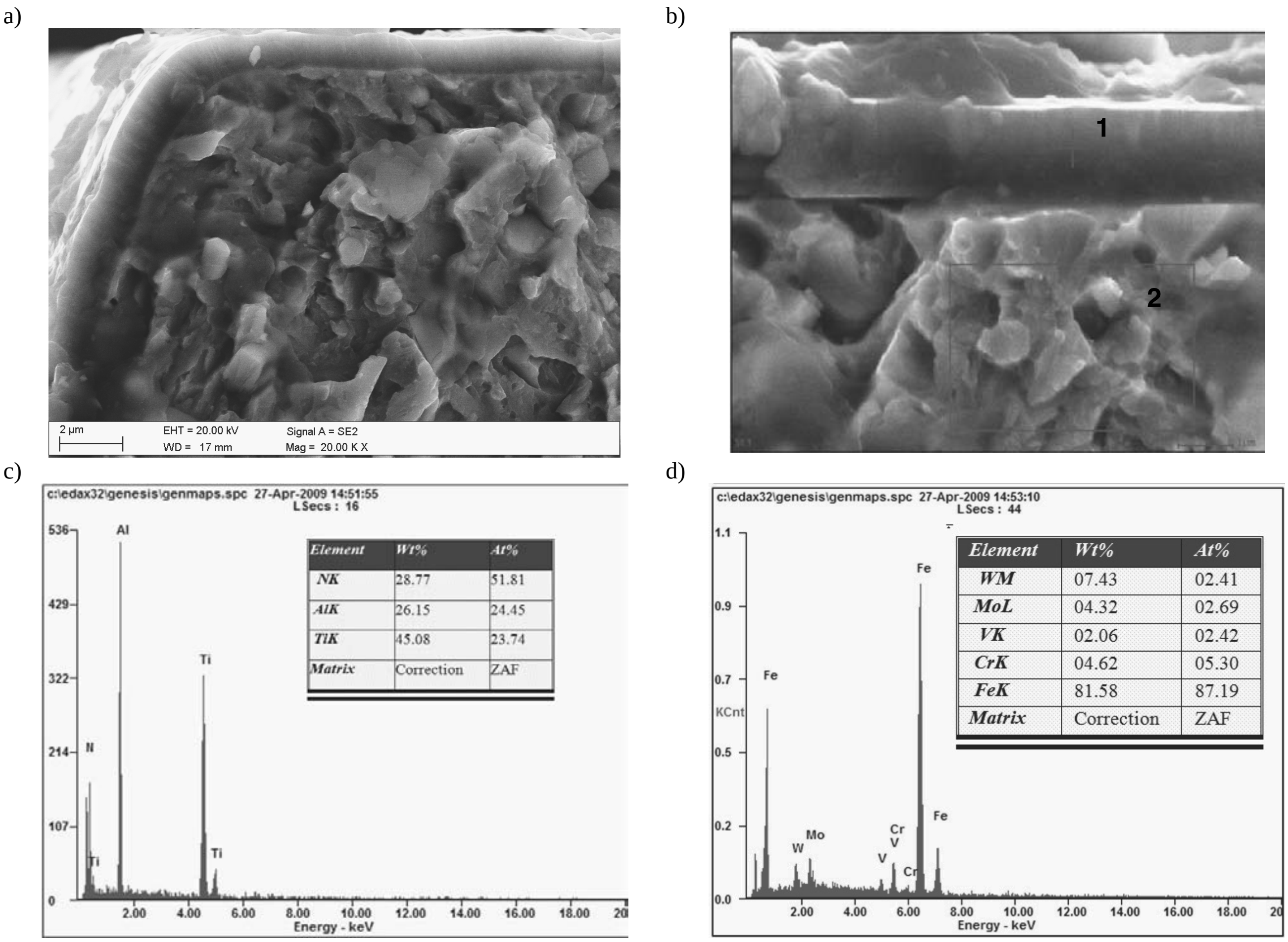


Fig. 5. a, b) Fracture surface of the (Ti,Al)N coating deposited on PIM HSSCM substrate, c) X-ray energy dispersive plot from the area 1, d) X-ray energy dispersive plot from the area 2

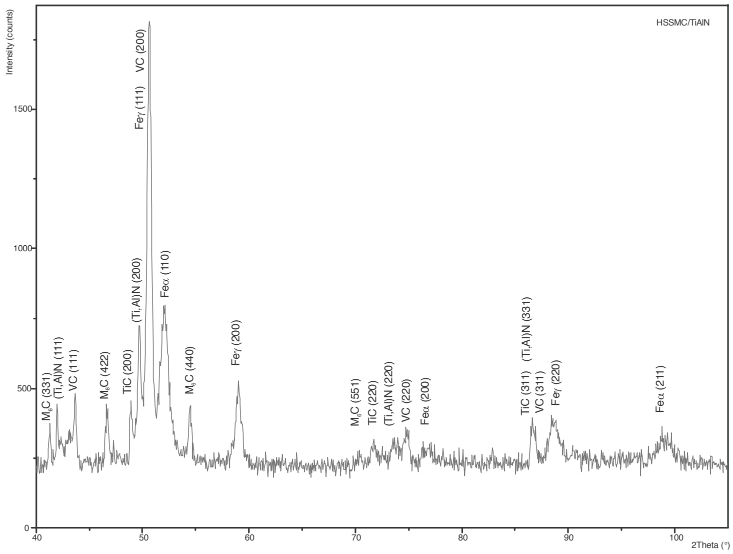


Fig. 6. X-ray diffractions pattern of the HS6-5-2/PLF HSSMC with the (Ti,Al)N gradient coating

Phase composition of developed composite tool materials with (Ti,Al)N was examined with use of X-ray qualitive phase analysis methods. Reflections of TiN, being in essence the most probably the composed nitride of (Ti,Al)N, come from PVD coating, as well as large number of reflections from substrates (e.g. infusible carbide phases of MC and M6C and Feα i Feγ) was stated. Differentiation of the TiN and (Ti,Al)N phases with use of diffraction methods is impossible because of isomorphism. (Ti,Al)N is in essence secondary solid solution on the base of titanium nitride TiN. It was demonstrated, using the X-ray qualitative phase analysis methods, that – according to the initial assumptions – coatings containing the (Ti,Al)N nitride phases, were developed on surfaces of the investigated substrates (Fig. 6).

Examinations of thin foils from (Ti,Al)N coatings confirm that, according to the original assumptions, coatings containing the TiN type phases were deposited onto the all substrates. It is not feasible to differentiate these phases from the diffraction point of view, due to isomorphism of the TiN and (Ti,Al)N phases. Structures of coatings deposited onto the substrates manufactured with use of PIM and PLF processes are presented in Fig. 7.

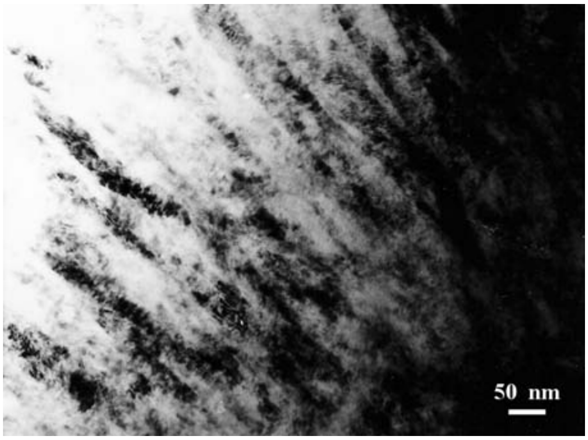
The gradient character of deposited coating and existance of interlayer between substrate and coatings causes the increase of adherence and also can improve the cutting ability of examined materials what was confirmed among others by researches made by the use of GDOES method. These researches confirm presence of titanium, aluminum, and nitrogen in the investigated coatings and of the substrate elements, among others Fe, W (Figure 8). The 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 about the existence of the interlayer between substrate material and the coating with earlier described diffusional 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 equivocally because of 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 disorption of substrate surface and the appearance of defects in the substrate in the conditions of coating deposition, especially in the PVD process.

It was revealed basing on the micro-hardness tests that the graded substrate hardness in surface area is 850-1100 $HV_{0,1}$. Deposition of the (Ti,Al)N coating onto the developed SMCs causes the significant surface layer hardness increase up to 2950 $HV_{0,1}$ (Table 2). The observed hardness increase of the surface layer compared to the uncoated substrate hardness is about 200%.

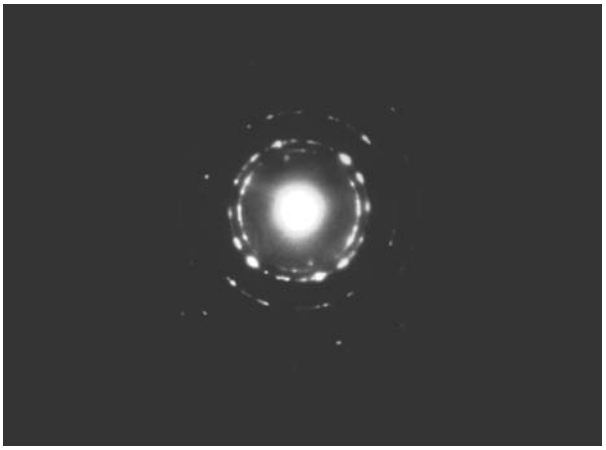
The critical load values Lc (AE) were determined using the scratch method with the linearly increasing load („scratch test"), characterising adherence of the investigated coatings to the substrate. The critical load was determined as the one corresponding to the acoustic emission increase signalling beginning of spalling of the coating. The coatings deposited onto the investigated substrate are characterised by very good adherence L_c = 51-62 N (Fig. 9, Table 2).

Depositing the wear resistant gradient (Ti,Al)N coatings onto developed SMCs results in a significant increase of the surface layer microhardness. Together with good adhesion of coatings achieved thanks to applied gradient structure of coatings, it may contribute to the decrease of the wear intensity of cutting tools' flanks or plastic forming tools made from the developed materials.

a)



b)



c)

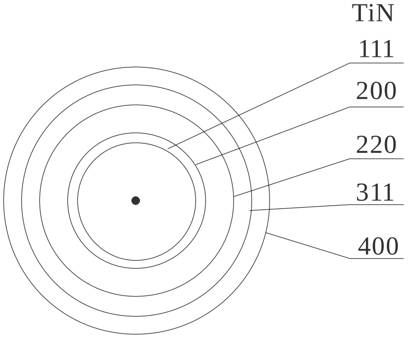


Fig. 7. a) Structure of the thin foil from the (Ti,Al)N coating deposited on HS6-5-2/PLF HSSMC substrate, b) diffraction pattern for the area as from figure a, c) solution of the diffraction pattern from figure c, (TEM)

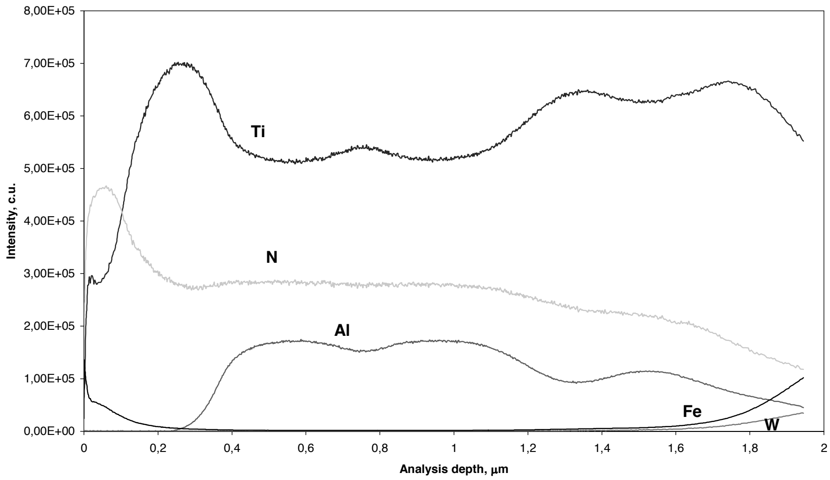


Fig. 8. Concentration changes of the (Ti,Al)N gradient coating elements, substrate material from the PIM HSSCM analysed in the GDOES spectrometer

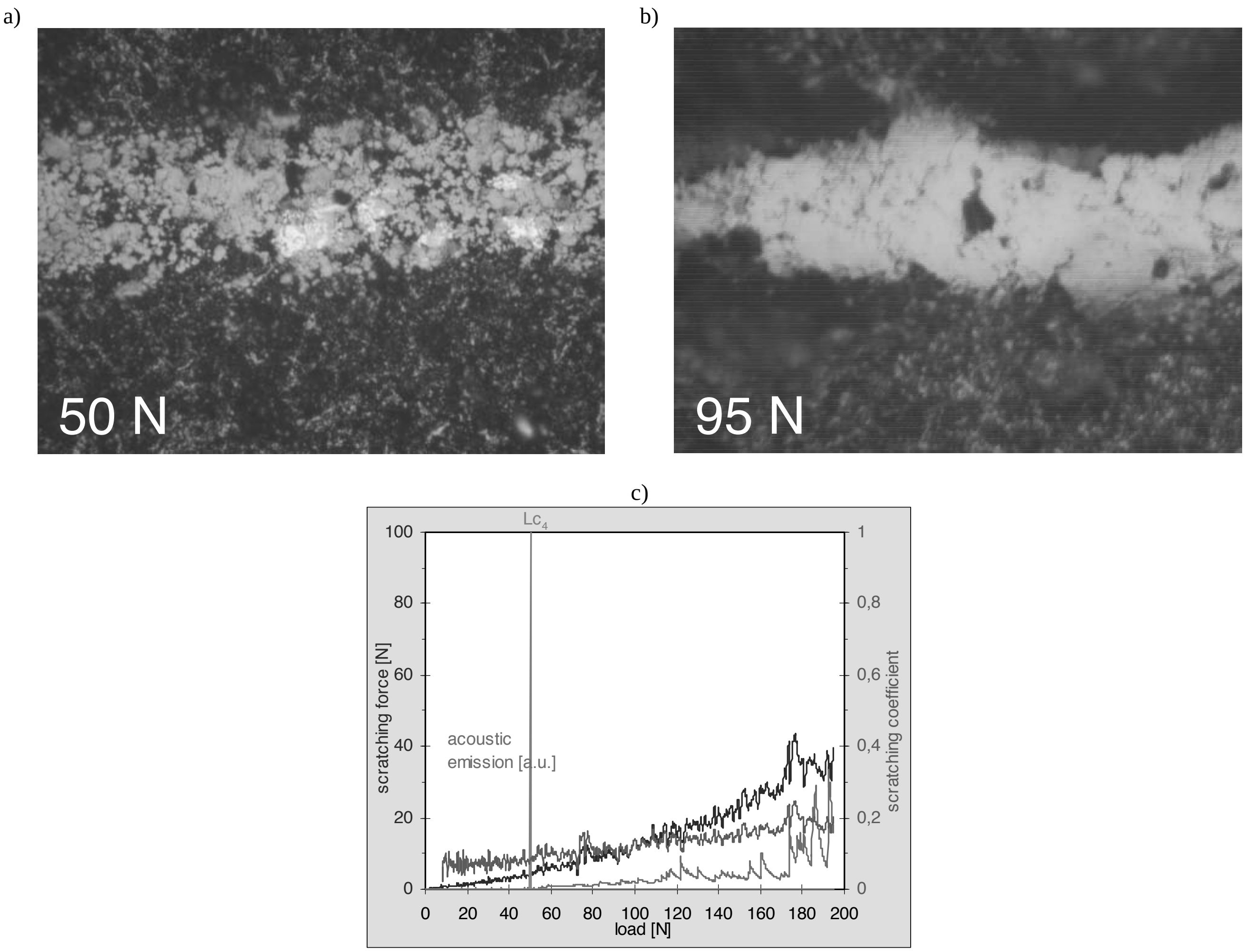


Fig. 9. a, b) Indenter trace with the optical L_c load, c) scratch test results of the (Ti,Al)N coating surface deposited on PIM HSSMC substrate

Table 2.
Characteristics of the HSS matrix composites with (Ti,Al)N gradient PVD coatings

Substrate	Coating		Porosity, %	Microhardness, HV	Critical load L_c, N
	Composition	Thickness, µm			
PIM	uncoated		0.65	1050	-
HS6-5-2/PLF			1.03	1100	-
41Cr4/PLF			0.78	850	-
PIM	(Ti,Al)N	1.6-1.8	-	2950	51.0
HS6-5-2/PLF			-	2850	62.5
41Cr4/PLF			-	2800	59.0

4. Conclusions

Hard, wear-resistant PVD coatings, like (Ti,Al)N differ in structure and properties from much less hard and more ductile SMC and HSSMC substrates. This is a reason of stress accumulation at coating/substrate connection zone occurring during plastic strain process. Such accumulation of internal stresses can be a reason of cracking and delamination of coating. Employed coatings characterized by gradient change of chemical composition can reduce this problem and make it possible to improve functional properties of developed tool materials.

Powder metallurgy PLF and PIM methods were used to fabricate the proposed gradient materials. Substrates was coated using the PVD method with (Ti,Al)N gradient coatings.

Depositing of gradient (Ti,Al)N coatings onto SMC materials meets the requirements connected with hybrid technology of production, joining powder metallurgy and physical vapour deposition techniques, in area of producing modern composite gradient tool materials. Sintered steel matrix composites reinforced with hard carbide phases and deposited with gradient PVD coatings can be widely employed in industry for tools, especially for machining and plastic forming processes.

It was stated, that modern methods of powders' forming application make possible to achieve gradient structure of tool, which is very advantageous in respect of mechanical properties. Employed consolidation of technologies joining powder metallurgy and physical vapour deposition techniques give the possibility to achieve high properties characteristic of cemented carbides with the high ductility characteristic of steels.

Depositing the wear resistant gradient (Ti,Al)N coatings onto developed SMCs results in a significant increase of the surface layer microhardness. Together with good adhesion of coatings achieved thanks to applied gradient structure of coatings, it may contribute to the decrease of the wear intensity of cutting tools' flanks or plastic forming tools made from the developed materials.

Acknowledgements

Research was financed partially within the framework of the Polish State Committee for Scientific Research Project N507 084 32/2398 headed by Dr Grzegorz Matula.

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