Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 43
ISSUE 1
November
2010

Chromium carbide coatings obtained by the hybrid PVD methods

M. Richert [a,*], A. Mazurkiewicz [b], J. Smolik [b]
[a] Faculty of Non-Ferrous Metals, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków
[b] Institute for Sustainable Technologies - National Research Institute, ul. Pułaskiego 6/10, 26-600 Radom
* Corresponding author: E-mail address: mrichert@agh.edu.pl

Received 11.09.2010; published in revised form 01.11.2010

Materials

ABSTRACT

Purpose: With the use of the Arc-PVD and Arc-EB PVD hybrid method, the chromium carbide coatings were deposited on steel substrate. Two kinds of coatings were obtained. The nanostructure coatings were formed by deposition of chromium carbide films by Arc PVD evaporation technique. The multilayer coatings were produced by Arc-EB PVD hybrid technology. In the second case the amorphous phase in majority was found in samples, identified by X-ray investigations.

Design/methodology/approach: The Arc PVD and combination Arc-EB PVD methods were used for carbide coatings deposition. The special hybrid multisource device, produced in the Institute for Sustainable Technologies – National Research Institute (ITeE –PIB) in Radom, was used for sample deposition. The microstructures of coatings were investigated by JEM 20101 ARP transmission electron microscopy (TEM), TESLA BS500 scanning electron microscopy (SEM) and Olympus GX50 optical microscopy (MO). The X-ray diffraction was utilized to identify phase configuration in coatings

Findings: The microstructure of deposited coatings differs depending on the deposition method used. The Arc PVD deposition produced nanometric coatings with the Cr_3C2, $Cr_{23}C_6$, Cr_7C_3 and CrC carbides built from nanometric in size clusters. In the case of the Arc-EB PVD hybrid technology in majority of cases the amorphous microstructure of coatings was found. The hybrid coatings consist of alternating layers of Ni/Cr-Cr_3C_2.

Practical implications: The performed investigations provide information, which could be useful in the industrial practice for the production of wear resistant coatings on different equipments and tools.

Originality/value: It was assumed that by using different kinds of PVD methods the different microstructures of coatings could be formed.

Keywords: PVD processes; Chromium carbide coatings; Nanomaterials; Amorphous phase

Reference to this paper should be given in the following way:
M. Richert, A. Mazurkiewicz, J. Smolik, Chromium carbide coatings obtained by the hybrid PVD methods, Journal of Achievements in Materials and Manufacturing Engineering 43/1 (2010) 145-152.

1. Introduction

Physical vapor deposition (PVD) processes are deposition processes in which ions or molecules of a material are vaporized from a solid or liquid source, transported in the form of a vapor through a vacuum or low – pressure gaseous environment and condense on a substrate. PVD processes are used to deposit films with the thickness range of a few angstroms to several dozen nanometers [1-4]. Typical PVD deposition rates vary from 0.1-10 nm/sec. The PVD coating techniques are vacuum evaporation, sputter deposition, arc evaporation, low voltage electron beam evaporation, cathode arc deposition, triode high voltage electron beam evaporation, ion planting and magnetron sputtering.

PVD coatings can be harder, have finer grain size and smoother surface morphology, be crack – free due to residual compression stresses. There are promising available nanometric features of coating. During last year's, nanostructured thin films have attracted considerable attention in several industrial applications [4-7]. Hard protective coatings of chromium carbide show excellent physical properties such as high hardness, strength, toughness, chemical stability and corrosion resistance [8, 9]. Chromium carbide coatings, which exhibit high hardness and excellent wear, have been extensively used as protective coating on various tools and dies. Because of these properties, they are widely used especially in tribological applications.

In recent years, an increasing effort has been made to obtain high-quality physical vapor deposition (PVD) chromium carbide coatings. However, in most cases, the obtained films were amorphous or with a not well-defined crystalline structure [10]. Coatings with the nanometric features were also deposited. In particular, the problem of finding the deposition conditions to obtain crystalline Cr_3C_2 remains still unsolved.

In the presented work, chromium carbide coatings deposited by Arc PVD and by the use of the Arc-EB PVD hybrid method, were investigated. The comparison of phase composition of coatings is presented. The great attention is put on microstructure investigations.

2. Experimental basis

2.1. Methods of carbide coatings deposition

High-density discharge located in the micro area of cathode spots is the basic phenomenon that can be observed in Arc-Evaporation method. As a result of the high-density discharge, the cathode material evaporates rapidly and is then ionized. A stream of highly ionized plasma, directed toward the surface of polarized negative potential ($U_{bias} \approx -150 \div -200V$) is created, and thus the coating material is crystallized. The process of arc evaporation of the metallic cathode in the reactive atmosphere allows the deposition of metal nitrides or carbides on the surface. The main objective of the Electron Beam Evaporation method is to cause the material placed in the melting pot to evaporate through its bombardment with high energy electron beam. In order to create the Ni/Cr-Cr_3C_2 multilayer coating the combination of two different surface treatment methods, i.e. the Electron Beam Evaporation method and Arc Evaporation method, into one hybrid the Arc-EB PVD was proposed (as shown in Fig. 1).

The configuration of the Arc-EB PVD hybrid method shown in Fig.1 enabled the separation of deposition zones of Cr_3C_2 carbide by the Arc-Evaporation method and the separation of Ni/Cr matrix using the EB Evaporation method. The introduction of the rotation of the substrate provides a selective deposition of individual materials as well as the composition of the multilayer structure.

In order to present the technical realization of hybrid technology shown in Fig. 1 the authors designed an original technological process implemented in the hybrid multisource device (Fig. 2), produced at the Institute for Sustainable Technologies – National Research Institute in Radom (Poland).

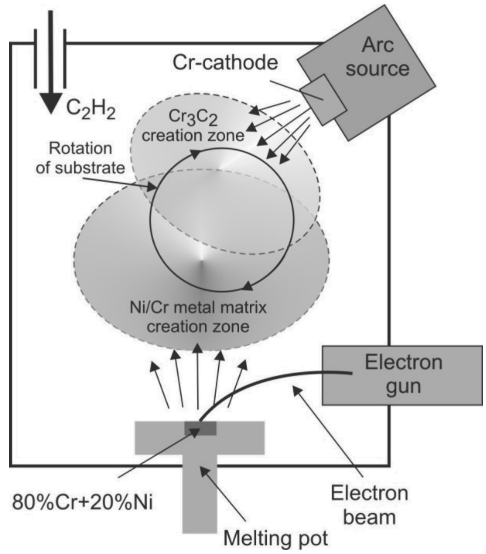

Fig. 1. Diagram of Arc-EB PVD hybrid surface treatment technology

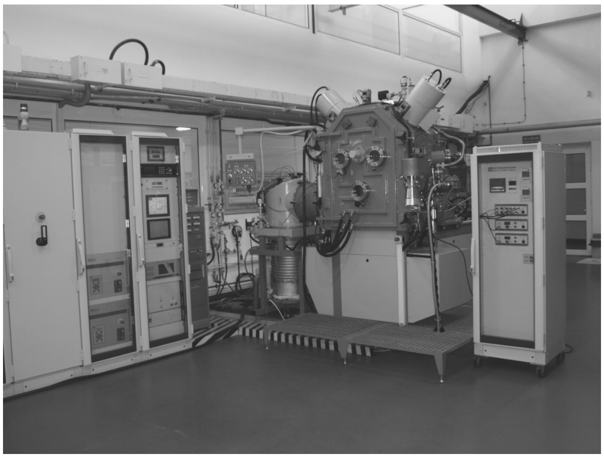

Fig. 2. Hybrid multisource device produced at the Institute for Sustainable Technologies – National Research Institute in Radom

The device has been equipped with two arc sources with the cathode diameter of ϕ=80 mm and with the 60kW electron gun with the dynamic electron beam deflection circuit and system. The device is equipped with modern, reliable power systems, a substrate polarisation system, multichannel process gases dosing system as well as the systems of monitoring and measuring the substrate temperature and the atmospheric gas pressure.

The optimisation of technological parameters of Cr_3C_2 carbide production through the Arc-Evaporation method and Ni-Cr matrix through Electron Beam Evaporation method was carried out in order to develop technological parameters of creating the Ni/Cr-Cr_3C_2 composite coating with the use of the Arc-EB PVD hybrid method.

2.2. Experimental procedure

Using Arc evaporation and hybrid Arc-EB evaporation PVD processes the Cr_3C_2 – NiCr coatings were deposited on the steel substrate.

In Table 1 the parameters of the using processes are presented.

Table 1
Parameters of applied PVD processes

Method and sample	Pressure	Atmosphere	Bias [U]	I
Arc PVD	$7x10^{-4}$mbar	Ar	-1000V	80A
Arc-EB PVD	$3x3^{-3}$mbar	C2H2	-300V	60A

The microstructure of coatings was studied by Olympus GX50 optical microscopy (MO), TESLA BS500 scanning electron microscopy (SEM) and under JEOL 2010 ARB transmission electron microscopy (TEM), provided with an Energy Dispersive Spectrometer (EDS) for the identification of chemical composition in micro-areas.

Thin foils for TEM investigations were prepared from cross sections by cutting, grinding and ion sputtering, using Struers and Gatan instruments. The samples for optical and scanning electron microscopy observations were polished mechanically applying the Struers equipment and technique. The samples were grounded, then polished by using OPS suspension and then with diamond pastes.

The phase composition of PVD coatings was investigated by Brucker D8 Discover-Advance diffractometer with copper tubing (40 kV, 30 mA, $\lambda = 1{,}540598$ A°). The method of superficial layer measurement and Diffract Plus Evaluation software were used to examine the composition of the layers.

3. Investigation Results

The microstructure of cross section of Cr_3C_2 coating is shown in Fig. 3. The characteristic elongated droplets were found inside coating, placed perpendicularly to the surface of the substrate. The observations of Cr_3C_2 external surface of coatings provide evidence for essential influence of finding inside coat droplets on the surface roughness (Fig. 4). The existence of droplets could contribute to the increase in the coatings surface roughness. The performed investigations show strong bond between the substrate and the chromium carbide film. Any voids and discontinuities were found between coats and substrate.

The cross section of coatings reveal columnar microstructure, characteristic for the PVD deposition (Fig. 5A). Fig. 5B shows the selected area diffraction pattern corresponding to the observed area visible in Fig. 5A. Such continuous diffraction rings demonstrate that chromium carbide coating could have amorphous or nanometric structure.

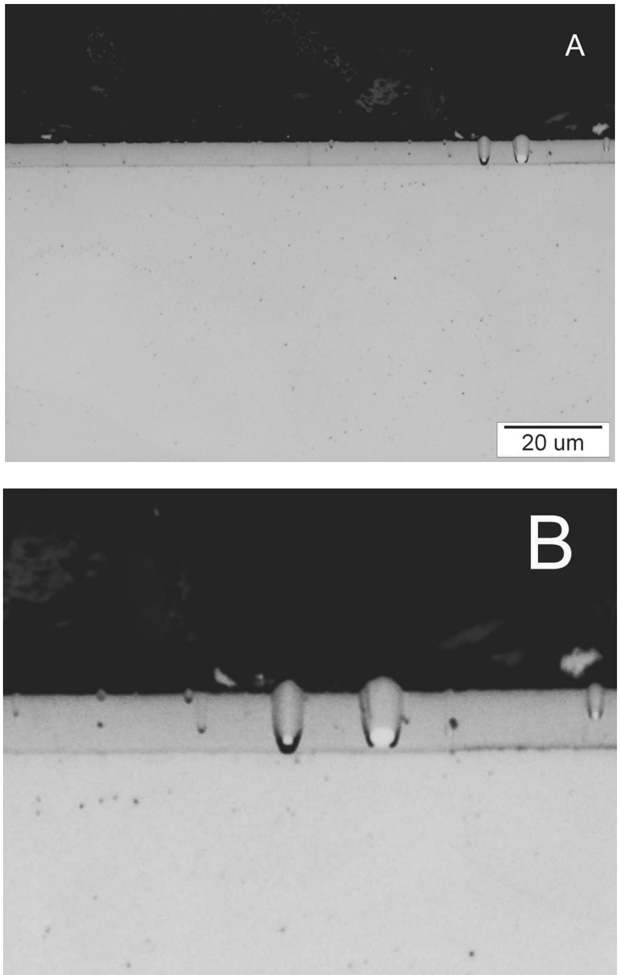

Fig. 3. Cross section of Cr_3C_2 coating deposited by Arc evaporation a) droplets inside coat, b) enlarger droplets (optical microscopy-MO)

The X-ray results of the Arc evaporation deposited sample are presented in Fig. 6. The Cr_3C_2, $Cr_{23}C_6$, Cr_7C_3 and CrC carbides inside the coating were identified. The broader peaks at 15°, between 30-40° and at 60° suggest nanometric kind of the microstructure.

The TEM investigations of microstructure contributed to the mentioned possibility of nanometric features of the sample. An examination of internal constitution of columnar microstructure separate the predictable nanometric clusters (Fig. 7). The nanometric in size carbide cluster were determined inside columns and provided satisfactory explanation to the growth of the columns (Fig. 7B). There are no data concerning the way of the formation of nanometric coatings. However, some deposition parameters and method of deposition can strongly influence the type of the microstructure coating.

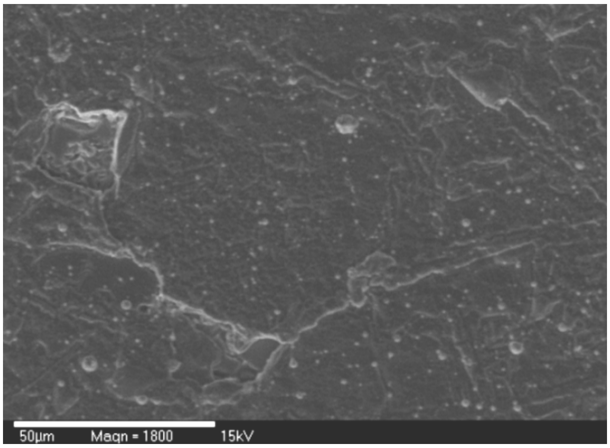

Fig. 4. Surface roughness of Cr_3C_2 coating deposited by Arc evaporation (SEM)

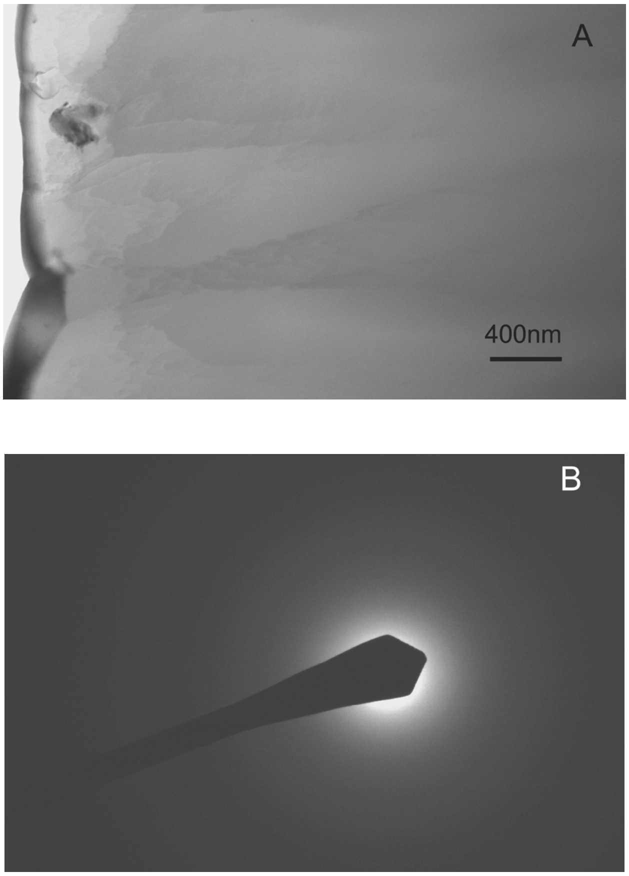

Fig. 5. Arc evaporation deposition, a) columnar microstructure of coating, b) diffraction pattern (TEM)

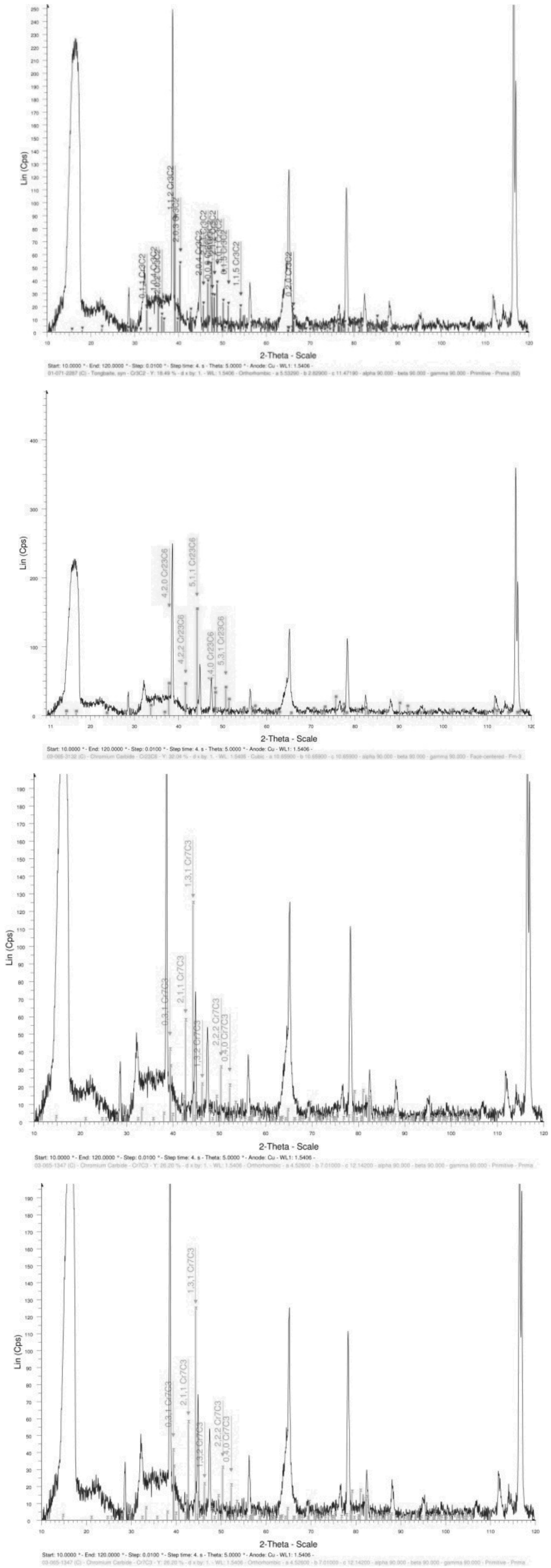

Fig. 6. X-ray profile of sample deposited by Arc evaporation, peaks from chromium carbides are identified

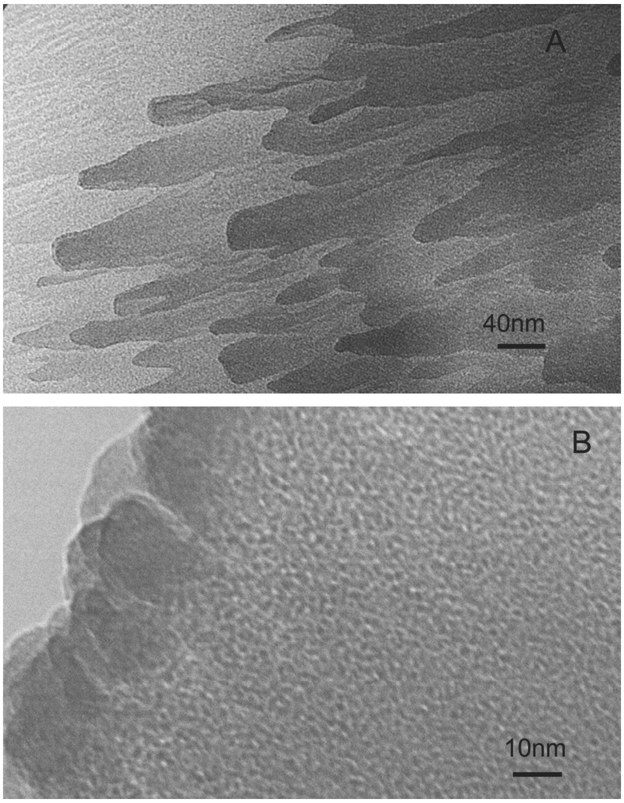

Fig. 7. Internal constitution of columnar microstructure of coating deposited by Arc evaporation, A) nanometric columns, B) nanometric clusters of carbides inside columns

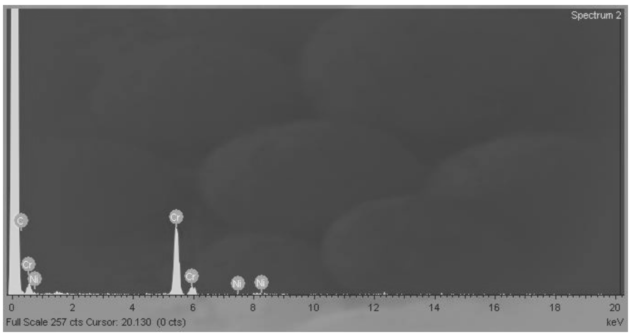

Fig. 8. EDX result of Arc evaporation deposition (TEM)

The deposition of Cr_3C_2 carbide coatings was the essential goal of the performed investigations. The existence of another kind of chromium carbides in coatings suggests the tendency to form the depletion in carbon carbides in the deposited material. The chemical composition of carbides requires to undertake the study to establish the kinetic and reaction mechanisms leading to the obtainmet of the material of desired properties.

With the use of the EDX technique the determination of elements in Arc PVD coating was performed. Such elements as: Cr, C and Ni were found (Fig. 8).

The second deposition technique used was the hybrid source treatment Arc-EB method. Fig. 9 presents the cross section trough the hybrid chromium carbide coating. The coating consists of from the alternating layers of Ni/Cr-Cr_xC_y.

What is characteristic is the broader layer deposited directly on the substrate. Its width is about 200 nm. The stacking of thinner layers is observed well. The summary thickness of the stacking layers is about 600 nm.

Typical microstructure of the hybrid coating deposited by hybrid source treatment with the use of the Arc-EB method observed TEM technique, is shown in Fig. 10, Fig. 11 and Fig. 12.

Fig. 10 presents the enlarged view of stacking layers. The layers have different thickness –varying from 6 nm to 20 nm. In the right upper part of Fig. 10, above the stacking layers area, the clearly visible layers with the inhomogeneous microstructure exist, which are characterized by dark, stripped contrast and width of about 20 nm. Fig. 11 and Fig. 12 show the details of the inhomogeneous layers.

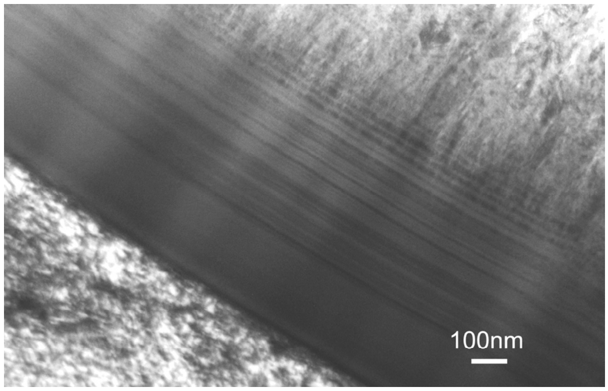

Fig. 9. Cross section trough the chromium carbide coating, Arc-EB hybrid PVD technology

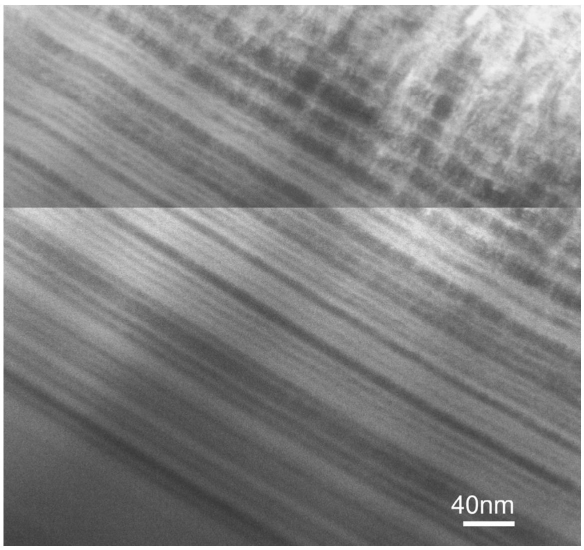

Fig. 10. Hybrid chromium carbide coating, area of the stacking layers

Fig. 11 demonstrated very characteristic interrupted contrast of layers. The thickness of layers is from a few to over a dozen nanometers. The layers with the interrupted contrast – dark and bright are additionally separated by bright smooth layers.

The layers observed in Fig. 12 are thicker than those observed in Fig. 11. They also show a changeable contrast between great and bright streaks.

The interrupted contrast could suggest some diversification of carbide and chromium elements inside the layers. Especially, it seems that places with a higher intensity of darkness are probably connected to the greater concentration of chromium carbides. The bright places are connected to the higher concentration of the Ni element. Probably very thin bright layers of about a few nanometers, which separated the layers with the interrupted contrast, are also connected to the areas rich of Ni.

The internal microstructure of broader layer deposited directly on the substrate is presented in Fig. 13. The characteristic columns, similar to ones observed in the Arc PVD coatings, are observed. Their position indicates front of deposition and shows direction of successive growth of coating. Inside broader columns, whose thickness is about 200 - 300 nm, it is possible to distinguish alternately placed dark and bright needle columns which thickness is about 10-30 nanometers.

The TEM high resolution TEM observations revealed the internal microstructure of the needle columns, observed in Fig. 13. They consist of stacks of atomic layers, which are visible inside the columns in the form of bulge traces (Fig. 14). Each column form different front of deposition and different angles of inclination of atomic layers. However, it is also possible to distinguish the common direction of crystallographic plains in all columns, which is inclined at of about 45^{o} to the direction of the column growth. The mutually crossing sets of plain traces are also observed inside columns.

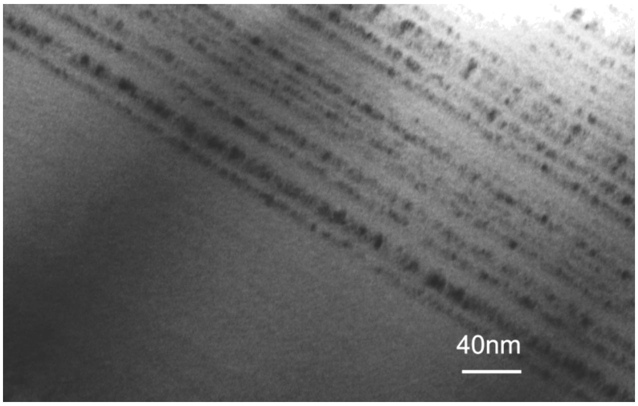

Fig. 11. Multilayer chromium carbide coating deposited by hybrid technology

The hybrid coatings difractograms are presented in Fig. 15, Fig. 16 and Fig. 17. A marked figures A show background, which is cut in B marked. What is characteristic is the high level of background with the broader extended peak, together with peaks corresponding to Fe - the background element . Due to the amorphous character of coatings, no peaks from chromium carbide phases are found.

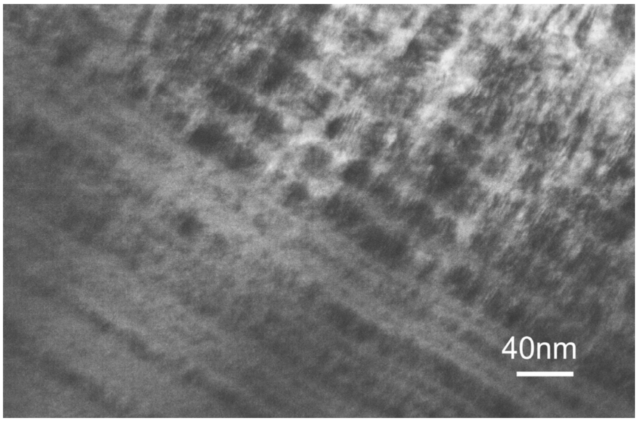

Fig. 12. Layers with the changeable contrast, Arc-EB hybrid PVD technology

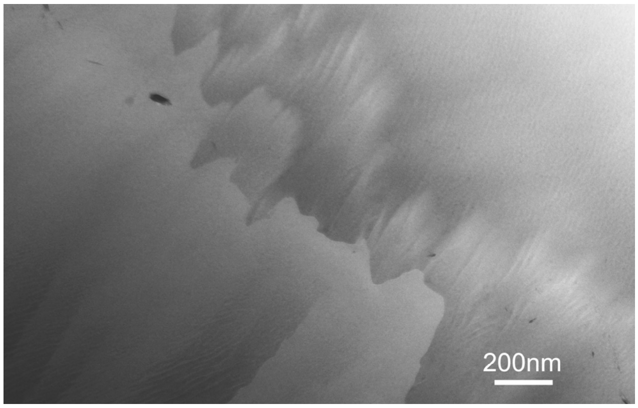

Fig. 13. Internal microstructure of layer deposited directly on the substrate, Arc-EB hybrid PVD technology

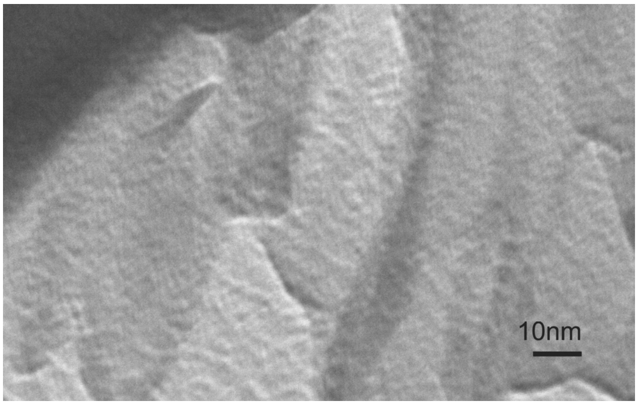

Fig. 14. The internal microstructure of columns, Arc-EB hybrid PVD technology

Such amorphous microstructure could be explained as existence of amorphous carbon rich carbide regions. Similar results were obtained during the investigations a carbide coatings for molding die applications presented in the work [7].

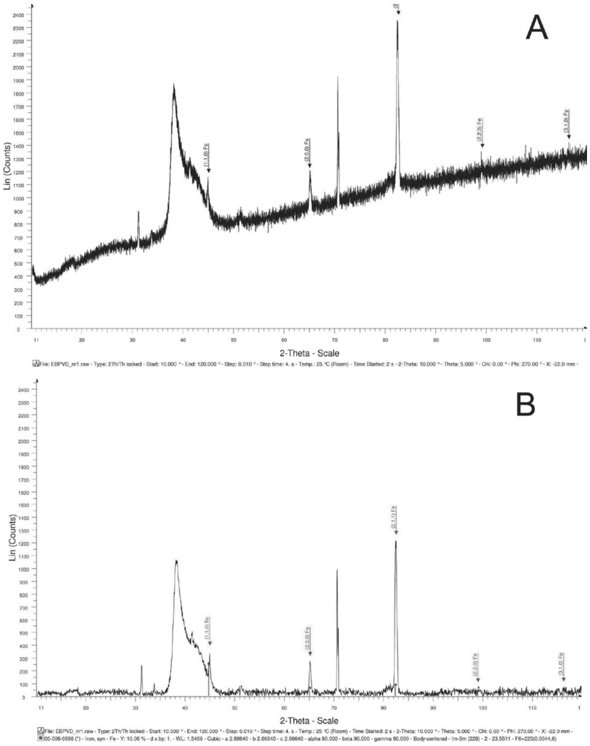

Fig. 15. Sample deposited by ARC EB hybrid technology, A) with background, B) without background

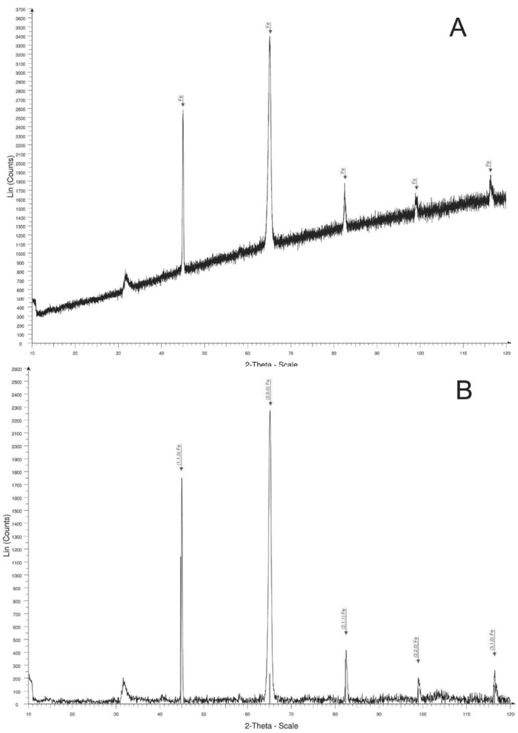

Fig. 16. Sample deposited by ARC EB hybrid technology, A) with background, B) without background

In Fig. 15 the broader peak between 35 – 48^{o} exists, not visible in Fig. 16 and Fig. 17. This suggest partly nanometric microstructure of this sample, similar to the results obtained for Arc PVD, presented in Fig. 6. However, in majority, the hybrid technology produced amorphous chromium carbide coatings.

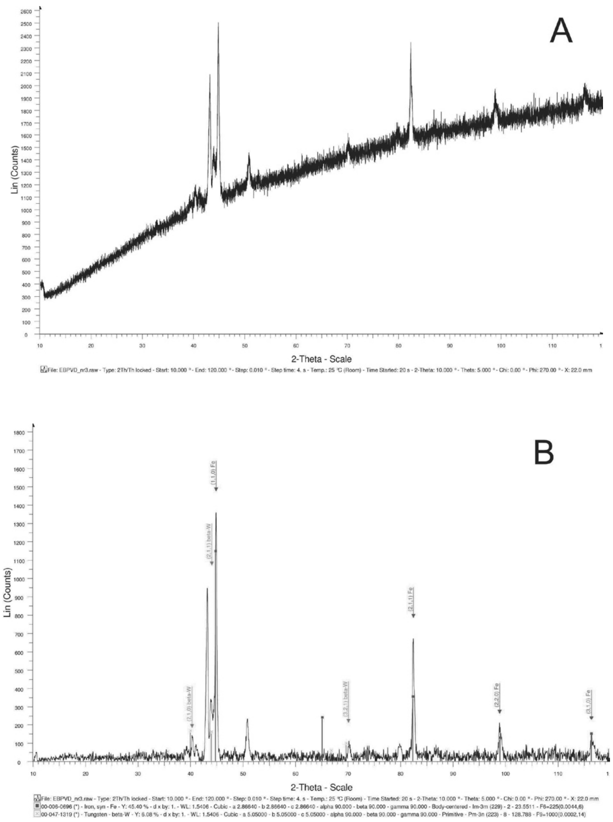

Fig. 17. Sample deposited by ARC EB hybrid technology, A) with background, B) without background

4. Discussion

The unique physical and chemical properties of carbide coatings like high melting point, extreme hardness, low coefficient of friction and chemical inertness make them candidates for wearing corrosion-resistant coatings [10,11]. The properties of coatings are influenced by their microstructure and composition which are dependent on the deposition technique used, such as different physical vapor deposition (PVD) methods. Using the same deposition technique, the microstructure and the composition of carbides are dependent on deposition parameters such as a reactive gas pressure, substrate temperature, power, and sputtering system geometry. However, despite further progress in surface analytical methods, the structure and the composition of the carbides formed are in many cases not yet well determined. Especially in many cases the amorphous phases are recognized in carbide coatings [10,11].

The presented results of chromium carbide coatings investigations shown that the microstructure of coatings strongly depend on the PVD method of deposition. The Arc evaporation method of deposition forms coatings, which contain the mixture of Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$ and CrC phases. The existence of such phases is difficult to isolate, due to the superposition of peaks from carbides. The Cr_3C_2 shows the broader peak between 30-42^0 suggesting the nanometric type of phase (Fig. 6). From the comparison of position of another kind of chromium carbides it could be stated that Cr_3C_2 is the dominating phase in the deposited coating.

The microstructure of nanometric coating deposited by the Arc PVD technique consists of the delicate outline columns of chromium carbide (Fig. 5A). The detailed observations show that columns are formed from nanometric in size chromium carbide clusters (Fig. 7).

The second deposition method used in the work was the Arc-EB hybrid PVD technology. This kind of deposition effect to the amorphous chromium carbide film, which phase consistence was documented by X-ray investigations.

The difractograms presented in Fig. 15, Fig. 16 and Fig. 17 illustrate the X-ray investigations. In one sample, besides the amorphous phase, partly nanometric one was found as well (Fig. 15).

In the work [12] it is reported that the amorphous phase of chromium carbides was obtained in coatings deposited by unbalanced magnetron sputtering in contrast with crystalline Cr_3C_2 obtained by deposition by arc evaporation. The presented data agree with the obtained results.

The amorphous microstructure of PVD coatings was also obtained by J.Esteve at all [7] and Chun-Chun Lin at all [8]. They reported the difractograms with the extended peaks typical for amorphous phase.

The amorphous microstructure of PVD coatings is often reported in literature, especially in PVD coatings. Nowadays the great effort is concentrated on the investigations leading to the identification and recognition of parameters responsible for the formation of this type of coatings microstructure.

5. Conclusions

The performed investigations show that:

1. Microstructures of coatings deposited by Arc PVD and hybrid Arc-EB PVD technology are different. The microstructure of Arc PVD coatings consists of a continuous film. The coatings deposited by hybrid technology are compound of the stacking of layers.
2. The internal microstructure of coatings in all techniques contained columns perpendicular to the substrate surface.
3. It was found that in the case of Arc PVD method the nanometric microstructure of coatings is formed. The hybrid method generally produced the amorphous kind of coatings.

Acknowledgements

The work was financially supported by polish project NR15 0001 06

References

[1] K. Lukaszkowicz, L.A. Dobrzański, A. Zarychta, L. Cunha, Mechanical properties o multilayer coatings deposited by PVD techniques onto the bras substrate, Journal of Achievements in Materials and Manufacturing Technology 15 (2006) 47-52.

[2] L.A. Dobrzański, K. Gołombek, J. Mikuła, D. Pakuła, Multilayer and gradient PVD coatings on the sintered tool materials, Journal of Achievements in Materials and Manufacturing Technology 31/1 (2008) 170-190.

[3] D. Pakuła, L. Dobrzański, Investigation of the structure and properties of PVD and CVD coatings deposited on the Si_3N_4 nitride ceramics, Journal of Achievements in Materials and Manufacturing Technology 24/1 (2007) 79-82.

[4] L.A. Dobrzański, L. Wosińska, K. Gołombek, J. Mikuła, Structure of multicomponent and gradient PVD coatings deposited on sintered tool materials, Journal of Achievements in Materials and Manufacturing Technology 20 (2007) 99-102.

[5] S. Gulizia, M.Z. Jahedi, E.D. Doyle, Performance evaluation of PVD coatings for high pressure die casting, Surface and Coatings Technology 140 (2001) 200-205.

[6] A. Jellad, S. Labdi, C. Malibert, G. Renou, Nanomechanical and nanowear properties of Cr3C2 thin film deposited by rf sputtering, Wear 264 (2008) 893-898.

[7] J. Esteve, J. Romero, M. Gomez, A. Lousa, Cathodic chromium carbide coatings for molding die applications, Surface & Coatings Technology 188-189 (2004) 506-510.

[8] Chun-Chun Lin, Wei-Jen Hsieh, Jain-Hong Lin, Uei-Shin Chen, Xing-Jian Guo, Han C. Shih , Formation and characterization of chromium carbide films deposited using a 90- bend magnetic filtered cathode vacuum arc system, Surface & Coatings Technology 200 (2006) 5052-5057.

[9] M. Roy, A. Pauschitz, R. Polak, F. Franek, Comparative evaluation of ambient temperature friction behavior of thermal sprayed Cr_3C_2 - 25(Ni20Cr) coatings with conventional and nano-crystalline grains, Tribology International 39 (2006) 29-38.

[10] A. Zalar_, J. Kovac, B. Pracek, P. Panjan, M. Ceh, Ion sputtering rates of C, CrxCy, and Cr at different Ar+ ionincidence angles, Vacuum 82 (2008) 116–120.

[11] Chun-Chun Lin, Wei-Jen Hsieh, Jain-Hong Lin, Uei-Shin Chen, Xing-Jian Guo, Han C. Shih, Formation and characterization of chromium carbide films deposited using a 90- bend magnetic filtered cathodic vacuum arc system, Surface & Coatings Technology 200 (2006) 5052-5057.

[12] Da-Yung Wang a, Ko-WeiWeng a, Chi-Lung Chang a, Wei-Yu Ho, Synthesis of Cr_3C_2 coatings for tribological applications, Surface and Coatings Technology 120–121 (1999) 622-628.