A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
Volume 57 2012 Issue 2
DOI: 10.2478/v10172-012-0053-0

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THE DEPOSITION OF WC-Co COATINGS BY EBPVD TECHNIQUE

OSADZANIE POWŁOK WC-Co TECHNIKAMI EBPVD

The WC-Co carbides are widely used to deposit protective coatings on engineering surfaces against abrasion, erosion and other forms of wear existence. The nanostructure coatings offer high strength, a low friction coefficient and chemical and thermal stability. WCo coatings were deposited using EBPVD technique realized in original technological process implemented in the hybrid multisource device, produced in the Institute for Sustainable Technologies – National Research Institute in Radom (Poland). The different kind of precursor sources was used. Depending on the source of precursors nanostructure of coatings forms continuous film or consist from nano-carbides. Nanocrystalline WC-Co coatings show hardness in the range of 510-1266 HV. The microstructure of coatings were observed by transmission electron microscopy (TEM). The phase consistence were determined byBrucker D8 Discover-Advance Diffractometer. The paper presents the original technological equipment, methodology, and technological parameters for the creation of the nanocomposite coatings WC.
Keywords: electron beam evaporation, WC-Co coatings, microstructure

Węgliki WC-Co są szeroko używane do osadzania na powierzchniach inżynierskich jako ochrona przeciwko tarciu, erozji i innym formom zużycia. Powłoki nanostrukturalne wykazują wysoką wytrzymałość, niski współczynnik tarcia oraz chemiczną i termiczną stabiność. Powłoki WC-Co zostały osadzane techniką EBPVD przy użyciu oryginalnego technologicznego procesu zhybrydowym źródłem prekursorów, w Instytucie Technologii Eksploatacji w Radomiu (Polska). Użyto różnego rodzaju źródeł prekursorów. W zależności od rodzaju użytego źródła prekursorów nanostrukturalne powłoki były zbudowane z ciągłych warstw lub z nano-węglików. Mikrotwardość nanokrystalicznych powłok mieściła się w zakresie 510-1266 μHV. Mikrostruktura powłok była obserwowana transmisyjnym mikroskopem elektronowym (TEM). Skład fazowy powłok określono za pomocą aparatu rentgenowskiego Brucker D8 Discover-Advance Diffractometer. Artykuł prezentuje oryginalne technologiczne urządzenie, metodologię i technologiczne parametry pozwalające na wytworzenie nanokompozytowej powłoki WC.

1. Introduction

Tungsten carbide (WC) hard coatings are materials of great interest due to their excellent properties and great technological applications. The tribological applications require high hardness and high strength, a low friction coefficient and chemical and thermal stability [1,2]. WC-Co and WC coatings offer a great opportunity to develop such properties. This kind of coatings have relative high hardness (about 2200HV) and high melting temperature (about 2800°C). The WC exhibited extremely high modulus of elasticity, well above 700 GNm^{-2}, a value exceeded only diamond, and has a high thermal conductivity of 1,2 J $(cm.s.K)^{-1}$[3].

It is difficult to obtain a pure WC phase, as W-C phase diagram shows a narrow range of homogeneity for WC. The different methods are used for tungsten carbide deposition; PVD, CVD, hybrid method as well as thermal spraying methods . Same investigations indicated the dependence of WC coatings on the PVD deposition parameters, for example gas composition or sputtering time [4]. This results proof that the deposition parameters can strongly influence on the microstructure, composition and properties of coatings. The influence of gas parameter flow on WC coatings was also investigated in the work [5]. It was found that the nanostructured WC-Co coatings show better mechanical and wear properties in comparison to coatings with the conventional microstructures [1]. The observations performed by TEM revealed that the nanoparticles of WC were embedded in the amorphic matrix [6]. It suggests that the coatings could be mixture of nanomaterials and amorphic

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materials. The detailed investigations of microstructure thorough the WC cross section coatings were presented in the work [7].

The kind of the precursor source could be the one of the parameters influencing the microstructure of WC-Co coatings deposited by PVD method. In the presented work two kinds of precursors were used in the electron beam physical vapour deposition method (EBPVD). The effects of their influence on microstructure and properties of WC coatings were investigated.

2. Esperimental

The tungsten carbide coatings have been deposited at aluminium alloy substrate by electron beam physical vapor deposition method (EB PVD). The coatings were prepared in multicatode hybrid evaporation system in Institute of Suitable Technologies in Radom, Poland. The two ways of precursor deposition were used. The first coating process was performed form precursor source consisting from WC-Co compacted powder evaporated in argon. The second process of deposition was performed by evaporation of tungsten in C_2H_2 atmosphere. Before the deposition the substrate was heating by arc etching using the Cr cathode.

The microstructure of coatings was observed by using transmission electron microscope JEM 2010 ARP. Thin foils, to microstructure observations, were prepared by the cross sections technique using Gathan materials and equipment. The phase composition of coatings was investigated by Brucker D8 Discover-Advance Diffractometer with copper tubing (40 kV, 30 mA, $\dot{A}$ = 1,540598 A°). The method of superficial layer measurement and Diffract Plus Evaluation software were used to examine the layers composition X-ray results. The scanning electron microscopy SU-70 with field emission gun thermally aided was used for investigation of chemical composition of deposited coatings. The microscopy was equipment with analyzers EDS UltraDry and WDS MagnaRay produced by Thermo Ecientific. The hardness of coatings was measured by Vickers method.

3. Results and discussion

Figure 1 presents the microstructure of WC-Co coating prepared from WC-Co compacted powder evaporated in argon. It could be visible that the microstructure of coating is very differentiate and consists from bright and dark layers (Fig. 1a). The higher magnifications show that layers are built from nanometric circular in shape particles with the characteristic cafe grain contrast (Fig. 1b, Fig. 1c). In dark layers particles have larger dimension than inside bright ones. Mostly particles have spherical shape, however also some elongated particles were also found (Fig. 1b).

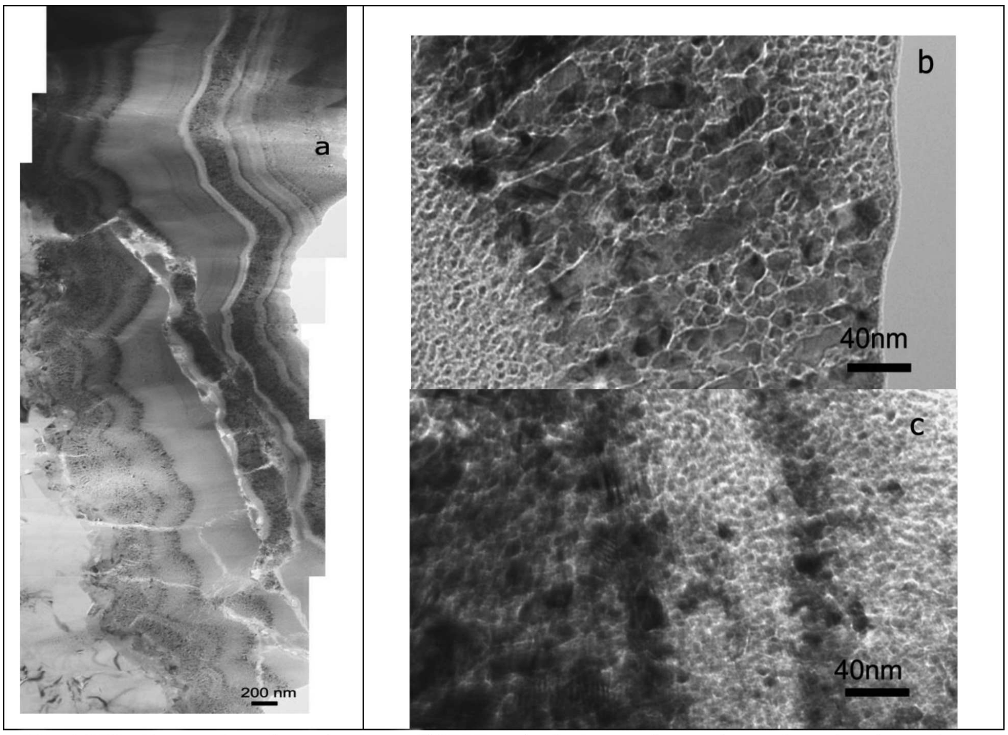

Fig. 1. WC-Co coating deposited by EBPVD technique, a) coating microstructure observed by transmission electron microscopy, b) outer layer of deposition, c) characteristic spherical particles

The investigations performed by EDS technique identified close to substrate face the Cr layer, which results from ion surface cleaning by Cr source in the PVD chamber, before the deposition (Fig. 2). The next layer of coating contains Co and C, respectively in proportion: C K_{α}–44,54% at to Co L – 55,46% at. The outer layer is enriched in carbon and corresponds to dark layers in Fig.1b and Fig.1c consisting from spherical black particles. The performed analysis indicates that the coating is generally build from the mixture of Co and C particles (Fig. 3). The tungsten appears on the very low level, as it informs the number of counts presented in the upper right corner of figures. In the case of tungsten the only 37 counts appeared (Fig. 2e) in comparison to the 1027 counts for Co (Fig. 2d).

The X- ray investigations, which results are presented in Fig. 4, show high level of background typical for amorphic phase. The picks from Al and Si background are only visible in the diagram. There were not found picks from WC phase, which confirms presented chemical identification of coating performed by the SEM EDS. It is possible that inside the Co layer exists some part of WC carbides but in very insignificant quantity.

The average 510 HV hardness of the deposited layers was found. It is rather lower value in comparison to the hardness of WC-Co coatings, which usually have the level of about 1800-2100 HV [8].

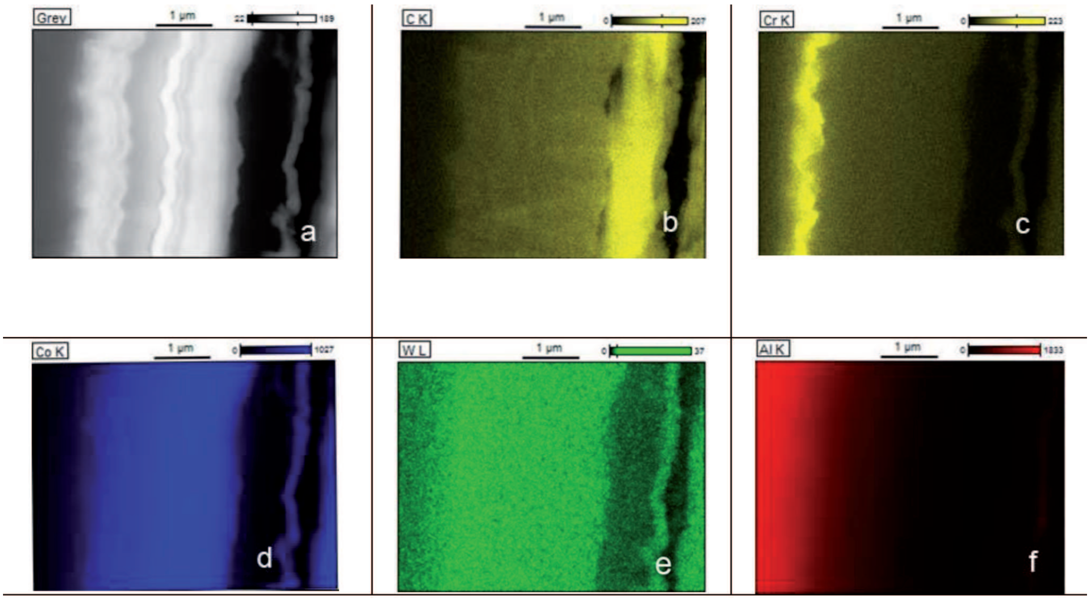

Fig. 2. SEM EDS mapping showing a) microstructure of coating, b) distribution of C element, c) distribution of Cr element, d) distribution of Co element, e) distribution of W and f) substrate element Al

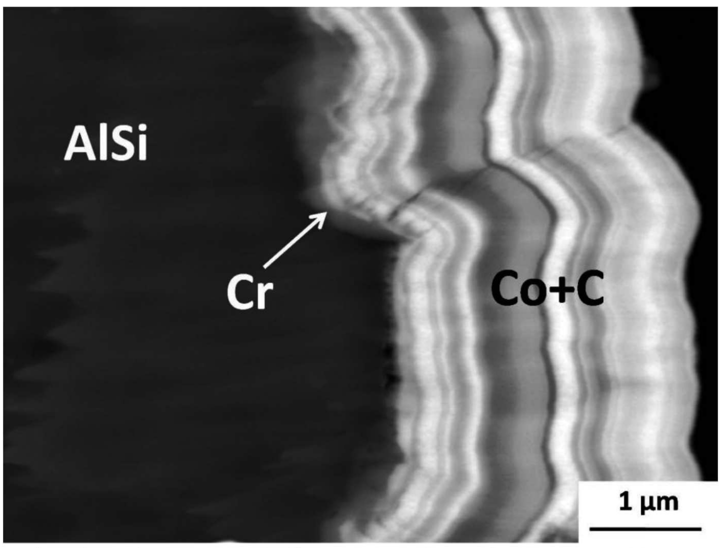

Fig. 3. Co + C coating deposited from WC-Co compacted powder evaporated in argon

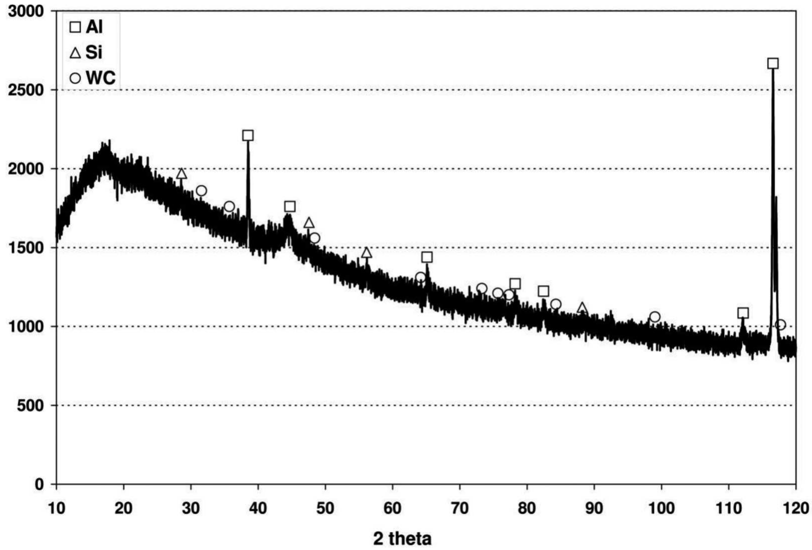

Fig. 4. X-ray diagram showing high level of background typical for amorphic phase

The microstructure of coating obtained by deposition from tungsten source in the C_2H_2 atmosphere using the PVD technique, observed by transmission electron microscopy, is presented in Fig. 5. The columnar microstructure was found. The detailed investigations show that column width has about 200-500 nm. The columns were built from narrow bands consisting from granules showing the nanometric dimensions (Fig.4c and Fig.4d).

Figure 5 presents the exemplary EDS maps of chemical element distribution. The number of counts for carbide and tungsten is comparable (C – 97, 71 – Fig. 5b, W – 81, 82 – Fig. 5e). It suggests WC carbide existence inside the investigated areas (Fig.7a). The investigations show that next the regions with the WC carbides, the W_2C carbides form, which example of occurrence is presented in Fig.7b.

The calculation of the stoichiometry composition of carbides was also performed on the base of intensity elements plot recorded during SEM investigations.

The X-ray investigations show that contrary to the deposition from WC-Co compacted powder evaporated in argon, coatings deposited from tungsten in C_2H_2 atmosphere exhibited amorphic and nanometric form, which can be concluded from both high level of background and the broader peaks in phase diagrams (Fig. 6). The discrete picks from WC suggests some part of nanometric phase.

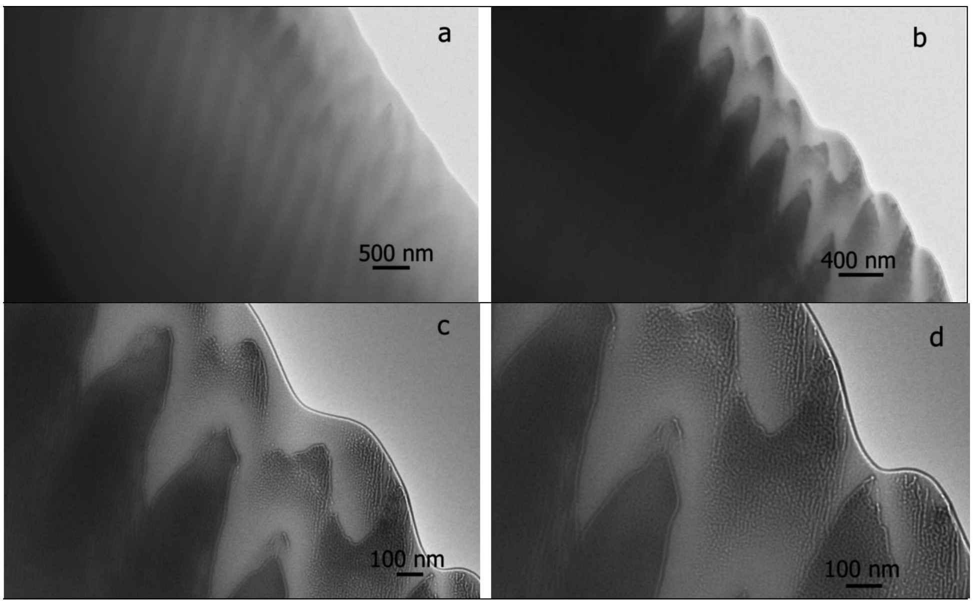

Fig. 5. Microstructure of WC coating deposited by EBPVD, a) column microstructure, b) spatial distribution of columns, c),d) internal microstructure of columns

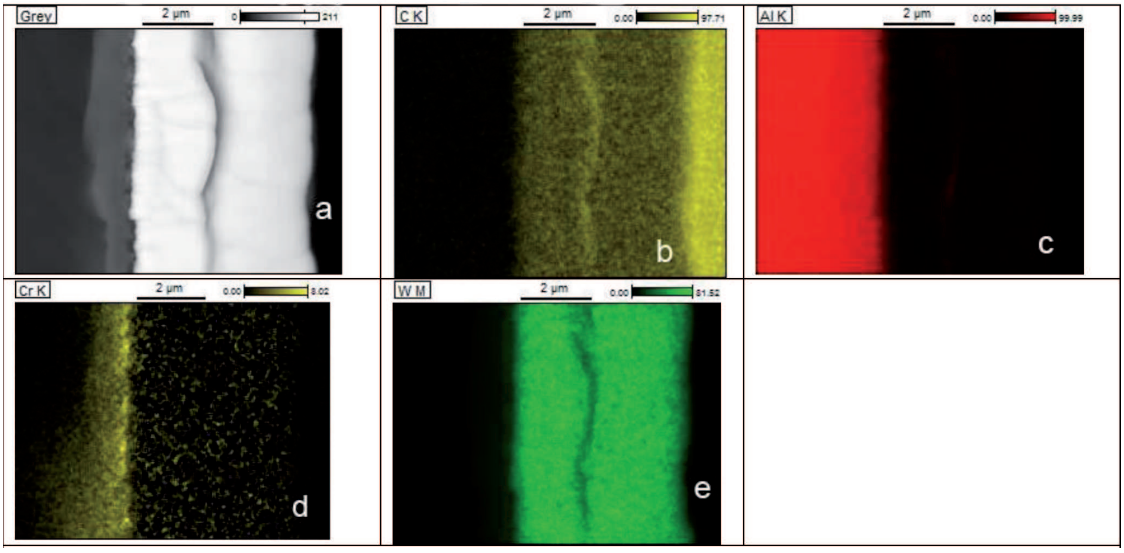

Fig. 6. The distribution of elements in coating, a) investigated area of coating, b) distribution of carbon, c) substrate element Al, d) distribution of Cr and e) distribution of tungsten

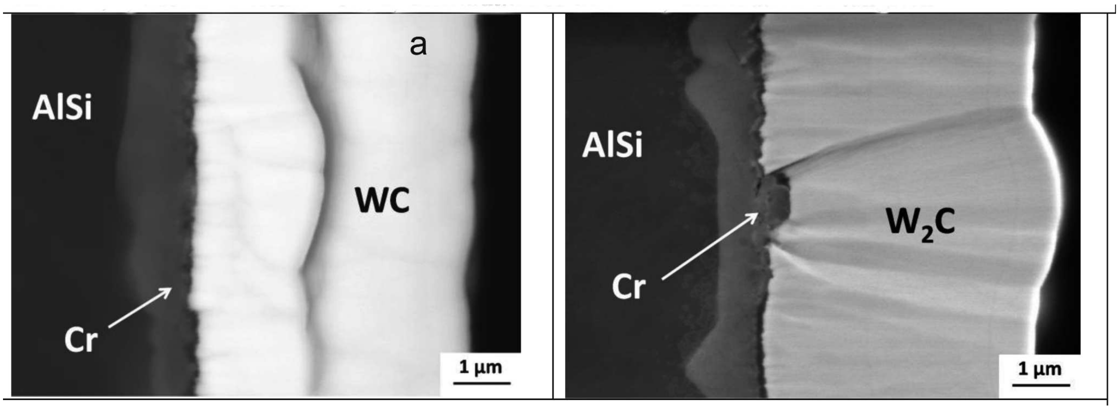

Fig. 7. WC coating deposited from tungsten source in the C_2H_2 atmosphere, a) area of occurrence of WC carbides, b) area of occurrence of W_2C carbides

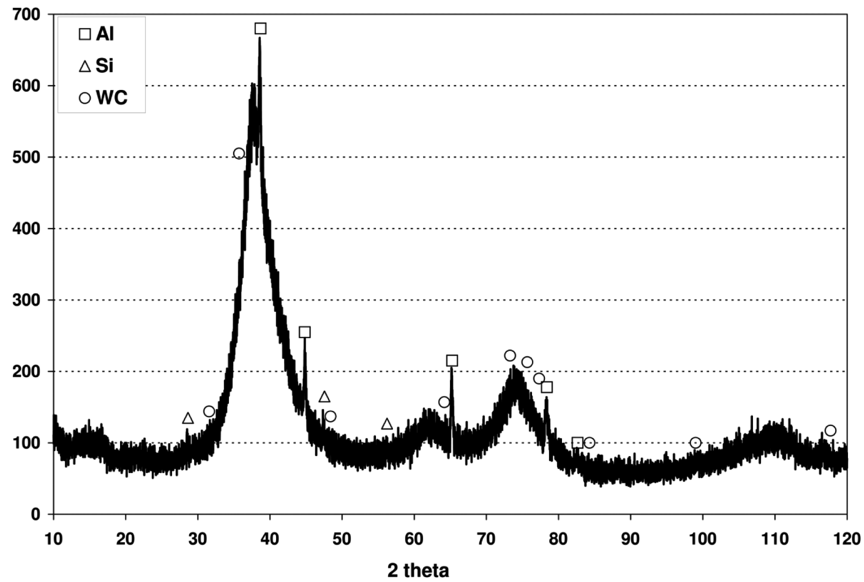

Fig. 8. X-ray diagram of WC coating, deposited from tungsten source in the C_2H_2 atmosphere, showing high level of background, some picks from Al, Si and discrete picks from WC are visible

4. Summary

Considering the presented results, the mechanism of Cr interlayer deposition during the cleaning surface process was isolated. This is the reason of the Cr interlayer occurrence. The results of the work [5] reported that interlayer of chromium can improve the adhesion of WC coatings. From this point of view existence of Cr interlayer is advantageous in the deposited coating composition.

The microstructure and phase composition of coating deposited from WC-Co compacted powder evaporated in argon in comparison to the coating obtained by deposition of tungsten source in the C_2H_2 atmosphere demonstrate essential differences. In the first case the only insignificant percentage of WC was found. The main dominating elements inside the coating was Co and carbon. The mixture of Co and C particles was typical microstructure in this analysed coating. Results presented in the work [4] shown appearance of the WC carbide coating deposited in argon gases onto carbon steel substrates. Therefore it is difficult to recognized the reason of the unsuccessful deposition of WC carbides from WC-Co compacted powder evaporated in argon in the performed work. Probably the vapour pressure of tungsten was too low to deposition of this element in the enough quantity. The understanding of this phenomenon requires additional investigations.

The deposition of tungsten in the C_2H_2 atmosphere was successful and WC and W_2C carbides were found inside the coating. Very characteristic is uniform structure of coating. The detailed investigations by TEM technique revealed that there exists very delicately visible internal columnar microstructure of coating having nanometric size of columns. The fine-structure coatings, deposited onto the sintered cutting toots we also found in the work [9].

On the basis of the experimental results of the X-ray investigations the phase consistence of coatings was characterized. In the both cases it has been found the mixture of the dominating amorphic phase and partly existence of nanometric state of coating. Especially in the case of coating deposited from tungsten source in the C_2H_2 atmosphere probably larger part of coating characterized the nanometric state.

The hardness of coating containing Co and C (coating deposited from WC-Co compacted powder) revealed level of about 510 HV. The hardness of coating containing WC and W_2C carbides is about twice time higher (1266 HV). The essential increase of hardness in the second case is connected with the existence of hard carbides, which were absent in the first kind of coating.

Acknowledgements

The work was financially supported by polish project N R15 0001 06.

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Received: 10 December 2011.