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## Structure of the PVD coatings deposited using the reactive magnetron sputtering method

L.A. Dobrzański<sup>a\*</sup>, K. Lukaszewicz<sup>a\*</sup>, K. Labisz<sup>a\*</sup>, L. Cunha<sup>b</sup>

<sup>a</sup>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

<sup>b</sup>Physics Department, University of Minho, Campus de Gualtar  
4710-057 Braga, Portugal

The paper presents investigation results of the structure and phase composition of hard monolithic nitride and multi-layer ceramic/metallic PVD coatings developed with the reactive magnetron sputtering method on the brass substrate.

### 1. INTRODUCTION

Deposition of hard layers of nitrides, carbides or oxides on material surface in the PVD processes is one of the most intensely developed directions of improvement of working properties of functional elements [1-3]. One of the PVD methods, merging the simplicity of the equipment and ease of process control, and also giving a possibility of putting down coatings both on very big surfaces and deposition of multi-layer sub-micrometer thick coatings, is the reactive magnetron sputtering method. An additional advantage of this method is a possibility of obtaining high throughput of the processes, at their relatively low costs, compared with other techniques of thin coatings deposition, which makes magnetron sputtering one of the most often used methods used for deposition of coatings.

Hard coatings with metal nitrides, like CrN, TiAlN, TiN, ZrN, etc., extend the life of the items that were covered with them, improving not only their wear resistance but also their resistance to the chemically aggressive environment, in comparison to the non-coated metal materials. This is an effect of the smaller grain size and higher extent of coating defectiveness. The hard coatings are usually chemically resistant at a reasonably elevated temperature, provided they are thick enough, tight, and do not display columnar structure [4-6]. Nitride coatings have the same crystallographic structure (face-centered cubic lattice), and similar properties, like: high melting temperature, high thermal and chemical resistance, high hardness and electrical conductivity. Mechanical properties of hard coatings deposited with the PVD technique depend in a great extent on their structure. In spite of the continuous interest of many research laboratories and industrial centres [7-8] many unexplained aspects remain connected with the process of coating development and its effect on its structure and properties.

The goal of this work is investigation of structure and phase composition, as well as texture of the coatings deposited with the PVD technique by the reactive magnetron sputtering onto the substrate from the CuZn40Pb2 brass.

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## 2. EXPERIMENTAL PROCEDURE

The investigations were made on specimens made from the CuZn40Pb2 brass covered in the PVD process with the hard coatings presented in Table 1, using the reactive magnetron sputtering method.

Table 1

Coating types and their deposition parameters: \*during metallic layers deposition, \*\* during ceramic layers deposition. During deposition the substrate temperature was always 300°C

| Coating type   | Substrate bias voltage [V] | Partial pressure, [Pa] |       | Thickness, [μm] | Number of layers |
|----------------|----------------------------|------------------------|-------|-----------------|------------------|
|                |                            | nitrogen               | argon |                 |                  |
| Ti/CrN × 1     | -50                        | 0*                     | 0,31  | 4,8             | 1                |
| Ti/CrN × 15    |                            | 0,15**                 |       | 4,5             | 15               |
| Ti/CrN × 150   |                            | 3,1                    |       | 150             |                  |
| Ti/ZrN × 1     | - 50                       | 0*                     | 0,29  | 2,1             | 1                |
| Ti/ZrN × 15    |                            | 0,10**                 |       | 1,6             | 15               |
| Ti/ZrN × 150   |                            | 1,9                    |       | 150             |                  |
| Ti/TiAlN × 1   | - 40                       | 0*                     | 0,38  | 2,3             | 1                |
| Ti/TiAlN × 15  |                            | 0,10**                 |       | 2,7             | 15               |
| Ti/TiAlN × 150 |                            | 2,2                    |       | 150             |                  |
| TiAlN/Mo × 1   | - 60                       | 0*                     | 0,45  | 6,2             | 1                |
| TiAlN/Mo × 15  |                            | 0,11**                 |       | 6,5             | 15               |
| TiAlN/Mo × 150 |                            | 5,9                    |       | 150             |                  |
| Cr/CrN         | - 50                       | 0*<br>0,15**           | 0,30  | 3,6             | 1                |
| Ti/TiN         | - 60                       | 0*<br>0,07**           | 0,25  | 2,4             | 1                |
| Zr/ZrN         | - 60                       | 0*<br>0,10**           | 0,29  | 2,0             | 1                |
| TiAl/TiAlN     | - 60                       | 0*<br>0,11**           | 0,45  | 2,3             | 1                |

The coatings were deposited onto the polished brass specimens by the reactive magnetron sputtering. Water cooled disks of the 200 x 100 x 6 mm size, containing pure metals (Cr, Ti, Mo) and the 50% Ti - 50% Al alloy, featuring substrates of the compound deposited on the charge, were used to deposition the coatings. The coatings were deposited in the atmosphere of the inert gas (argon) or/and reactive gas (nitrogen). The distance between each of the disks and the coated brass specimens is 65 mm.

The structures of the deposited coatings were examined on the cross sections in the Philips XL-30 scanning electron microscope. Detection of secondary electron was used for generation of fracture images.

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.

Phase composition of the investigated coatings was determined using a Dron 2.0 X-ray diffractometer, with the step recording using the  $K\alpha_1$  filtered X-ray radiation with the  $\lambda = 1.79021$  nm wavelength from the cobalt anode lamp powered with the voltage of 35 kV with heater current of 8 mA. Measurements were made within the  $2\theta$  angle range from 35-100°. Seifert-FPM XRD7 X-ray diffractometer equipped with the texture add-on was used for evaluation of the coatings' structures. X-ray radiation of the Co  $K\alpha$  cobalt lamp powered with 35 kV voltages with the heater current of 40 mA. Analysis of the texture of the examined coatings was made using the inverse pole figures.

### 3. DISCUSSION OF INVESTIGATION RESULTS

The examination of cross section of the coatings by SEM reveals a compact structure, without any visible delamination or defects. In case of the single layer coatings their columnar structure is clearly visible (Fig.1). Examinations of the multi-layer coatings' fractures on the scanning microscope indicate to the lack of the columnar structure. It was confirmed, however, in case of the multi-layer coatings, that 15 alternating layers were deposited (Fig.2). In coatings with 150 layers observing each of the individual layers was not possible due to their small thickness.

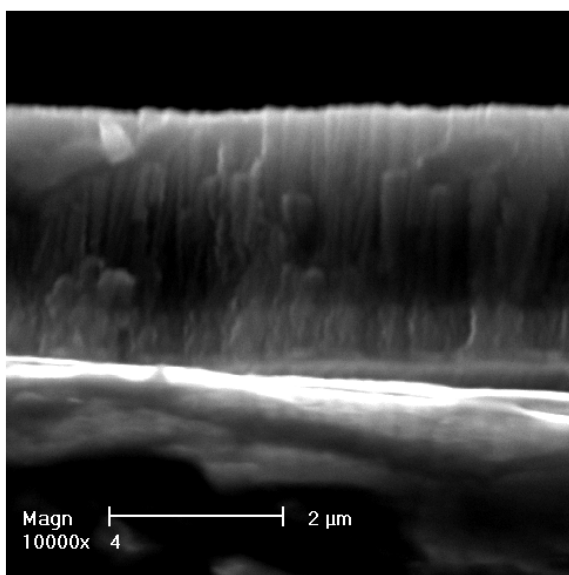


Fig. 1. Fracture of the Ti/TiAlNx1 coating deposited onto the CuZn40Pb2 substrate

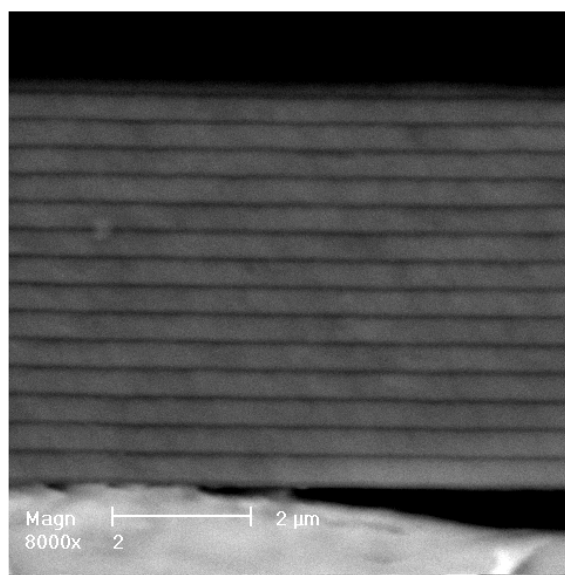


Fig. 2. Fracture of the Ti/CrNx15 coating deposited onto the CuZn40Pb2 substrate

The morphology of the coatings' surfaces deposited on the brass substrate is characterized by a significant in homogeneity connected with occurrences of the multiple near-drop-shaped or close to spherical particles, which is connected with the essence of the employed PVD process for depositing the coatings and is consistent with the previous research results [9-10]. This is caused by presence in plasma of the metallic drops of metal sputtered from the magnetron disc that take part in forming the coating. The sizes of the drop-shape particles are differentiated in the range from several tenths of a micrometer to about 8  $\mu\text{m}$ . Their diameter is within the range of  $2,5\div 8$   $\mu\text{m}$  in most cases.

Fractographic examinations of the investigated coated brass specimens' fractures reveal a sharp transition zone between the substrate and coatings. In general, however, there are no premises that might suggest the epitaxial growth of even fragments of the investigated coatings.

Observations of TEM data showed that the coatings have fine crystallites. Basing on observations in the bright and dark fields their average size was evaluated as about  $50 \div 160$  nm, depending on the coating type. The structure of the selected coatings deposited onto the brass substrate is presented in Fig. 3. The dark field image was obtained from (111) reflexes.

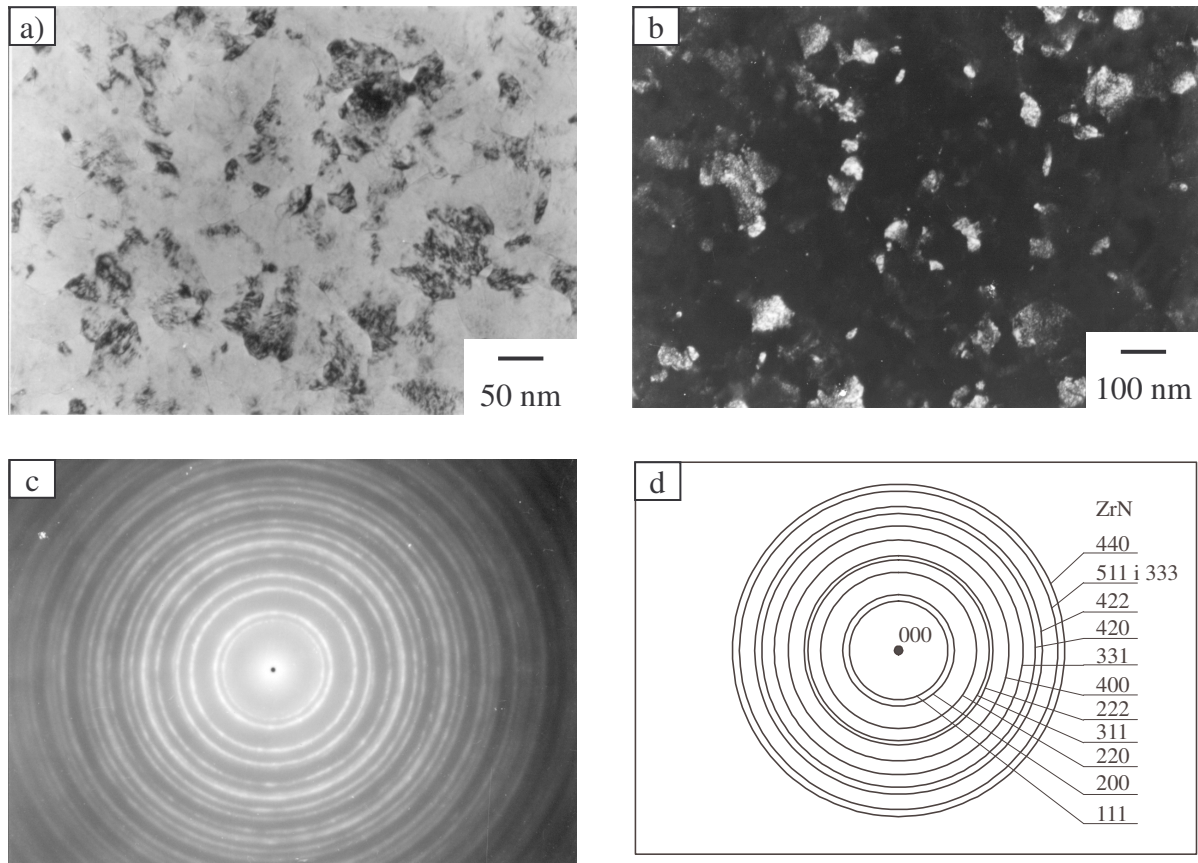


Fig. 3. a) Structure of the thin foil from the Zr/ZrN coating deposited onto the CuZn40Pb2 brass substrate, b) dark field from the ZrN (111) reflex, c) diffraction pattern from the area as in figure a, d) solution of the diffraction pattern from figure c

Using the X-ray qualitative phase analysis methods (Fig. 4) it was found out, according to the initial assessment, that onto the CuZn40Pb2 brass surface coatings were deposited presented in Table 1. The CrN phases in case of the Ti/CrN and Cr/CrN coatings, ZrN in case of the Ti/ZrN and Zr/ZrN coatings, TiAlN in case of the Ti/TiAlN and TiAl/TiAlN coatings, Mo in case of the TiAlN/Mo coatings, Zr in case of the Zr/ZrN coating, and TiN in case of the Ti/TiN coatings reveal the privileged crystallographic orientation. The diffraction lines of the TiAlN phase are shifted to higher deflection angle values in comparison with the TiN phase. This is caused by decreasing of the lattice parameter with the NaCl structure, typical for TiN with 0,423 nm to 0,418 nm because of substitution Ti atoms ( $r = 0,146$  nm) by Al atoms

( $r = 0,143$  nm). Moreover, reflexes coming from phases  $\alpha$  - (Cu, Zn) and  $\beta$  - CuZn occurring in the brass were found in the diffraction patterns. This is caused by a small thickness of coatings deposited onto the brass substrate, smaller than penetration depth of X-ray radiation into the material.

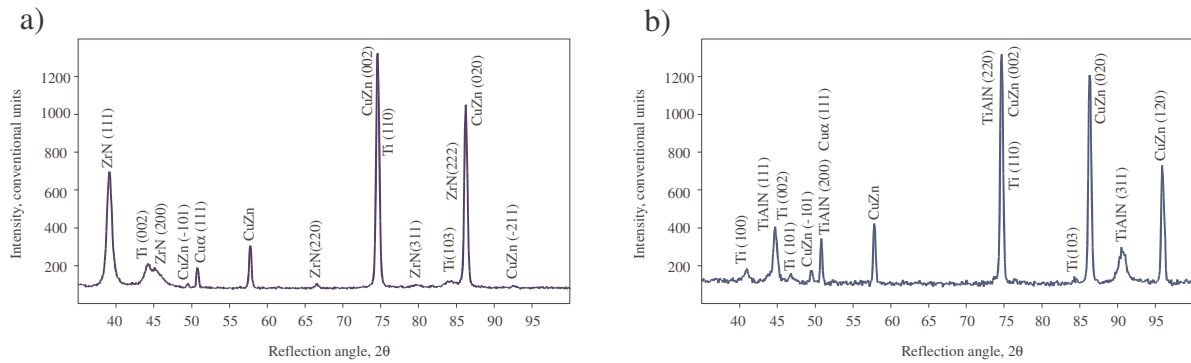


Fig. 4. Results of the X-ray phase analysis of the coatings: a) Ti/ZrN  $\times$  15, b) Ti/TiAlN  $\times$  1 deposited onto the CuZn40Pb2 substrate

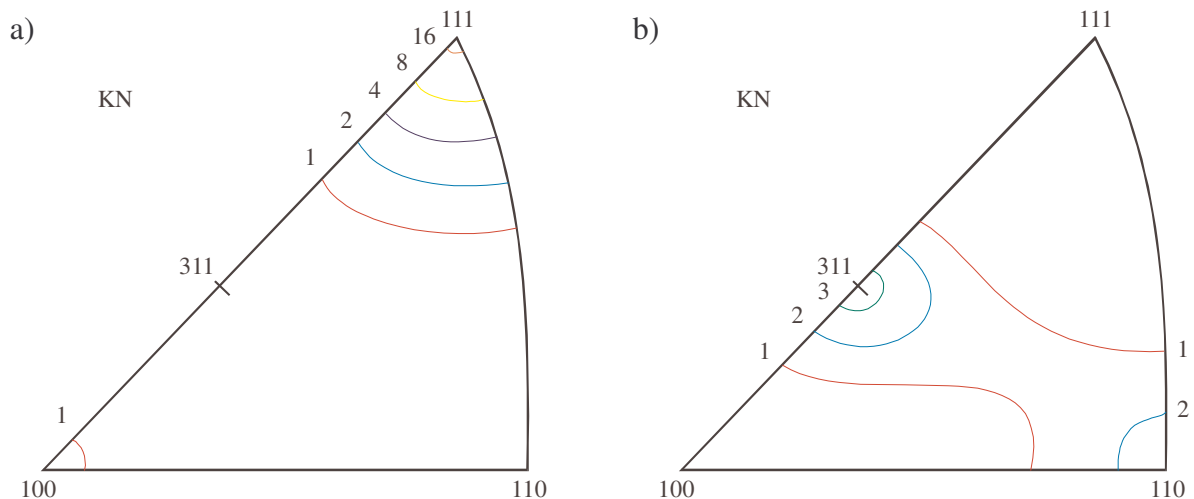


Fig. 5. Inverse pole figure representing the distribution of normal to the deposited coating surface: a) Ti/ZrN  $\times$  15, b) Ti/TiAlN  $\times$  1 in the (001)-(011)-(111) base triangle

The texture analysis of the examined coatings was carried out with the inverse pole figures method. It was found out that the coating texture has the axial character, however, the discriminated axis is deviated from the normal to the coating surface even by several degrees. However, the diffraction lines of the deposited nitride layers are often very weak. They overlap sometimes partially lines coming from the substrate. Therefore, to make the uniform texture presentation possible for the examined coatings, the decision was taken not to use the simple pole figures method for texture analysis, but to employ the inverse pole figures method instead, representing the distribution of the normal to coating surface in the base triangle (100)-(110)-(111). Intensities were analyzed of the following diffraction lines: {111}, {200}, {220}, and {311}. Intensities of the diffraction lines: {111}, {200}, {220} and {311} were

analyzed. Intensity increase of any line indicates to occurrence of the discriminated crystallographic plane, related to this line. To achieve full comparability of results, the pole figures were made as quantitative figures, in which contour line values are given as multiples of normal densities related to the particular crystallographic orientation, compared to the density in the material without texture. The pole figures are presented in Fig. 5. 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. 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}. 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 cyclic changes in time of delivering the reactive gases in case of the multi-layer coatings 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. SUMMARY

The hard PVD coatings deposited by the reactive magnetron sputtering method demonstrate structure composed of fine crystallites, resulting with the increase of strength and hardness of coatings. In case of single-layer coatings the columnar structure occurs causing deterioration of the corrosion resistance of coatings. The binary texture occurring in coatings is not connected with the substrate texture and epitaxy phenomenon, but results from development of a new, independent texture in the constituted coating.

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