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Hard gradient (Ti,Al,Si)N coating deposited on composite tool materials

L.A. Dobrzański*, L.W. Żukowska, J. Mikuła, K. Gołombek, T. Gawarecki
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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ABSTRACT

Purpose: This paper presents investigation of gradient coating of (Ti,Al,Si)N deposited on the Al_2O_3+$SiC_{(w)}$ oxide ceramics substrate deposited with the PVD process.

Design/methodology/approach: Structure of substrate and coating was investigated with use of scanning electron microscopy (SEM); The X-Ray Photoelectron Spectrometry (XPS) and Auger Electron Spectrometry (AES) examinations was carried out for proving the gradient character of the (Ti,Al,Si)N coating. The investigation includes also microhardness and roughness tests of the deposited coating and used substrate. Scratch test results was analysed to introduce adherence of the investigated coating.

Findings: Gradient structure and main properties of the investigated materials were introduced. It has been stated, that properties of the coated with gradient (Ti,Al,Si)N coating oxide tool ceramic increase in comparison with uncoated material.

Practical implications: Depositing the wear resistant gradient coating onto the Al_2O_3+$SiC_{(w)}$ oxide tool ceramic results in a significant increase of the surface layer microhardness, contributing most probably in this way in machining to the decrease of the wear intensity of cutting tools' flanks made from the Al_2O_3+$SiC_{(w)}$ oxide tool ceramic.

Originality/value: 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.

Keywords: Gradient coatings; XPS; AES, PVD; Oxide ceramics; Whiskers

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MATERIALS

1. Introduction

SiC whisker-reinforced ceramic composites were an innovation that came into importance for potential structural applications because of the significant improvements in the mechanical properties these materials offered as compared to the monolithic materials. The incorporation of SiC whiskers into Al_2O_3 ceramics resulted in increases in strength, fracture toughness, thermal conductivity, thermal shock resistance and high temperature creep resistance. These discoveries initiated several years of intense study into this class of composites [1, 9, 3, 4, 14].

Ceramic tools containing the SiC whiskers have the life exceeding other tool materials, allowing at the same time very high cutting speeds. One of the disadvantages of the reinforced ceramics is decay of whiskers in case of machining alloys containing iron, which significantly limits its use [1,4, 5, 14, 16, 17].

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. Gradient coatings can be deposited onto cutting tools in the PVD processes made as well from the high speed steels, cemented carbides, cermets, and also from ceramic materials. PVD processes are a technique of the thin wear resistant coatings. In the development of new, contemporary materials the functionality is often improved by combining materials of different properties into composites. Coating composites are designed to specifically get better properties such as tribological, electrical, optical, electronic, chemical and magnetic [2-7, 10-13, 15].

X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) have long been used as a surface analytical methods for the determination of composition and chemistry of the elements in a material. are well-established techniques for surface analysis and also (when combined with sputter depth profiling) for thin film and interface analysis [1].

This paper presents investigation of gradient coating of (Ti,Al,Si)N deposited on the Al_2O_3+$SiC_{(w)}$ oxide ceramics substrate deposited with the PVD process.

2. Experimental procedure

Experiments were carried out on Al_2O_3+$SiC_{(w)}$ oxide ceramics. Cathodic arc evaporation PVD process was employed for deposition of (Ti,Al,Si)N gradient coating. Deposition conditions: substrate temperature 500 °C, negative bias of – 200V and total pressure of 0,2 Pa (0,002 mbar). Specifications of the investigated materials are presented in Table 2.

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

The microhardness using the Vickers method was made on the Hanemann tester. The tests were made with the load of 0.9 N, making it possible to eliminate to the greatest extent the influence of the substrate material on the measurement results.
Structure and surface of the developed coatings was examined on the transverse fractures on the SUPRA 25 scanning electron microscope (SEM). To obtain the fracture images the Secondary Electrons (SE) detection method and In-Lens detection method were used with the accelerating voltage in the range of 15-20 kV and maximum magnification 100 000x.

Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) are surface chemical analysis techniques, used in the analysis of atoms and molecules on surfaces. This methods are sensitive to the outermost atom layers at the surface and operate in ultra-high vacuum. Therefore they are used to analyses materials at surfaces to the single atomic layer level (Fig.1).

The X-Ray Photoelectron Spectrometry (XPS) examination was carried out for proving the gradient character of the (Ti,Al,Si)N coating deposited onto Al_2O_3+SiC substrate. The XPS technique has been chosen because of highly surface specific achieved due to the short range of the photoelectrons that are excited from the solid. The energy of the photoelectrons leaving the sample are determined using a two metal hemispheres (CHA) and this gives a spectrum with a series of photoelectron peaks.

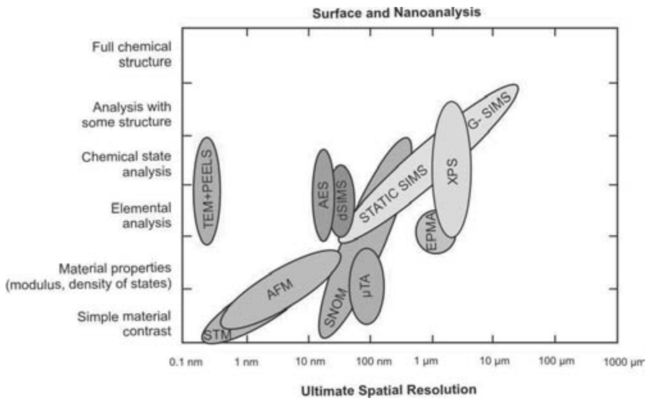

Fig. 1. Techniques for surface and nanoanalysis [8]

The binding energy of the peaks are characteristic of each element. The peak areas can be used (with appropriate sensitivity factors) to determine the composition of the materials surface. The shape of each peak and the binding energy can be slightly altered by the chemical state of the emitting atom. The schematic diagram of the X-ray photoelectron spectrometry has been shown on Fig. 2. The investigations has been carried out with use of the PHI 5700/660 Physical Electronics spectrometer.

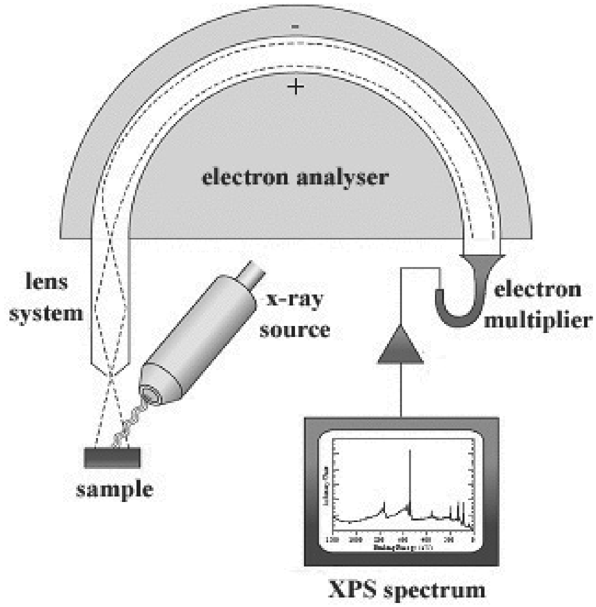

Fig. 2. Schematic diagram of X-Ray Photoelectron Spectroscopy (XPS)

The Physical Electronics model PHI 660 Scanning Auger Microprobe (SAM) surface technique was used to determine elemental compositions of investigated materials. It was also used in depth profiling applications in conjunction with ion beam sputtering. The PHI 660 system is composed of a conventional scanning electron microscope with a lanthanum hexaboride (LaB_6) cathode, a secondary electron detector, and an axial cylindrical mirror analyzer to detect Auger electrons produced during electron imaging. Very small spot sizes are available, down to 200A for imaging, and several thousand angstroms for rapid Auger data acquisition using high beam currents. Inert gas sputtering is used to clean surface contamination from samples and to remove material from a small area on the surface for depth profiling. Several modes of operation are available, including survey, line, profile, and elemental mapping. Technical parameters of the spectrometer used in investigation has been shown in Table 1.

Table 1.
Parameters of AES investigation at potential of 914 eV

Parameters	Value
Ray flux, [nA]	10
Ray energy, [keV]	10
Beam section, [nm]	< 3*
Sensitivity, [cps]	> 40 000

* initial value.

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) 200 N/min, penetrator's travel speed (dx/dt) 10 mm/min, acoustic emission detector's sensitivity AE 1. The critical load L_C, at which coatings' adhesion is lost, was determined basing on the registered values of the acoustic emission AE and friction coefficient F_t. Additionally L_C was determined optically.

3. Discussion of the experimental results

Ceramics with whiskers are obtained mostly by the isostatic hot sintering and by the uniaxial hot pressing. The increase of the whiskers portion to 15-20% causes increase of the ceramics strength. Further increase of the SiC whiskers portion deteriorates the mechanical properties because of the increased probability of the development of whiskers agglomerates, featuring the cracking propagation source.

Occurrences of whiskers with the diameters of d=0.5-0.8 µm in the Al_2O_3+$SiC_{(w)}$ tool oxide ceramics sinter were revealed during examinations on the electron scanning microscope, reinforcing the structure and thus ensuring brittle cracking resistance due to the crack bridging process (Figs. 3).

The fractographic examinations that have been carried out give grounds to state that the coating was deposited uniformly onto the investigated substrate material and that coating adhere tightly to the substrate (Fig. 4).

Table 2.
Specifications of the investigated materials

Coating	Thickness, µm	Roughness, µm	Microhardness, HV
uncoated	-	0.07	1890
gradient (Ti,Al,Si)N	2.6	0.18	2650

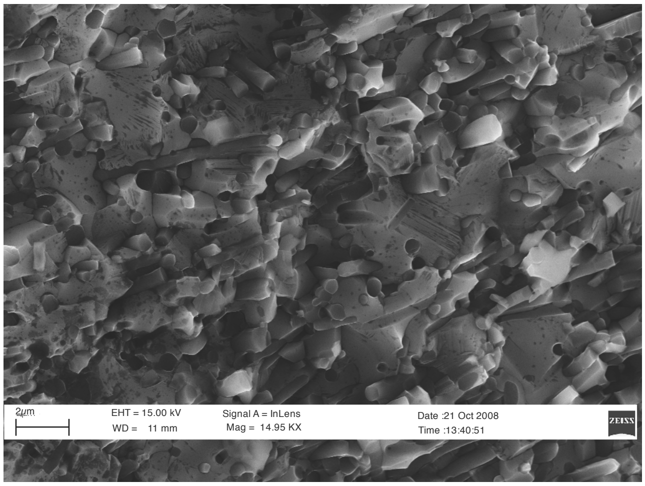

Fig. 3. Structure of the Al_2O_3 oxide tool ceramic reinforced with SiC whiskers

Roughness of the substrate defined by R_a parameter is 0.07 µm. Depositing the gradient (Ti,Al,Si)N coating onto the examined substrate causes increase of the roughness parameter to R_a=0.18 (Table 2). Increase of the roughness parameter is connected with occurrence of the drop shaped micro-particles on the surface of coating. The occurrence of the droplets is most probably connected with titanium micro-particles dropping out immediately after completion of the coating deposition process (Fig. 5).

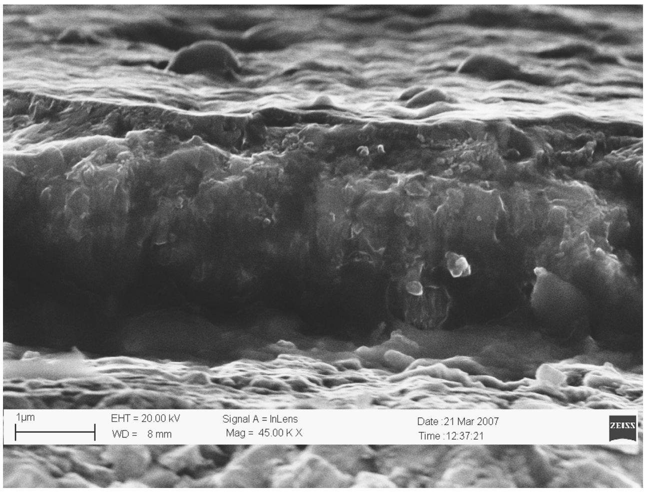

Fig. 4. Fracture surface of the gradient (Ti,Al,Si)N coating deposited onto the Al_2O_3+$SiC_{(w)}$ oxide tool ceramic

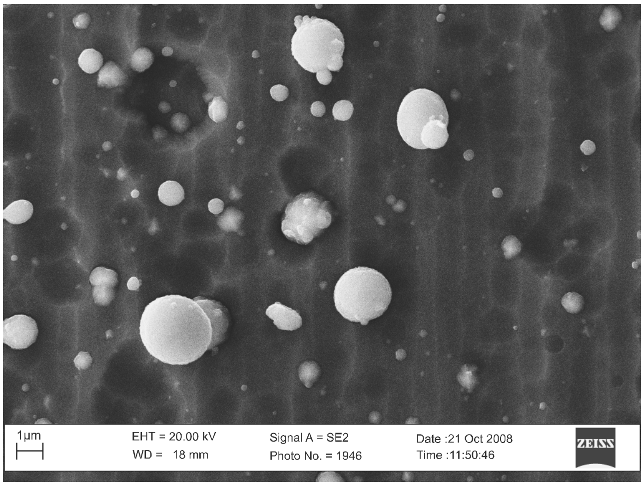

Fig. 5. Topography of the gradient (Ti,Al,Si)N coating surface, deposited on the Al_2O_3+$SiC_{(w)}$ oxide tool ceramic

Depositing the wear resistant gradient coating onto the Al_2O_3+$SiC_{(w)}$ oxide tool ceramic results in a significant increase of the surface layer microhardness, contributing most probably in this way to the decrease of wear intensity of cutting tools' flanks during machining process (Table 2).

During the the X-Ray Photoelectron Spectroscopy (XPS) investigations $Al_{K\alpha}$ monochromatic beam of X-ray radiation was used. Depth profile analysis was obtained after 1000 min of sputtering by Ar+ ions at the accelerating voltage of 2 kV. In one-one-minute cycles of sputtering ion gun scanned the area of square. Side of a square was 2 mm. After each of the cycles the measurement of characteristic peaks of nitride, titanium, aluminium, silicon, carbon and oxygen connected with atomic chemical composition analysis was made in area of the 0,4 mm circle in the centre of scanned square. Two surface spectra in different areas (0.4 mm circle and 2 mm x 0.8 mm rectangle) was made after depth profile analysis (Figs. 6, 7). In spite of the meaningful difference of analysed areas of the surface spectra there is no significant difference of the chemical composition results. It speak volumes for high homogeneity of the surface pickled with Ar+ ions and precise setting of the sputtering ion gun towards the analysed area. Strong peaks characteristic for nitride, titanium, aluminium and weaker peaks characteristic for silicon, as well as photoelectron peak O1s of oxygen was identified. This indicate, that the intermediate area between the coating and Al_2O_3+$SiC_{(w)}$ oxide ceramic substrate was reached.

It was found out as a result of depth profile chemical composition analysis (Fig. 8), that investigated (Ti,Al,Si)N coating is characteristic of the gradient structure changing significantly concentration of aluminium and titanium in direction from the surface of coating to the substrate.

During the 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 gradient coating deposited on the Al_2O_3 oxide tool ceramic reinforced with SiC whiskers was carried out (Fig. 9). 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. It was found that developed coating is homogeneous in respect of topography (Fig. 10) and chemical composition (Fig. 11).

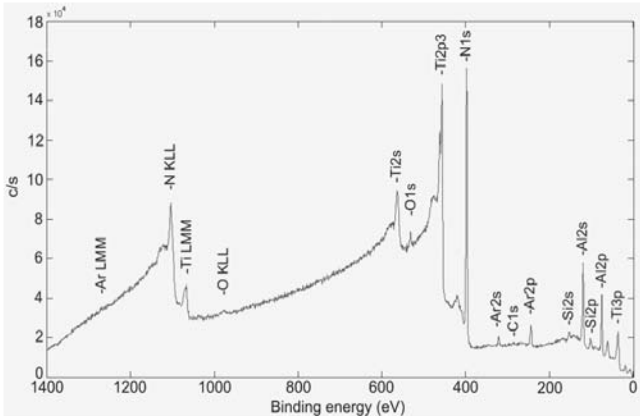

Fig. 6. Surface spectrum of (Ti,Al,Si)N gradient coating deposited on the Al_2O_3 oxide tool ceramic reinforced with SiC whiskers obtained with XPS method (area of analysis: 0.4 mm circle)

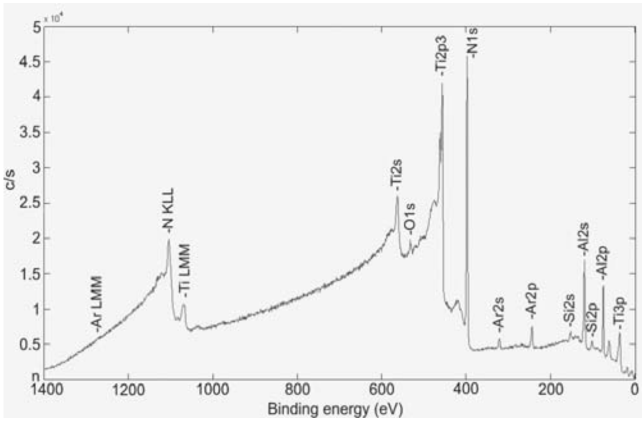

Fig. 7. Surface spectrum of (Ti,Al,Si)N gradient coating deposited on the Al_2O_3 oxide tool ceramic reinforced with SiC whiskers obtained with XPS method (area of analysis: 2 mm x 0.8 mm rectangle)

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 PVD coating 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 coating deposited onto the Al_2O_3+$SiC_{(w)}$ substrate is characterised by good adherence

(L_C= 38 N), (Fig. 12). Basing on the acoustic emission AE registered during the test and microscope observations (using classification of critical forces: L_{C3} – scratch edge flaking, L_{C4} – partial delamination of coating, L_{C5} –total delamination of coating) and L_C(Ft) – it was found, that relatively high value of AE registered in range of 40-135 N can be effected by specific topography of investigated coating with micro particles of titanium developed in the coating deposition process. Basing on the metallographic examinations it was found, that scratch edge flaking take place at value of force 135 N, while delamination of coating takes place at value of force 175 N (Fig. 13).

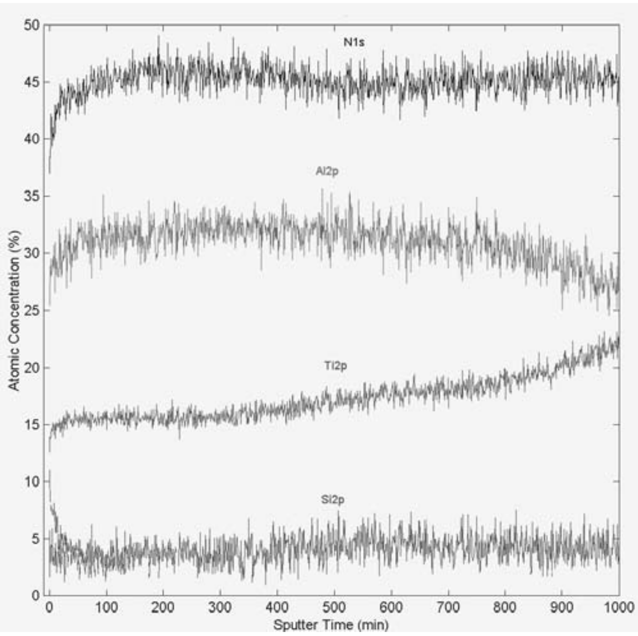

Fig. 8. Depth profile of the chemical composition obtained with XPS method on the (Ti,Al,Si)N coating

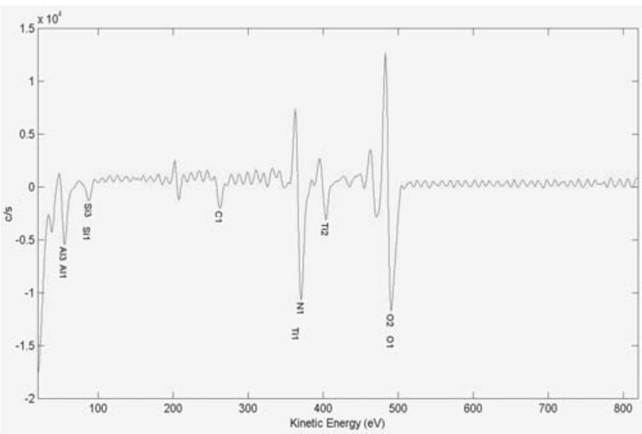

Fig. 9. Auger survey spectrum of (Ti,Al,Si)N gradient coating deposited on the Al_2O_3 oxide tool ceramic reinforced with SiC whiskers after 3450 min ion etching

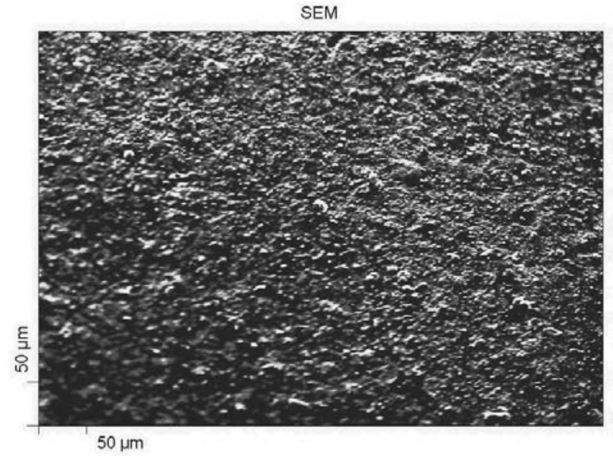

Fig. 10. Topography of the gradient (Ti,Al,Si)N coating surface, deposited on the Al_2O_3+$SiC_{(w)}$ oxide tool ceramic after 450 min min ion etching (Scanning Auger Microprobe)

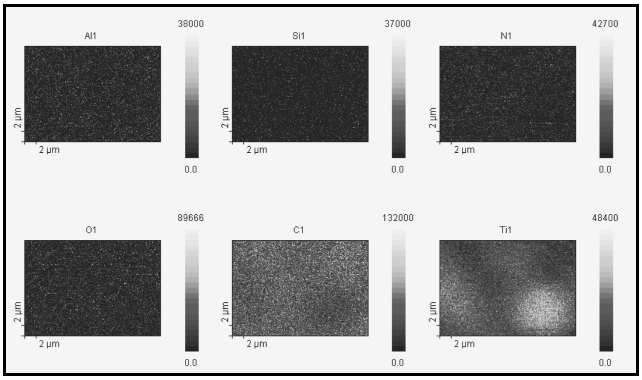

Fig. 11. Comparison of elemental mappings: Al, Si, N, O, C i Ti of the gradient (Ti,Al,Si)N coating surface, deposited on the Al_2O_3+$SiC_{(w)}$ after 450 min min ion etching (Scanning Auger Microprobe)

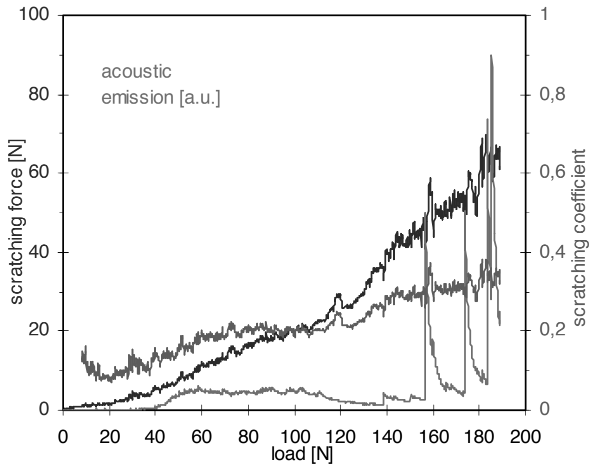

Fig. 12. Scratch test results of the TiAlSiN coating surface deposited on Al_2O_3+$SiC_{(w)}$ substrate

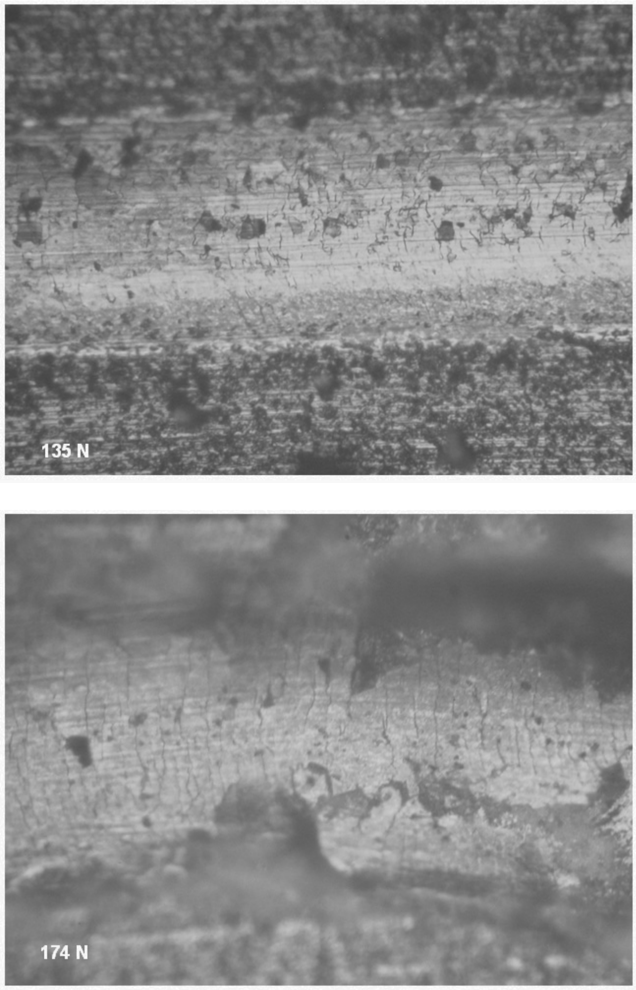

Fig. 13. Indenter trace with the optical L_c load of the TiAlSiN coating surface deposited on $Al_2O_3+SiC_{(w)}$ substrate

4. Conclusions

The results of the investigations gradient (Ti,Al,Si)N coating deposited onto $Al_2O_3+SiC_{(w)}$ oxide tool ceramic with use of the cathodic arc evaporation CAE-PVD method are given in the paper. Gradient PVD coating deposited on $Al_2O_3+SiC_{(w)}$ oxide tool ceramics with whiskers have a dense, compact structure and their fracture surface topography attests their high brittleness, characteristic especially for the oxide ceramic materials. The coating were deposited uniformly onto the investigated substrate materials and have a fine-graded structure.

It was found out as a result of depth profile chemical composition analysis made with use of X-Ray Photoelectron Spectroscopy (XPS) and Scanning Auger Microprobe (SAM), that investigated (Ti,Al,Si)N coating is characteristic of the gradient structure changing significantly concentration of aluminium and titanium in direction from the surface of coating to the substrate.

The results of roughness and microhardness tests confirm the advantages of the gradient (Ti,Al,Si)N coating. Depositing the wear resistant gradient coating onto the $Al_2O_3+SiC_{(w)}$ oxide tool ceramic results in a significant increase of the surface layer microhardness, contributing most probably in this way in machining to the decrease of the wear intensity of cutting tools' flanks made from the $Al_2O_3+SiC_{(w)}$ oxide tool ceramic

Investigated oxide ceramics with the gradient (Ti,Al,Si)N coatings deposited with the PVD method in the cathodic arc evaporation process CAE qualify for the widespread industrial use on cutting tools.

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