



XPS and AES analysis of PVD coatings

L.A. Dobrzański ^{a,*}, L.W. Żukowska ^a, J. Kubacki ^b, K. Gołombek ^a, J. Mięka ^a

^a 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

^b A. Chelkowski Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland

* Corresponding author: E-mail address: leszek.dobrzanski@polsl.pl

Received 23.04.2008; published in revised form 01.08.2008

ABSTRACT

Purpose: The X-Ray Photoelectron Spectrometry (XPS) and Auger Electrons Spectroscopy (AES) analysis of PVD coatings were performed for samples, made from cemented carbides, cermets and composite gradient tool materials.

Design/methodology/approach: The Ti(C,N) gradient coating was investigated by XPS and AES method with multifunctional PHI 5700/660 spectrometer. The characteristic of surface region coating were determined from XPS depth profile. The transition region between Ti(C,N) coating and substrate was analyzed by AES method as line profile.

Findings: The coating consists mainly of TiC and TiN compound. The oxygen impurities of investigated coating is below 2%. The “fresh” surface of Ti(C,N) coating is covered by thin films TiO₂. There was observed homogeneous distribution of carbon, titanium and nitrogen elements in the surface region. The ratio of C/N obtained for surface region is characteristic for deposited coating. The transition region is also homogeneous between coating and cermet substrate.

Practical implications: PVD deposition techniques making it possible to obtain surface layers with the varying thickness values, respectively, with the structure changing across the layer depth along with the change of its chemical or phase compositions for improvement of its properties, and especially for the advantageous combination of the very high abrasion wear resistance of the surface along with the relatively high ductility of the core of materials used for, respectively, blanking tools and for hot working, profile cutting tools with ductility high enough and for the heavy duty very high speed cutting tools.

Originality/value: Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are an excellent tools for performing surface analysis and for determining elemental composition as a function of depth. AES or XPS analyzes the residual surface left after a certain sputtering time with rare gas ions. In this way composition depth profiles can be obtained that provide a powerful means for analyzing worked layers, modified layers, thin films, multiple-layered coatings, lubricants, reaction film products, transferred films, and their interfaces.

Keywords: Spectroscopy; XPS; AES; PVD

METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

1. Introduction

The contemporary technologies of materials forming employed in the machining, casting, and also plastics forming domains call for using more and more efficient tool materials. Deposition of hard wear resistant coatings features one of the fastest developing directions of research, stimulated by the growing service requirements of machines

and equipment, making definite improvement of the sintered tool materials possible (sintered high speed steels, cemented carbides, cermets, ceramics). PVD deposition techniques making it possible to obtain surface layers with the varying thickness values, respectively, with the structure changing across the layer depth along with the change of its chemical or phase compositions for improvement of its properties, and especially for the advantageous combination of the very high abrasion wear resistance of the surface along with the relatively high

ductility of the core of materials used for, respectively, blanking tools and for hot working, profile cutting tools with ductility high enough and for the heavy duty very high speed cutting tools [1-6].

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are powerful analytical tools for material science. AES and XPS methods are one of the most frequently used methods of quantitative analysis. Those methods are an excellent tools for performing surface analysis and for determining elemental composition as a function of depth. AES or XPS analyzes the residual surface left after a certain sputtering time with rare gas ions. In this way composition depth profiles can be obtained that provide a powerful means for analyzing worked layers, modified layers, thin films, multiple-layered coatings, lubricants, reaction film products, transferred films, and their interfaces [7-13].

In paper results of XPS and AES analysis was introduced as one of the most commonly employed surface analytical techniques for analyzing multilayer nanostructure compositions of surface layers, thin coatings and other components of a sample.

2. Methodology of research

The investigations were carried out on samples made from cemented carbides, cermets and gradient tool materials obtained by using the powder metallurgy of the chemical composition corresponding to the HS6-5-2 high-speed steel reinforced with the WC and TiC type hard carbide phases with the growing portions of these phases in the outward direction from the core to the surface. All substrates were coated using the PVD method of Ti(C,N) gradient coating. Thickness of the investigated gradient coating is in range 1.5-1.8 μm .

The TiCN gradient coating was investigated by XPS and AES method with use of multifunctional PHI 5700/660 spectrometer. The measurements were performed with use of monochromatized Al k_{α} x-ray source ($h\nu = 1486.6$ 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 vapor 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. The transition region between Ti(C,N) coating and substrate was analyzed by AES method as line profile from Ti(C,N) coating to substrate area.

3. Results

The XPS investigations of the Ti(C,N) gradient coating deposited on substrates showed that "fresh" surface of Ti(C,N) coating included small value of silicon impurities (about 1%). The most of atomic concentration calculated for oxygen and carbon suggests that after PVD process surface of sample was covered by adsorbates, mainly carbon oxides and oxygen atoms (Figure 1a). The complex structure of C1s peak include at least three components. Two components is clearly visible at 284.8 eV and

282.1 eV. The peak with most intensity at 284.8 eV can be assigned to "surface" carbon. The peak with lower energy at 282.1 eV is typical for carbides. The small complex peak observed at about 288 eV corresponds to adsorbate carbon oxides. Intensities of peaks for "surface" carbon and carbon oxides decreased after successive sputter time. After 20 minutes of sputtering the only one peak corresponding to carbides was observed. Similar situation was observed for titanium. The spectrum of Ti2p level is presented on Figure 2. It consists of two groups of peaks Ti2p_{3/2} and Ti2p_{1/2} due with spin-orbit coupling. The first pair of Ti peak with higher binding energy corresponds to Ti atoms in TiO₂ [14] while next pair with lower binding energy corresponds to Ti atoms in Ti(C,N) coating. After 4 minutes of sputtering only one pair of peaks was observed. It can indicate that "fresh" surface of Ti(C,N) coating is covered by thin films of titanium oxides, mainly TiO₂. Combine results for Ti and C can suggest that Ti and C atoms exist in Ti(C,N) coating as titanium carbides.

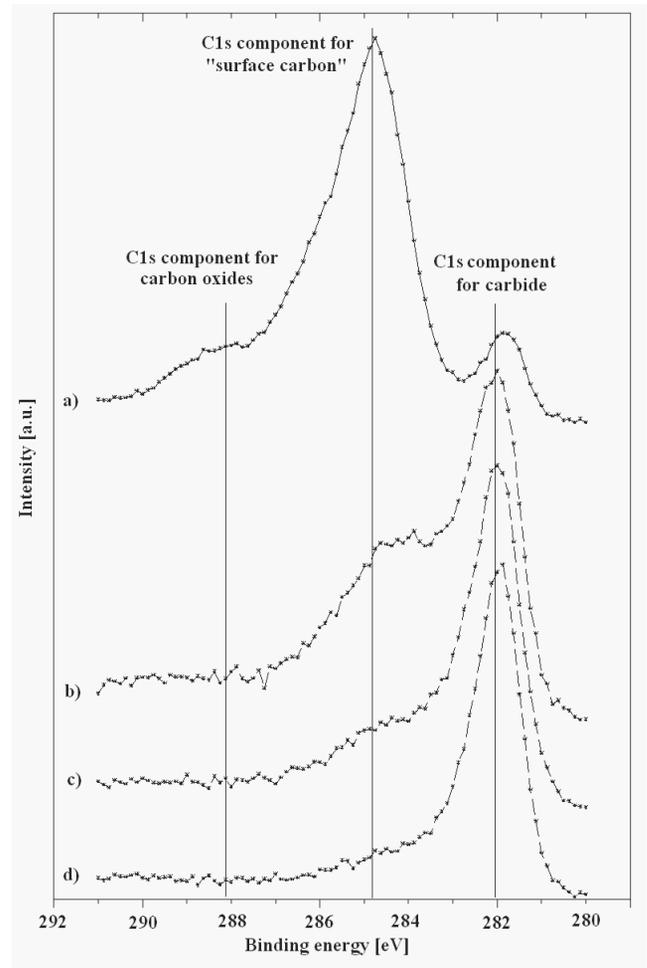


Fig. 1. The shapes of C1s lines obtained by XPS method for Ti(C,N) coating; a) „fresh” *ex situ* surfaces, b) after sputtering Ar⁺ ions for t=2min, c) after sputtering Ar⁺ ions for t=4min, d) after sputtering Ar⁺ ions for t=20min

The chemical composition of Ti(C,N) coating "free" from adsorbates is presented in Table 1. 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 Figure 3. 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 [15].

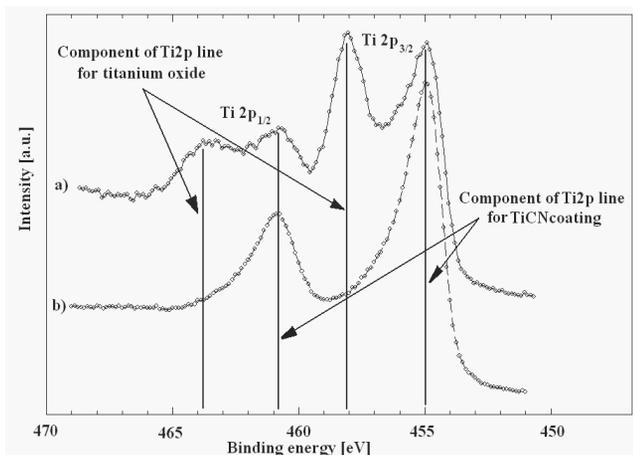


Fig. 2. The shapes of Ti2p lines obtained by XPS method for Ti(C,N) coating from: a) „fresh” *ex situ* surfaces, b) after sputtering Ar⁺ ions for t=4min

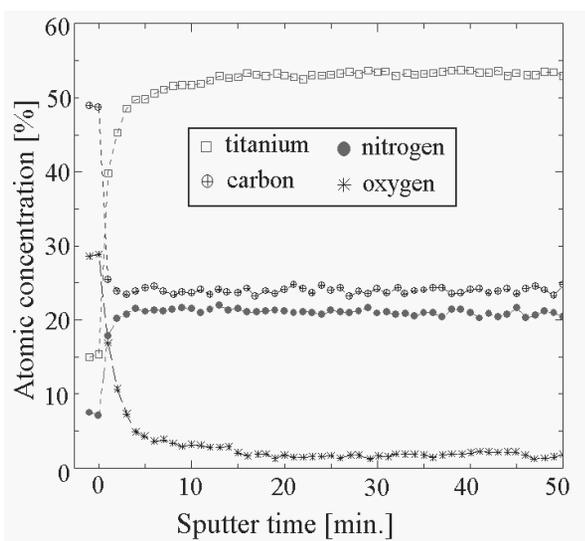


Fig. 3. The distribution of atomic concentration of elements in the surface region of Ti(C,N) coating (XPS)

Table 1. Chemical composition of investigated coating Ti(C,N) obtained by XPS method

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

The close examination of transition region was performed by AES method. *Ex situ* surface of coating Ti(C,N) was bombarded by Ar⁺ ions with energy 4 kV in time 90 minutes. The bottom of formed crater is presented on the Figure 4. The profile of this crater was determined along the line "L" from the scale of grey colour. It is only demonstrative profile without the Y-scale. The diameter of obtained bottom crater is about 500 μm. However, the size of sputtering crater is depended on several parameters, like set-up of raster size and collimating beam of argon ions.

The transition region between the Ti(C,N) coating and substrate is presented on Figure 5a with profile of created crater topography. The dark region correspond to the top of Ti(C,N) coating, the bright region correspond to the substrate. The area between these regions is transition zone with profile noticeable along the profile line. The line profile measurement of coating and substrate elements was performed along the mark line for expand region (presented on Figure 5b). Points presents topography of this region. The distribution of particularly elements occurring in transition zone is presents on Figure 5c. The intensities for all measured elements were calculated to atomic concentration. Unfortunately the nitrogen has a differential auger line at 389 eV within a complex groups auger peaks of titanium. It caused the analyse of this element impossible with use of AES method. The ratio of atomic concentration C/Ti obtained for Ti(C,N) coating with use of XPS is equal 0.53 (Table 1). The similar value C/Ti = 0.47 was obtained from AES spectra. This ratio was dramatically change for cermet substrate, where received ratio was about unity. It is clearly visible at the Figure 5c. The tungsten has the most (about 4%) and nickel has a least (below 2%) of atomic concentration in the substrate. The fix transition region between coating and substrate across the sputtering crater has a dimension about 200 μm. The change of atomic concentration of gradient coating occur rather smoothly than step.

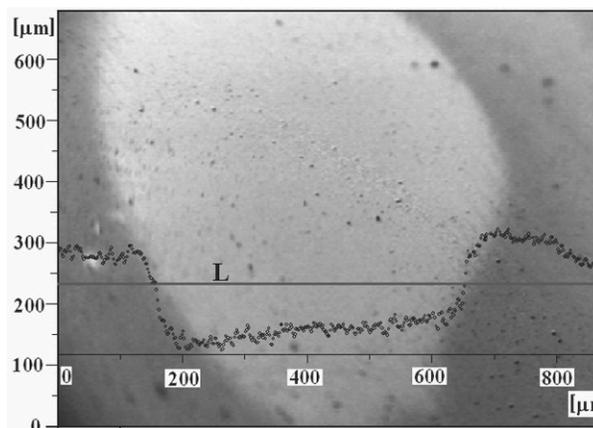


Fig. 4. SEM picture of area with sputter crater

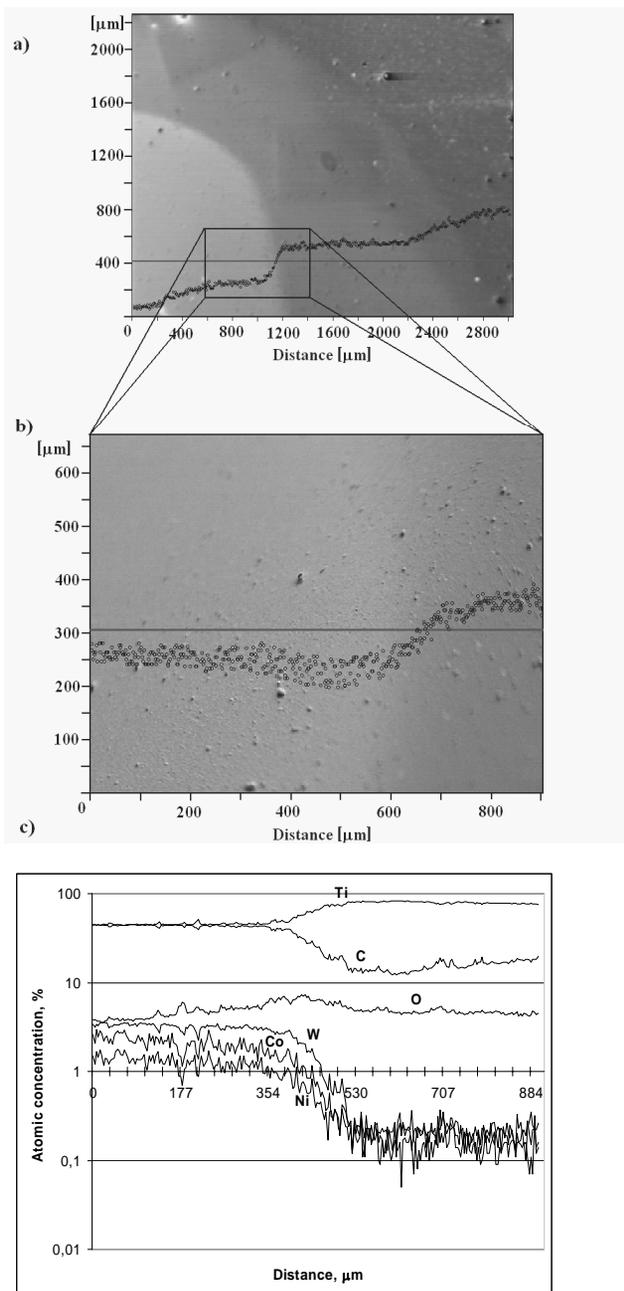


Fig. 5. SEM picture of transition zone of sputter crater (a, b) and line profile of chemical composition (c) (AES)

4. Conclusions

The X-Ray Photoelectron Spectrometry (XPS) and Auger Electrons Spectroscopy (AES) examinations was carried out for detailed chemical analysis of the Ti(C,N) gradient coating deposited onto several substrates. The oxygen impurities of investigation coating was below 2%. The “fresh” surface of Ti(C,N) coating is covered by thin films TiO₂. There was observed homogeneous distribution of carbon, titanium and nitrogen elements in the surface

region. The ratio of C/N obtained for surface region is characteristic for deposited coating. The transition region is also homogeneous between coating and substrate materials.

Acknowledgements

Research was financed partially within the framework of the Polish State Committee for Scientific Research Project N N507 2068 33 headed by Dr Jaroslaw Mikula.

References

- [1] L.A. Dobrzański, J. Mikula, K. Gołombek, Structural characteristic of the modern sintered tool materials, *Materials Science Forum* 530-531 (2006) 499-504.
- [2] L.A. Dobrzański, K. Gołombek, J. Mikula, D. Pakula, Improvement of tool materials by deposition of gradient and multilayers coatings, *Journal of Achievements in Materials and Manufacturing Engineering* 19/2 (2006) 86-91.
- [3] L.A. Dobrzański, K. Lukaszowicz, J. Mikula, D. Pakula, Structure and corrosion resistance of gradient and multilayer coatings, *Journal of Achievements in Materials and Manufacturing Engineering* 18 (2006) 75-78.
- [4] 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.
- [5] L.A. Dobrzański, L. Wosińska, J. Mikula, 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.
- [6] L.A. Dobrzański, L.W. Żukowska, J. Mikula, K. Gołombek, T. Gawarecki, Hard gradient (Ti,Al,Si)N coating, *International Journal of Materials and Product Technology* (2007) (in print).
- [7] M. Bizjak, A. Zalar, P. Panjan, B. Zorko, B. Pracek, Characterization of iron oxide layers using Auger electron spectroscopy, *Applied Surface Science* 253 (2007) 3977-3981.
- [8] R. Kosiba, J. Liday, G. Ecke, O. Ambacher, J. Breza, P. Vogrincic, Quantitative Auger electron spectroscopy of SiC, *Vacuum* 80 (2006) 990-995.
- [9] J. Kovac, M. Bizjak, B. Pracek, A. Zalar, Auger electron spectroscopy depth profiling of Fe-oxide layers on electromagnet sheets prepared by low temperature oxidation, *Applied Surface Science* 253 (2007) 4132-4136.
- [10] A.R. Chourasia, D.R. Chopra, *Auger Electron Spectroscopy, Handbook of analytical chemistry*, Prentice Hall, 1997.
- [11] M.A. Baker, S.J. Greaves, E. Wendler, V. Fox, A comparison of in situ polishing and ion beam sputtering as surface preparation methods for XPS analysis of PVD coatings, *Thin Solid Films* 377-378 (2000) 473-477.
- [12] K. Miyoshi, *Surface Analysis and Tools*, National Aeronautics and Space Administration Report NASA TM-2002-211815, 2002.
- [13] J.E. deVries, Surface characterization methods-XPS, TOF-SIMS, and SAM a complimentary ensemble of tools, *Journal of Materials Engineering and Performance* 7 (1998) 303-311.
- [14] R.P. Netterfield, P.J. Martin, C.G. Pacey, W.G. Sainty, Ion-assisted deposition of mixed TiO₂-SiO₂ films, *Journal of Applied Physics* 66 (1989) 1805-1809.
- [15] J. Chastain, R.C. King, Jr, *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics, 1995.