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Structure of TiBN coatings deposited onto cemented carbides and sialon tool ceramics

L.A. Dobrzański*, M. Staszuk, J. Konieczny, W. Kwaśny, M. Pawlyta
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: The aim of this paper was investigated structure of sintered carbides WC-Co type and sialon tool ceramics with wear resistance ternary coatings TiBN type deposited by cathodes arc evaporation process (CAE-PVD).

Design/methodology/approach: Observation of fracture and topography studied coatings were done by scanning electron microscope. Chemical composition was determine by energy dispersive spectrometry (EDS) method. Thin foils of substrates and coatings by transmission electron microscopy (TEM) was done. Phases composition analysis carried out by XRD and GIXRD method.

Findings: The investigated PVD gradient coatings deposited by CAE-PVD method are demonstrating fine-grained structure. The TiN, TiB and TiB_2 phases were found in coatings and β-Si_3N_4 phase was found in sialon tool ceramics. Coating onto sialon tool ceramics reveal shallow pinhole while coating onto cemented carbide is without discontinuity.

Research limitations/implications: In the future investigations will progress for mechanical properties, e.g. roughness, microhardness, adhesion strength and operating properties.

Originality/value: In this work the influence of parameters deposited coatings by CAE-PVD technique on structure and phases composition the ternary TiBN gradient coatings were investigated.

Keywords: Tool materials; Thin & Thick coatings; Sialon; Cemented carbides; TEM; SEM

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Machining has given geometrical shape producing subjects and elements in a main aim. However, there are made higher and higher demands with regard to assurance suitable dimensional precision and quality workable surface. Moreover, economical and ecological regards has gained more crucial importance. Process parameters, which are connected with tool application, its geometry, material cutting edge, as well thickness of take off layer, has a decisive influence on quality workable material and cost-effective, and capacity machining [1-8].

Ceramic materials on base nitride silicon are pleased huge interest. Pure Si_3N_4 reveals perfect qualities in wide range temperatures, however it is susceptible on chemical interaction workable material and on oxidation with work in range above 1000 ºC [6-8]. In search of much perfect a tool material in 70 years XX century, it has been begun interested in compounds such as: ox nitrides silicon and aluminum, because it was found that introducing aluminum and oxygen into silicon nitride has created new possibilities. Leading researches have pointed out that silicon nitride β-Si_3N_4 about a hexagonal lattice dissolve aluminum oxide Al_2O_3 creating constant solution β', which is expressed in formula $Si_{6-z}Al_zO_zN_{8-z}$. A number z determines atoms numbers Al, which are replaced Si toms with Si_3N_4 system and contains in range from 0 to 4.5. Tool are made by sialons are designed to turning and milling of steels and hard workable alloys such as: cast irons workable thermal, nickel alloy, titanium and aluminum [6-12].

Huge scientific and industrial (technological) interest has pleased coatings type TiBN for the sake of their high properties in last years. The addition of boron into TiN coatings was found to improve the structural, mechanical and tribologicalproperties of this coatings. At this point, researches have shown that the coatings are consisting of one or two ingredients, three ingredinets phases are not present. Diagram of triple phase system Ti-B-N is presented in figure 1 and it contains five areas appearance individual phase depending on chemical composition. The TiBN coatings receive on a basis of metastable constant solutions with multicomponent and multiphase compositions can belong to a modern perspective group of coating materials on inserts tools for machining. [3, 13-17].

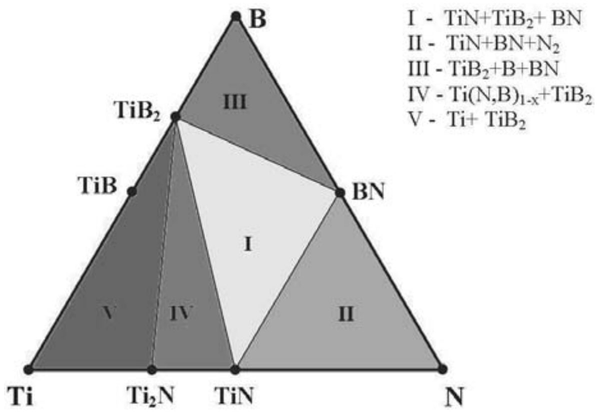

Fig. 1. Phase diagram of Ti-B-N system [8-10]

The various applications and usage of coated cutting tools for machining of different groups of materials performs position of the art technology at present. The produce wide range of different hard nitridic and oxidic films and next to deposit them on various tool substrates as monolayer, multilayer or composite coatings is possible thanks to increase different developments in coating equipment and processes. Rising demands, which are put into relation cutting tool such as: hight speed machining, machining of hard materials, bring higher and higher interest in technology development of depositing thin and wear resistant coatings. Investigations presents that the improvement of the property of usable tool materials can be obtained through coating sputtering in the process of physical deposition from the gas phase PVD [1-3,6,7,19,20].

In this work the structure of cemented carbide and sialon tool ceramics inserts coated by ternary TiBN coatings were done by following methods: SEM, TEM and XRD. Chemical composition analysis was carried out by the EDS method. Coatings were synthesized by cathodes arc evaporation technique from TiB targets with a presence nitrogen reactive gas.

2. Experimental

Films deposition were carried out using arc evaporation machine with two TiB targets. The mixture of Ar and N_2 gases were used. Before deposition the chamber was evacuated to a 5×10^{-6} mbar using a turbo molecular pumps system. The temperature deposition was approximately 350 °C. Coating was depositing onto sintered carbides WC-Co type and sialon tool ceramics inserts, ultrasonic cleaned in acetone. Before deposition substrates were electron heated. After that they were ion cleaned in vacuum chamber. The duration time was 25 min.

The TiBN coating of varying nitrogen concentration was deposited on the substrate with change of nitrogen flow gas. Nitrogen content was increased by increasing flow of nitrogen in the process from 0 sccm to 250 sccm (Fig. 2) during initial 5 minutes of process. Further 10 minutes process the flow nitrogen gas was constant, equal 250 sccm. The flow of inert gas – Argon – was equal to 20 sccm. The current of two TiB (95:5 % at.) targets was constant and equal to 70A. During the deposition process BIAS voltage was equal to -100V. Due to non-conductive SiAlON substrate this inserts were put down on a steel target, which was connected with bias. Sample holders were set in the rotatory movement.

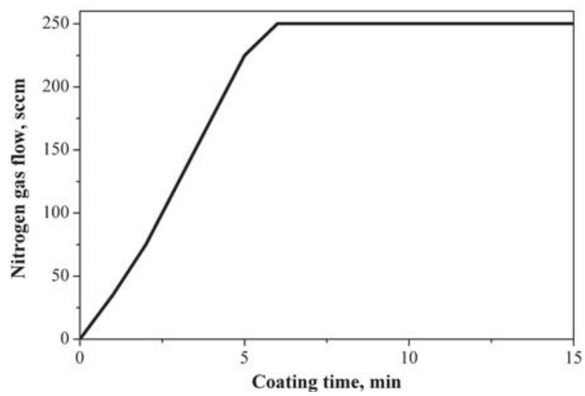

Fig. 2. Change concentration of reactive gas flow during TiBN coating deposited process

Phase composition analyses of investigated samples were made on the PANalytical X'Pert PRO diffractometer, working in goniometer system (using the filtered X-ray Co Kα, step 0.05, time of counting 10 sec.) at the voltage of 40 kV and tube current of 30mA. Moreover, phase analysis by low incidence beam angle diffraction method was performed.

Observation of coatings structure was carried out by use of ZEISS SUPRA 35 scanning electron microscopes with Oxford detector. The Secondary Electrons (SE) technique were used with the accelerating voltage of 15÷20 kV. Chemical composition examinations was made with use of Energy Dispersive Spectrometry (EDS) method.

The investigations of structure and diffraction of thin foils were made with use of the JEOL 3010 transmission electron microscope at the accelerating voltage of 300 kV. The electron diffractions from TEM were solved with use of Eldyf computer program.

3. Results

The phase composition of sialon tool ceramics was determined by X-ray diffraction methods. Figure 3 presents a diffraction spectra from investigated sialon ceramics. All peaks on diffraction pattern are derived from β-Si_3N_4 phase. Observation of thin foil from a sialon substrate was pointed out that sialon structure is a fine-grained, because majority of grains from this ceramic is smaller than 500 nm. Diffraction analysis of thin foils confirms XRD researches that structure of sialons is consisted of β-Si_3N_4 phase (Fig. 4). It is a hexagonal structure from a space group P63/m, in which siliceous atoms occupy position 6h, while nitrogen atoms occupy position 6h and 2c. Moreover, there was observed inside grains numerously lattice defects in a dislocation form (Fig. 5).

As the result of a fracture observation in the scanning electron microscope it was found that a coating was uniformly deposited on all substrate and it was tighten adhered to substrate from a cemented carbide and sialon tool ceramics. The TiBN coating structure

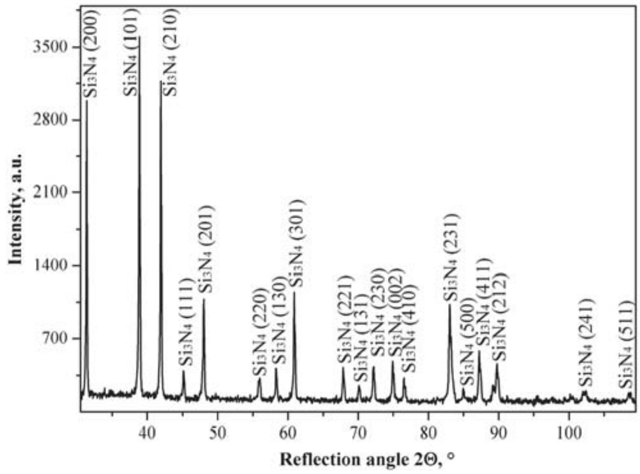

Fig. 3. X-ray diffraction pattern of sialon tool ceramics

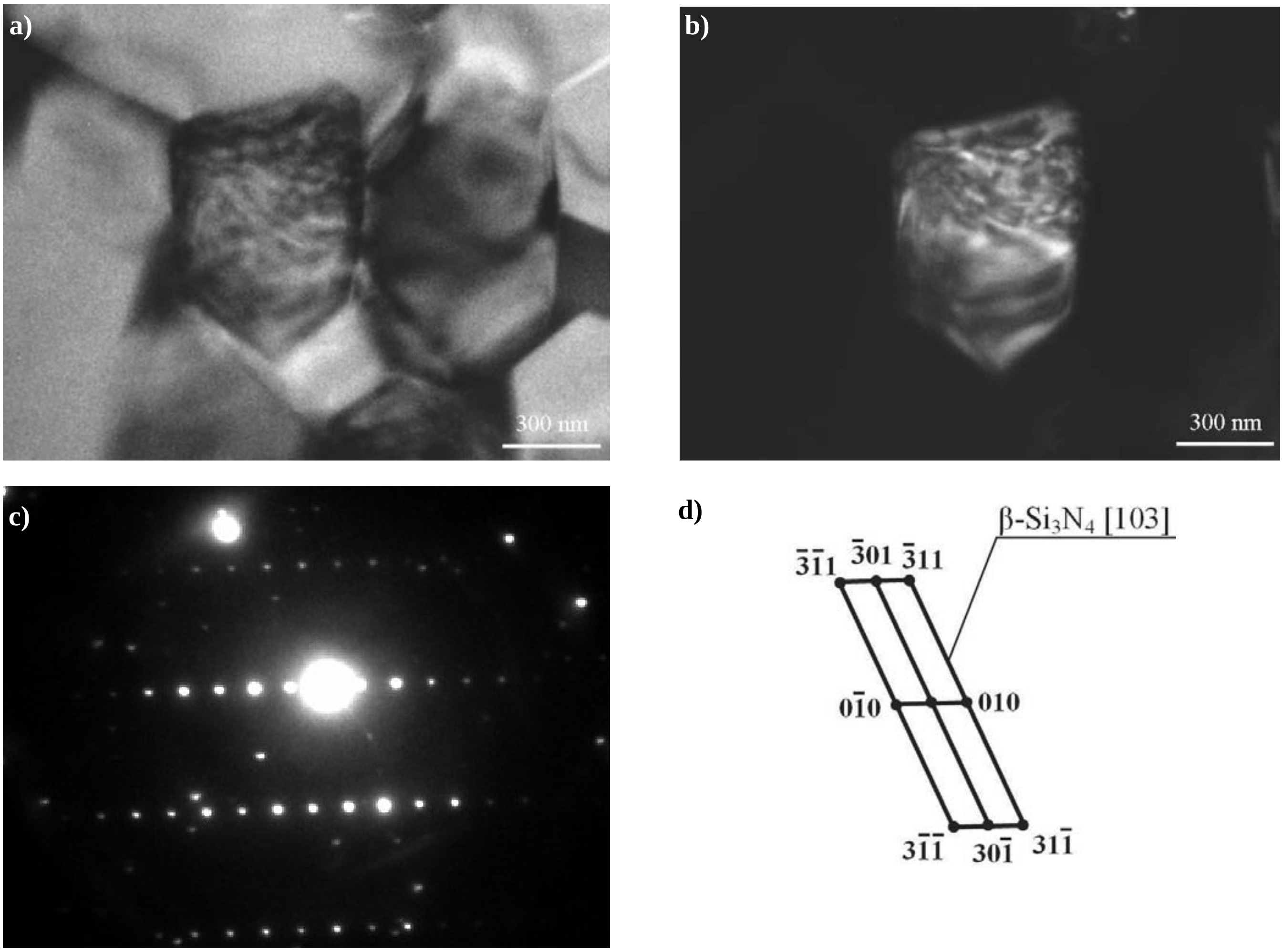

Fig. 4. Structure of sialon substrate: a) bright field; b) dark field from 3-31 reflex; c) diffraction pattern from area b and d) solution of the diffraction pattern

deposited on substrate from a cemented carbide WC+Co type is a typical structure of a zone T according to a Thornton's model with fine compact fibrous crystallite (Fig. 6), which riseing is stimulated by big mobility of atoms as a result of substrate temperature increase during depositing. Whereas, a TiBN coating on a sialon substrate shows a structure close to a zone III of a Thornton's and Mowczan-Demcziszin's model. Probably it is caused smaller mobility of atoms during depositing a coating on ceramics substrate and this is caused too low a substrate temperature. This is a result of this a sialon substrate does not conduct electric current and does not connect to a BIAS voltage polarization during a depositing process, so energy of bombing particles is lower rather than in a case of substrate from a cemented carbide. This can also influence on the mechanical properties studied coatings.

Fig. 5. Structure of sialon substrate, visible numerous dislocations

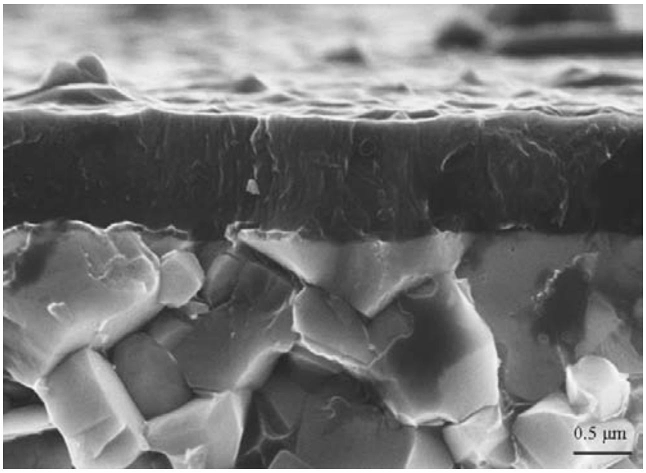

Fig. 6. Fracture of the TiBN coating deposited onto the cemented carbide substrate

Observations of a surface topography coating on cemented carbide show that obtained a coating is characterized of compact structure without pores and it does not point out apparent defects. Whereas, a coating on a sialon tool ceramics includes some defects in form of insignificant pinholes (Fig. 7a). Observations of fractures were revealed that pores did not reach into substrate (Fig. 7a left bottom frame). Surfaces of investigated coatings show inhomogeneity, which is caused occurrence of many micro-drops, formed during a depositing coating process in the consequence sprinkle of drops, sputtering from targets. Researches of chemical composition with use of EDS spectrometer confirm presence a titanium in micro droplets (Fig. 7b). Micro-droplets receive diversified shape from a regular to lengthwise and flat. Molecule size is also diversification and contained in range from several decimal micrometry to 3 micrometers. Moreover, quantity observed agglomerate forming in effect connecting a few small drops is not big.

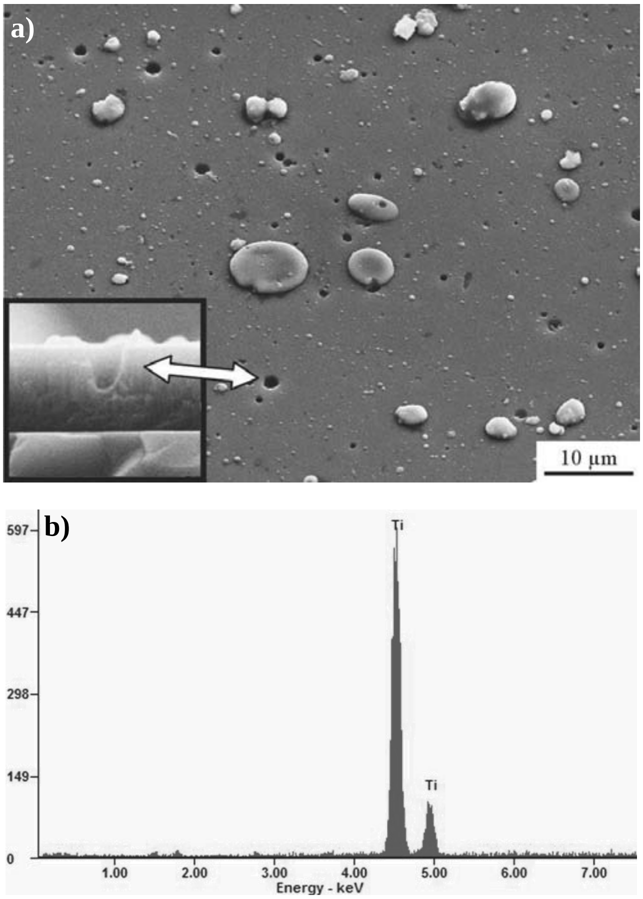

Fig. 7. The TiBN coating deposited onto the sialon tool ceramics substrate a) topography image, b) EDS spectra from a drop area

There were done the XRD analysis in goniometric system with use of X'Celerator detector in order to determine phases composition of investigated coatings. Further researches were applied a grazing incidence X-ray diffraction method (GIXRD) with use of the parallel beam collimator in order to get much accurately information from a surface layer analyzed coatings. Exists of TiN phase in examinated coatings was pointed out by the

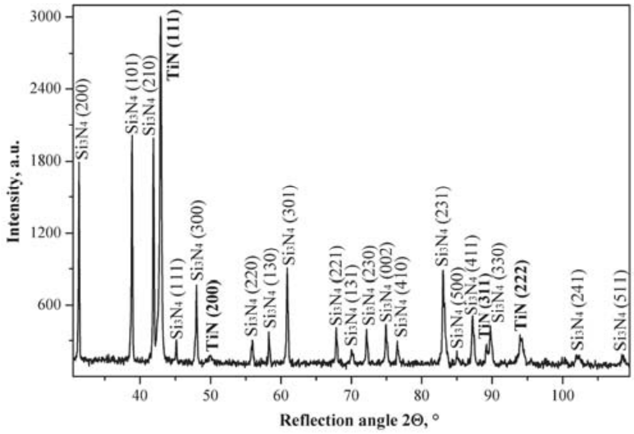

Fig. 8. X-ray diffraction pattern of TiBN coating deposited on sialon tool ceramics

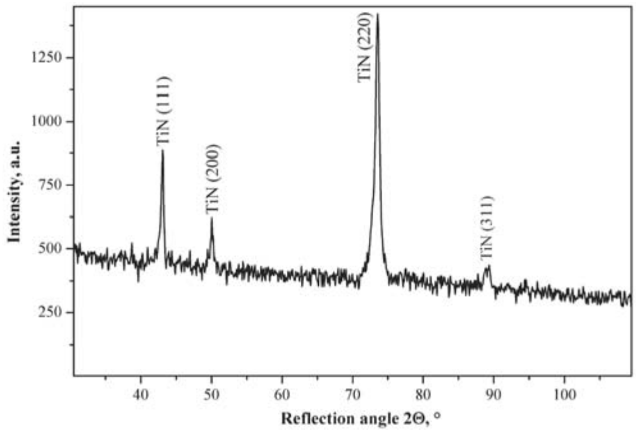

Fig. 9. X-ray diffraction pattern of TiBN coating deposited on sialon tool ceramics obtained by GIXRD method (α=1)

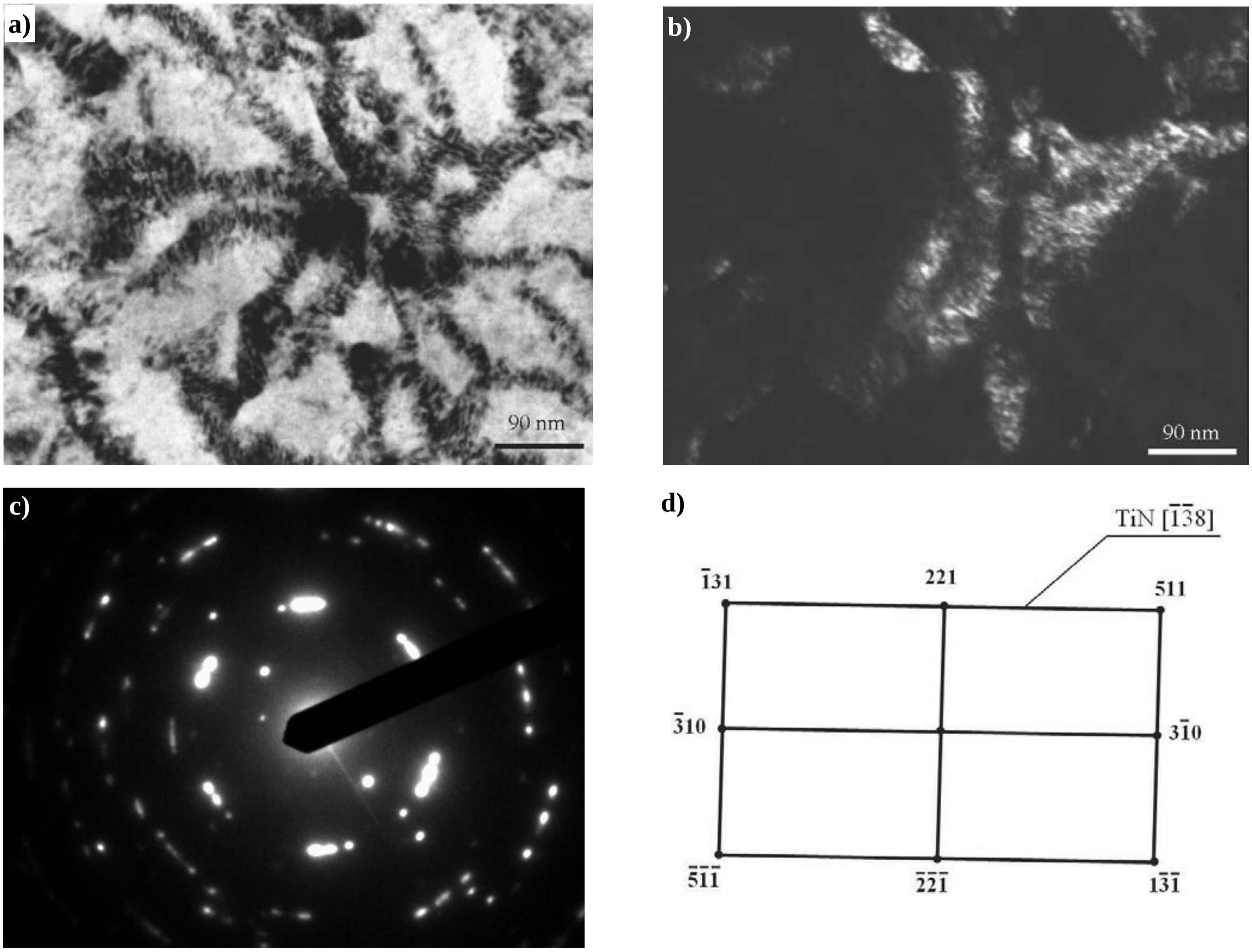

Fig. 10. Structure of thin foil from TiBN coating a) bright field; b) dark field from 221 reflex; c) diffraction pattern from area a and d) solution of the diffraction pattern

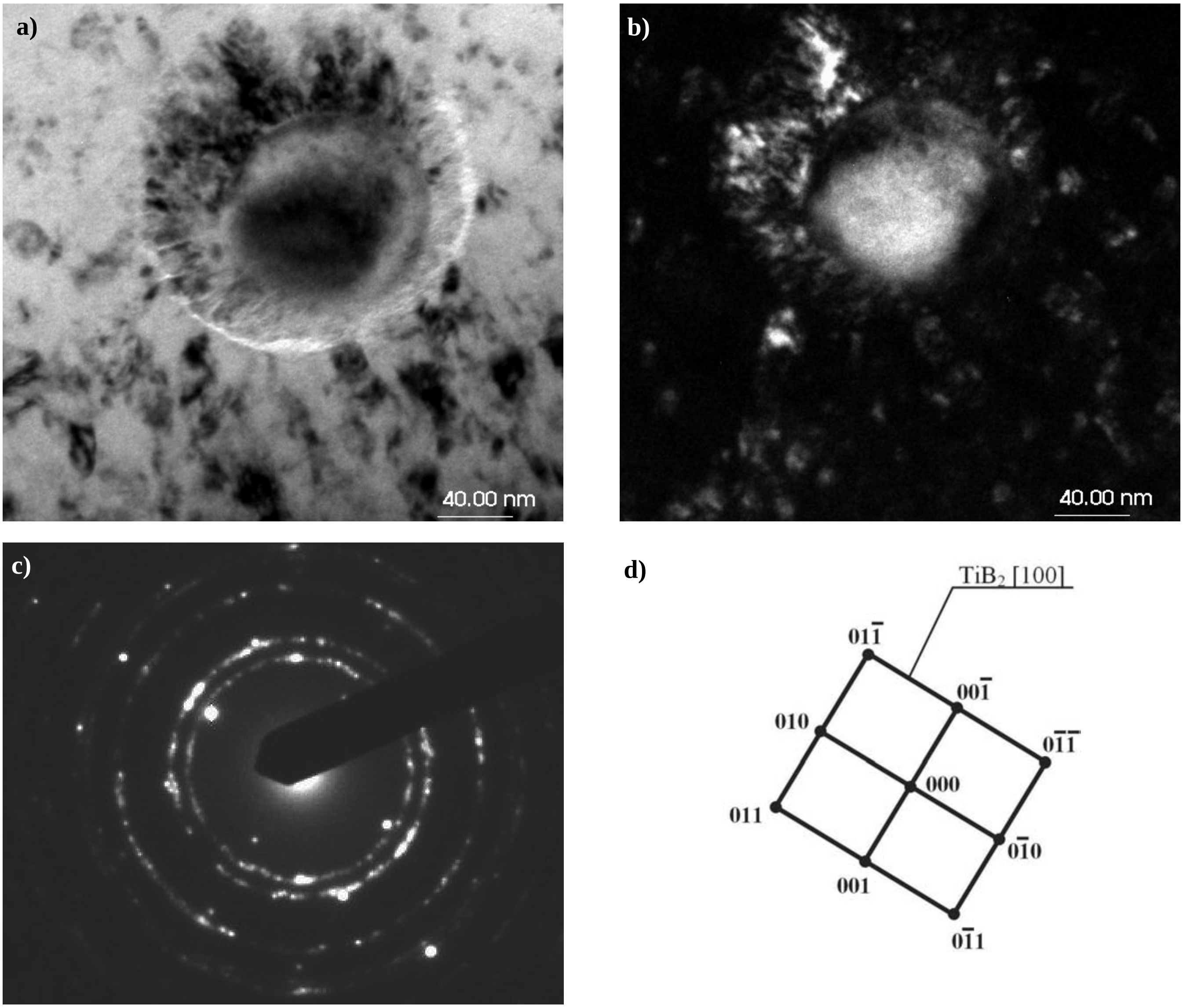

Fig. 11. Structure of TiBN coating: a) bright field; b) dark field from -111 reflex; c) diffraction pattern from area b and d) solution of the diffraction pattern

classic XRD method. The X-ray diffraction were shown the highest intensity of picks for a (111) fcc TiN phase (Fig. 8). The other peaks from this phase were slight or covered clearly with peaks from the substrate. The GIXRD diffraction spectra was showed a distinctly picks from coatings without picks from substrates. In booth cases were found picks for titanium nitride phase (Fig. 9). The TiB_2 and BN phases were not found by the XRD method.

The researches of thin foils from coatings has confirmed occurrence a typical phase fcc TiN (space group Fm3m) in a deposited coatings. The observation in light field was carried out that a coating structure is characterized by fine-grained (Fig. 10a). Moreover, a diffraction (Fig. 11) is shown an existing hexagonal structure TiB_2 (space group P6mmm) according to a phase diagram, which is presented in figure 1 and small quantity of precipitation TiB phase with a orthorhombic lattice (space group Pnma). According to information published in [18] it is a phase with a less hardness than TiB_2. The researches of thin foils do not confirm occurrence of BN phase in structure of analyzed coatings. The absence of this phase and what is more occurrence TiB phase can be connected with relative low a process temperature of deposited coatings. Figure 11 shows the thin foil structure of TiBN coating deposited on tool ceramics. The image visible in this figure was identify as solidify of micro-drops due to intense local evaporation provoked by microarcs during a depositing process. Carried out of diffraction analysis can confirm this assumption, because the TiB_2 phase was identified there. Moreover, from the light field it follows that this droplet is coherent with warp of coating.

Thus, the identification of chemical composition coatings by means of X-ray diffraction an researches of thin foils, shows that there was obtained coatings, which are variation regular mixture TiN, hexagonal TiB_2 and orthorhombic TiB, by a CAE-PVD method.

4. Summary

The paper includes the results of investigated cemented carbide WC+Co type and sialon tool ceramics uncoated and coated by gradient coating made utilization by cathodes arc evaporation process. The influence of depositing parameters and a kind of substrate on a ternary structure of TiBN coating were examined. The following investigations were done:

- Researches of structure sialon ceramics by XRD method and observations of thin foil showed that this material reveals hexagonal structure β-Si_3N_4 phase. Observations revealed numerous dislocations inside crystallite. The structure was qualify as fine-grained.
- The fracture observations, which were deposited during a CAE-PVD process were revealed that coatings are characterized by fine-grained, a columnar and compact structure, well adhered to a substrate.
- The coatings topography onto sialon reveals small pinholes, while a coating onto cemented carbides is free from discontinuity. The coatings inhomogeneity in both cases is connected with occur micro drops, characterized for this kind of PVD technique.
- It was shown that coatings contain a titanium nitride phase by made use of methods such as: X-ray diffraction and grazing incidence X-ray diffraction method.
- The thin foils investigates from coating let reveal their internal structure. It was shown that coating consists of fine-grained structure TiN grains. There was found into coating, what is more TiB and TiB_2 phases.

While there was not found a BN phase, what can testify about too low process temperature of deposited coatings for creating a boron nitride. The fine-grained structure nano-crystalline let think about good quality of these coatings. Mechanical properties of these coatings will be done in the close future, there will be examined a cutting ability tools in a technological test continuous machining.

References

[1] H. Holzschuh, Deposition of Ti–B–N (single and multilayer) and Zr–B–N coatings by chemical vapor deposition techniques on cutting tools, Thin Solid Films 469–470 (2004) 92–98.
[2] L.A. Dobrzański, M. Staszuk, M. Pawlyta, W. Kwaśny, M. Pancielejko, Characteristic of Ti(C,N) and (Ti,Zr)N gradient PVD coatings deposited onto sintered tool materials, Journal of Achievements in Materials and Manufacturing Engineerting, 31/2 (2008) 629-634.
[3] L.A. Dobrzański, K. Gołombek, Structure and properties compound coatings TiN+gradient or multi (Ti,Al,Si)N+TiN types deposited onto cermet tools, Proceedings of the Scientific Conference "Materials, Mechanical and Manufacturing Engineering", M3E 2005 133-140.
[4] K. Lukaszkowicz, L.A. Dobrzański, M. Staszuk, M. Pancielejko, Comparison of the PVD gradient coatings deposited onto X40CrMoV5-1 and HS6-5-2 tool steel substrate, Journal of Achievements in Materials and Manufacturing Engineerting, 27/1 (2008) 79-82.
[5] L.A. Dobrzański M. Staszuk, J. Konieczny, J. Lelątko, Structure of gradient coatings deposited by CAE-PVD techniques, Journal of Achievements in Materials and Manufacturing Engineerting, 24/2 (2007) 55-58.
[6] P. Cichorz, Cutting tools, WNT, Warszawa 2006 (in Polish).
[7] M. Wysiecki, Modern tool materials, WNT, Warszawa 1997 (in Polish).
[8] L. Przybylski, Contemporary ceramics tool materials, Cracow University of Technology Press, Kraków 2000 (in Polish).
[9] M. Sopińska-Lizer, Sialon ceramic obtained from a powder by carbothermic reaction – physical-chemical production bases and properties, Scientific books, Silesian University of Technology Publishing House, Gliwice 2000.
[10] S. Hampshire, Silicon nitride ceramics – review of structure, processing and properties, Journal of Achievements in Materials and Manufacturing Engineering 24/1 (2007) 43-50.
[11] K.H. Jack, Review: SiAlONs and related nitrogen ceramics, Journal of Materials Science 11 (1976) 1135-1157.
[12] L.A. Dobrzański, Engineering materials and materials design. Fundamentals of materials science and physical metallurgy, WNT, Warsaw-Gliwice, 2006 (in Polish).
[13] Y. He, I. Apachitei, J. Jhou, W. Walstock, J. Duszczyk, Effect of prior plasma nitriding applied to a hot-work tool steel on the scratch-resistant properties of PACVD TiBN and TiCN coatings, Surface & Coatings Technology 201 (2006) 2534–2539.
[14] T.P. Mollart, J. Haupt, R. Gilmore, W. Gissler, Tribological behaviour of homogeneous Ti-B-N, Ti-B-N-C and TiN/h-BN/TiB_2 multilayer coatings, Surface and Coatings Technology 86-87 (1996) 231-236.
[15] W. Gissler, P.N. Gibson, Titanium implantation into born nitride films and ion-beam mixing of titanium born nitride multilayers, Ceramics International 22 (1996) 335-340.
[16] Y.H. Lu, Z.F. Zhou, P. Sit, Y.G. Shen, K.Y. Li, Haydn Chen, X-Ray photoelectron spectroscopy characterization of reactively sputtered Ti–B–N thin films, Surface & Coatings Technology 187 (2004) 98– 105.
[17] Z. Werner, J. Stanisławski, J. Piekoszewski, E.A. Levashov, W. Szymczyk, New types of multi-component hard coatings deposited by ARC PVD on steel pre-treated by pulsed plasma beams, Vacuum 70 (2003) 263–267.
[18] S. Stolarz, High-melting compounds and phases, "Śląsk" Publishing House, Katowice 1974 (in Polish).
[19] K. Gołombek, J. Mikuła, D. Pakuła, L.W. Żukowska, L.A. Dobrzański, Sintered tool materials with multi - component PVD gradient coatings, Journal of Achievements in Materials and Manufacturing Engineerting 31/1 (2008) 15-22.
[20] L.A. Dobrzański, K. Gołombek, Gradient coatings deposited by Cathodic Arc Evaporation: characteristic of structure and properties, Journal of Achievements in Materials and Manufacturing Engineerting, 14 (2006) 48-53.