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Structure of monolayer coatings deposited by PVD techniques

L.A. Dobrzański*, K. Lukaszkowicz, K. Labisz
Division of Materials Processing Technology 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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Methodology of research

ABSTRACT

Purpose: The aim of the research is the investigation of the structure of coatings deposited by PVD technique (reactive magnetron sputtering method) onto the substrate from the CuZn40Pb2 brass.

Design/methodology/approach: Microstructure was characterised using optical metallography, scanning and transmission electron microscopy.

Findings: The hard PVD coatings deposited by reactive magnetron sputtering method demonstrate structure composed of fine crystallites. In case of the monolayer coatings the columnar structure occurs. Examinations of the PVD coating textures reveal that in most cases they have the binary textures {111} and {100} or {110} and {311}.

Research limitations/implications: In order to evaluate with more detail the possibility of applying these coatings in tools, further investigations should be concentrated on the determination of the mechanical and tribological properties of the coatings.

Originality/value: The paper contributes to better understanding and recognition the structure of thin coatings deposited by PVD techniques.

Keywords: Electron microscopy; PVD coatings.

1. Introduction

Deposition of hard layers of nitrides, carbides or oxides on surface of the engineering materials in the PVD processes features the most intensely developing direction of extending the functional elements' life [1-5]. Reactive magnetron sputtering method is one of the many PVD methods making it possible to obtain the high throughput of the coating deposition processes at the relatively low running-costs, compared to other methods. Capability of putting down the multi-layer, sub-micrometer thick coatings, and also the possibility of deposition of coatings on very big surfaces, as well as simplicity of the equipment and ease of the process control, feature an additional advantage of this method, making reactive magnetron sputtering one of the methods commonly used for deposition of the protective coatings. Undoubtedly, the PVD coatings owe their advantageous properties to the highly defected, amorphous structure, and smaller grain size. The hard coatings are usually chemically resistant at a reasonably elevated temperature, provided they are thick enough, tight, and do not display columnar structure [6-8]. Mechanical properties of hard coatings deposited with the PVD technique depend to a great extent on their structure.

The X-ray diffraction examinations (XRD), examinations on the transmission electron microscope (TEM), and on the scanning electron microscope (SEM) make it possible to determine thoroughly the essential details of the crystalline structure of the coatings [9-12]. The chemical composition analysis is connected inseparably with them, making it possible to identify the elements and their concentrations both from the surface and within the material using, e.g., the Auger's electron spectrometry. Selection of the substrate material onto which the investigated coatings were deposited by PVD technique in the presented project was not incidental either. It turns out that brass, because of its good castability and machinability, remains still a willingly used material; however the high requirements pertaining to its properties stimulated employment of other methods, ecologically clean and giving a chance to obtain more diversified coating coloration and also more advantageous functional properties.

Table 1.
Coating types and their deposition parameter: *during metallic layers deposition; ** during ceramic layers deposition

Coating type	Numbers of layers	Substrate bias voltage, V	Chamber pressure, Pa	Partial pressure, Pa		Temperature, °C
				nitrogen	argon	
Ti/CrN	1	-50	0.58	0* 0.15**	0.31	300
Ti/ZrN	1	-50	0.34	0* 0.10**	0.29	
Ti/TiAlN	1	-40	0.40	0* 0.10**	0.38	
Cr/CrN	1	-50	0.39	0* 0.15**	0.30	
Ti/TiN	1	-60	0.25	0* 0.07**	0.25	
Zr/ZrN	1	-60	0.35	0* 0.10**	0.29	
TiAl/TiAlN	1	-60	0.49	0* 0.11**	0.45	

2. Investigation methodology

The coatings were produced by reactive dc magnetron sputtering using metallic pure targets. They were deposited on CuZn40Pb2 brass substrates. The nitride coatings were deposited when the substrates were static in front of the target in an Ar and N_2 atmosphere. The thin intermediate metallic layers were deposited when the substrates were static in front of the target in an Ar atmosphere. Some deposition conditions are summarized in Table 1.

Targets containing pure metals (Ti, Cr, Zr) and the 50% Ti - 50% Al alloy, were used for deposition the coatings.

Metallographic examinations were made on the coated brass specimens and on brass alone on the LEICA MAEF4A light microscope with the Leica-Qwin computer image analysis system at magnifications up to 1000 ×. The micro sections were prepared using STRUERS equipment, and afterwards they were etched in a ferric chloride aqueous solution (10 ml ferric chloride, 30 ml hydrochloric acid, and 100 ml distilled water) to reveal the brass structure.

The structures of the deposited coatings were examined on transverse sections in a Philips XL-30 scanning electron microscope. Detection of secondary electron was used for generation of fracture images, the accelerating voltage was 20 kV, and the maximum magnification was 10000×. The notched specimens were cooled in liquid nitrogen before fracturing to eliminate plastic deformation and to ensure the brittle fracture.

Seifert-FPM XRD7 X-ray diffractometer equipped with the texture add-on was used for evaluation of the coatings' textures. X-ray radiation was used of the Co Kα cobalt lamp powered with 35 kV voltage with the heater current of 40 mA. Analysis of the textureof the examined coatings was made using the inverse pole figures.

The investigations of diffraction and structure of thin foils were made on the JEOL 2000 FX transmission electron microscope at the accelerating voltage of 160 kV. Thin foils were made by mechanical grinding and further ion polished using the Gatan apparatus.

3. Investigations results

Examination of thin foils obtained from coatings revealed that coatings were made up from fine crystallites. Basing on observations in the bright and dark fields their average size was evaluated as about 50 ÷ 160 nm, depending on the coating type. The average grain size was greater in case of the mono-layer TiAl/TiAlN coatings only and was about 250 nm. The structure of the selected coatings deposited onto the brass substrate along with the diffraction patterns showing spectral lines coming from phases occurring in the coatings is presented in figure 1. The dark field image was obtained from (111) reflexes.

It was confirmed in metallographic examinations made on the light microscope that the investigated coatings are characterized by uniform thickness on their entire area and good adhesion to the substrate. The diphase CuZn40Pb2 brass structure visible in the pictures consists of the α phase (light grains), β phase (dark grains) and of the fine grained, uniformly distributed Pb precipitations (fig. 2).

Fractographic examinations of the investigated coatings' fractures, made in the electron scanning microscope, confirmed initial statement that the coatings were put down correctly. The coatings display compact structure without visible delamination or defects. Single layer coatings display columnar structure (fig. 3), which can be recognized as consistent with the Thornton's model (I zone). Fractographic examinations of the fractures of specimens made from brass with the coatings deposited on their surfaces revealed the sharp transition zone between the substrate and the coatings. There are, in general, no premises that might suggest epitaxial, at least, growth of the examined coatings' fragments.

The texture analysis of the examined coatings was carried out with the inverse pole figures method. Intensities were analyzed of the following diffraction lines: {111}, {200}, {220}, and {311}. The texture of the examined specimens is an axial one, in which the discriminated crystallographic axes are normal to the {100}, {110}, {111}, or {311} planes. In most coatings the binary texture occurs, in which – in varying proportions – two planes, parallel to the deposition plane, are discriminated. The Zr/ZrN coating has the binary texture {100} + {111} of the ZrN phase, where the {111} orientation prevails. The Cr/CrN coating has the uniform {100} texture of the CrN phase.

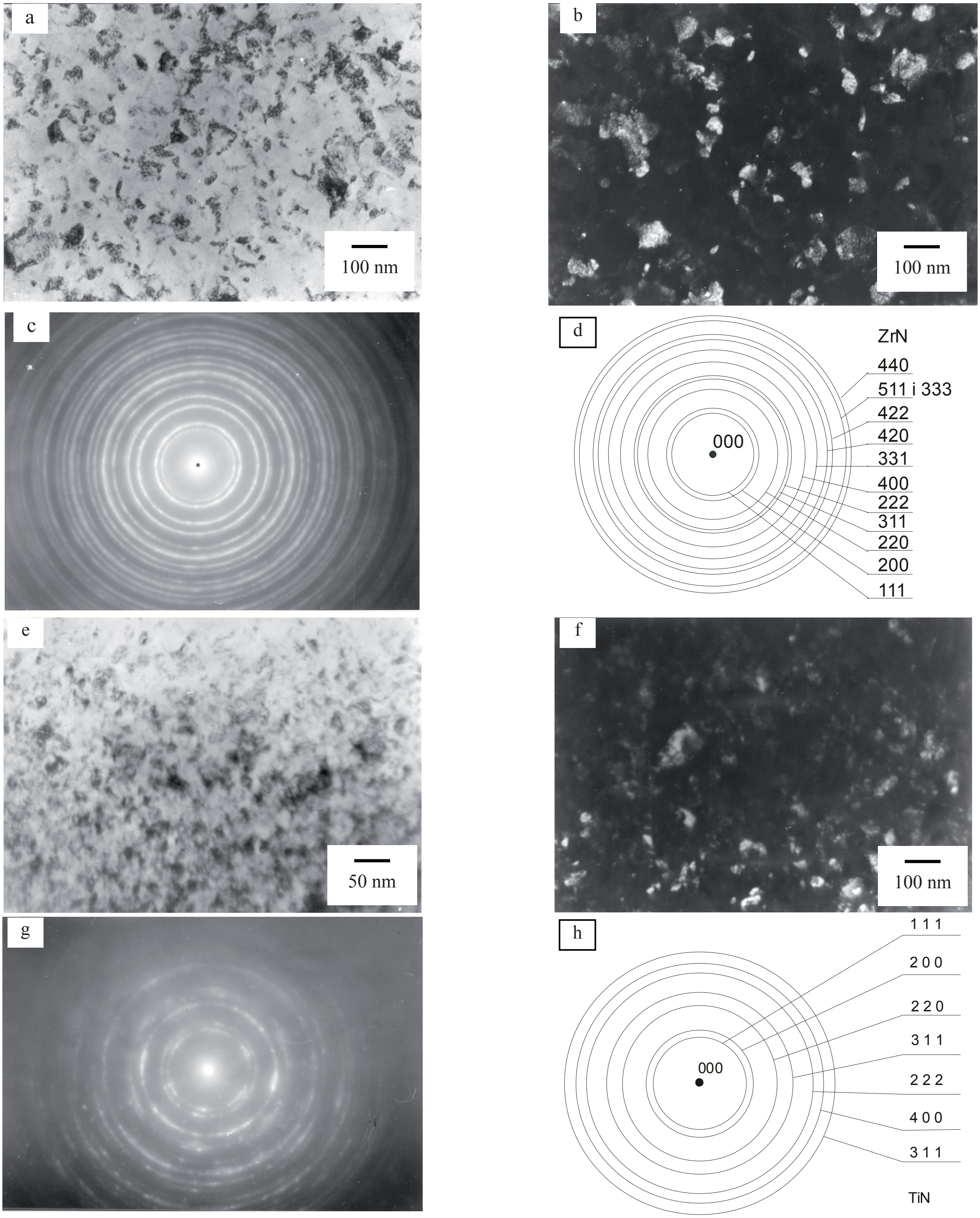

Fig. 1. Thin foil structure from the coating: a) Zr/ZrN, e) Ti/TiN deposited on the CuZn40Pb2 brass substrate, dark field from the (111) reflex: b) ZrN, f) TiN, c) diffraction pattern from the area as in figure a, d) solution of the diffraction pattern from figure c, g) diffraction pattern from area as in figure e, h) solution of the diffraction pattern from figure g

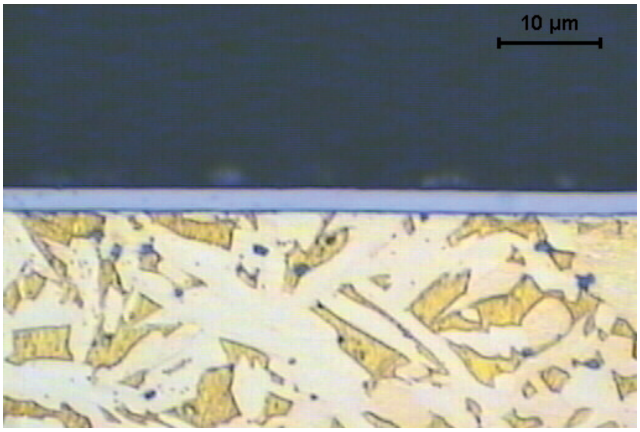

Fig. 2. Ti/CrN coating deposited onto the CuZn40Pb2 substrate

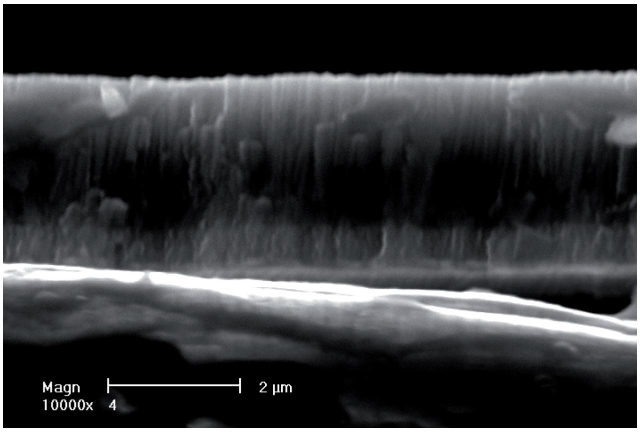

Fig. 3. SEM micrograph of fracture in Ti/TiAlN sample

The Ti/TiN coating has the {111}+{311} binary texture of the TiN phase where the component {111} prevails. The TiAl/TiAlN coating has the {110}+{311} texture of the TiAlN phase, however the {110} component prevails slightly. The Ti/CrN coating is characterized by a not so strong binary texture, in which the discriminated planes are: {100} and {111} of the CrN phase. The Ti/ZrN coating is characterized by the same texture type, however, the strong ZrN phase {111} component prevails decidedly. The Ti/TiAlN coating has the binary texture {110} + {311} of the TiAlN phase.

In case of the analyzed coatings one can judge that the preferred orientation should be {111}, as this is the plane with the dense packing of atoms. Examinations of the PVD coating textures reveal that in most cases they have the binary textures {111} and {100} or {110} and {311}. The binary texture of the coatings is not connected with the substrate texture and the epitaxy phenomenon, as the texturing level of the substrate from brass, on which the coatings were put down is low. Changes of crystallographic orientations of the examined coatings result from their positions in respect to the magnetron axis, temperature effect, unstable conditions during their deposition resulting from changes in time of delivering the reactive gases in case of the nitride coatings or thin metallic layers and slightly changing current – voltage conditions, which in consequence change the direction of the resulting energy vector, according to which the condensate is oriented.

4. Conclusions

The hard PVD coatings deposited by reactive magnetron sputtering method demonstrate structure composed of fine crystallites. In case of the monolayer coatings the columnar structure occurs, causing deterioration of the corrosion resistance of the coatings, resulting from the possibility of easier penetration of the corrosive agent into the material [3]. Investigated coatings reveal the binary texture in most cases. The binary texture occurring in the coatings is not connected with the substrate texture and the epitaxy phenomenon but is a result of development of the new independent texture in the constituted coating.

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