



# Structure, texture and chemical composition of coatings deposited by PVD techniques

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## ABSTRACT

**Purpose:** The aim of the research is the investigation of the structure, texture and chemical composition of coatings deposited by PVD technique (reactive dc magnetron sputtering method) onto the substrate from the CuZn40Pb2 brass.

**Design/methodology/approach:** Microstructure was characterised using optical metallography, scanning and transmission electron microscopy. Changes of the chemical composition of the coatings were examinations made on the glow discharge optical spectrometer (GDOS).

**Findings:** The hard PVD coatings deposited by reactive dc 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.

**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

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## METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

### 1. Introduction

The quality of a hard PVD coatings depends on the following parameters [1-5]:

- microhardness,
- coating thickness,
- composition and structure of the coating,
- adhesion and tension between the substrate and the coating,
- temperature resistance of the coating.

The system involving bulk material, interface, surface coating or modified surface layer is very complex and, together, yields the systems properties, which are requested by the designer, with every part playing an important role. Multiple information connected with structure of coatings deposited by PVD technique is particularly useful for further improvement of the coating deposition process and studying causes of their destruction or defects [6]. The structure of the PVD deposited coating is influenced by many parameters. The coatings are usually chemically resistant at a reasonably elevated temperature, provided

they are thick enough, tight, and do not display columnar structure [7-10]. Mechanical properties of hard coatings deposited by PVD technique depend to a great extent on their structure. One can use a great number of interactions to characterise composition and structure of coatings. Different methods, namely, 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. The chemical composition analysis is connected with them, making it possible to identify the elements and their concentrations both from the surface and within the material using, e.g., the glow discharge optical spectrometry (GDOS), interaction with electrons yielding X-rays (EDX), interactions with electron or photons yielding auger and photo electrons (AES, XPS) [11-14].

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

## 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<sub>2</sub> 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 $\times$ .

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 $\times$ .

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 K $\alpha$  cobalt lamp powered with 35 kV voltage with the heater current of 40 mA. Analysis of the texture of the examined coatings was made using the inverse pole figures.

Changes of the chemical composition of the coatings in the direction perpendicular to their surfaces and changes of concentration in the transition zone between the coating and the substrate material were evaluated basing on examinations made on the Leco Instruments GDOS-750 QDP glow discharge optical spectrometer. The tests were made with the following conditions of the spectrometer's Grimm lamp:

- inner diameter of the lamp – 4 mm;
- supply voltage of the lamp – 700 V;
- lamp current – 20 mA;
- working pressure – 100 Pa;
- analysis time period – 400 s.

The continuous concurrent spectrometer in the Paschen-Runge system was used in this device, with the focal distance of 750 mm and the holographic mesh with 2400 lines per millimeter. The maximum depth of the chemical composition analysis is about 10  $\mu$ m.

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

On the basis of the investigations of thin foils of the obtained coatings one has stated that the coatings are made of 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.

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*<br>0.15**         | 0.31  | 300             |
| Ti/ZrN       | 1                 | -50                       | 0.34                 | 0*<br>0.10**         | 0.29  |                 |
| Ti/TiAlN     | 1                 | -40                       | 0.40                 | 0*<br>0.10**         | 0.38  |                 |
| Cr/CrN       | 1                 | -50                       | 0.39                 | 0*<br>0.15**         | 0.30  |                 |
| Ti/TiN       | 1                 | -60                       | 0.25                 | 0*<br>0.07**         | 0.25  |                 |
| Zr/ZrN       | 1                 | -60                       | 0.35                 | 0*<br>0.10**         | 0.29  |                 |
| TiAl/TiAlN   | 1                 | -60                       | 0.49                 | 0*<br>0.11**         | 0.45  |                 |

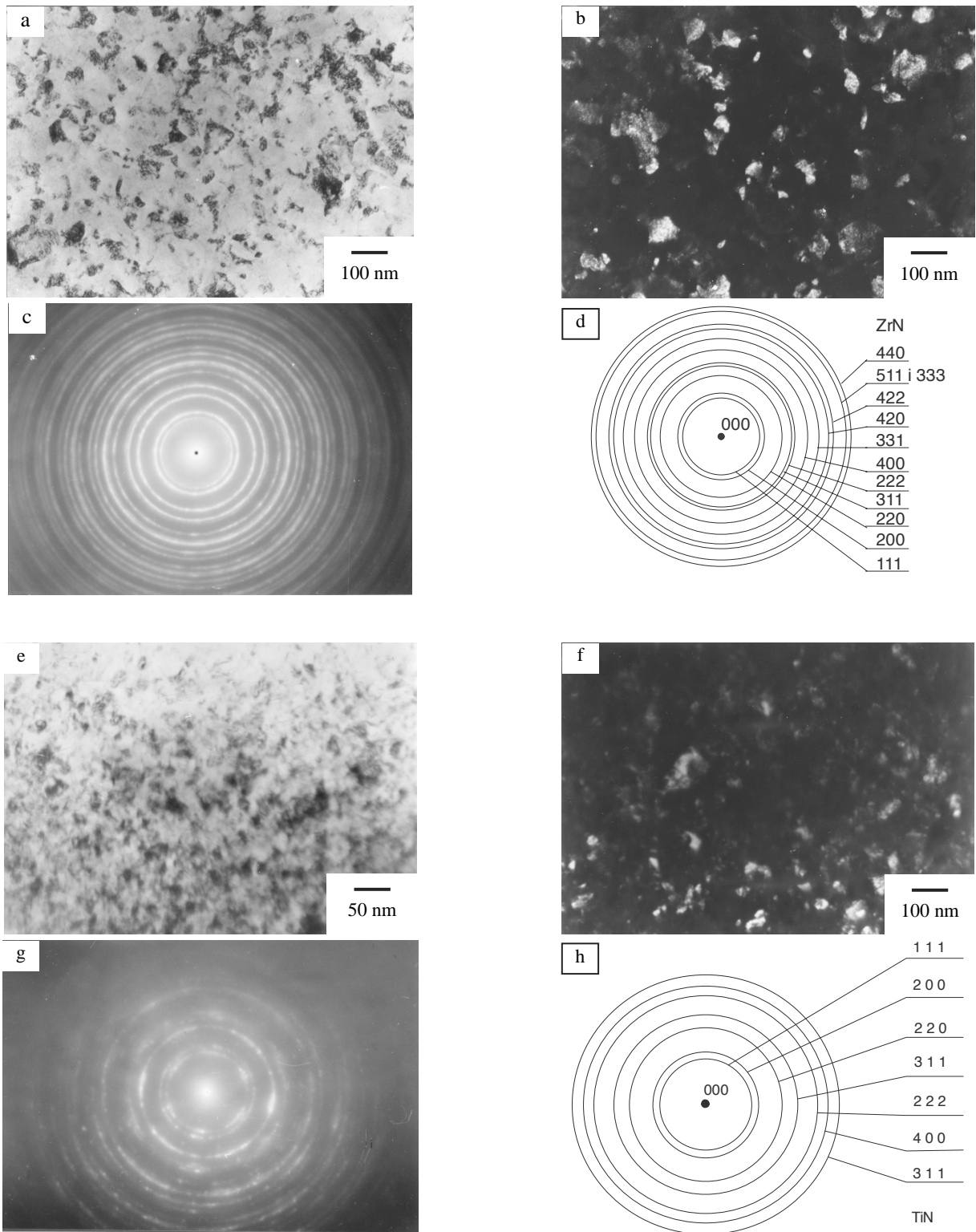


Fig. 1. Thin foil structure from the coating: a) Zr/ZrN, e) Ti/TiN deposited on the CuZn40Pb2 brass substrate, dark field from the (111) reflex: b) ZrN, f) TiN, c) diffraction pattern from the area as in figure a, d) solution of the diffraction pattern from figure c, g) diffraction pattern from area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

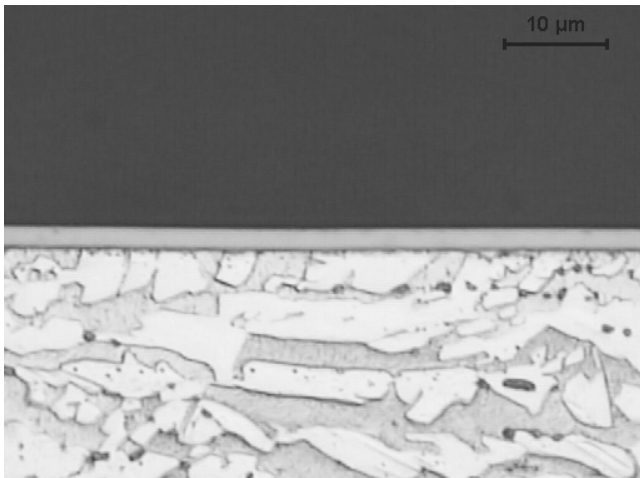


Fig. 2. Ti/TiN coating deposited onto the CuZn40Pb2 substrate

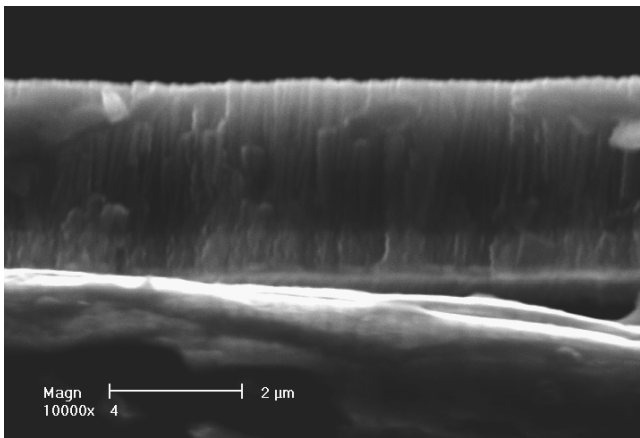


Fig. 3. SEM micrograph of fracture in Ti/TiAlN sample

In case of TiAl/TiAlN monolayers the average size of grains is bigger, but the size of the phase particles does not exceed 250 nm. The structure of the selected coatings deposited onto the brass substrate together with the diffraction patterns demonstrating spectral line coming from phases appearing in the coatings are presented in Fig. 1. The dark field image was obtained from (111) reflexes.

A visible in the image structure of a two-phase CuZn40Pb2 brass substrate consists in  $\alpha$  phase (bright grains),  $\beta$  phase (dark grains) and fine, evenly distributed Pb releases (Fig. 2). The coatings are characterized by a tight adhesion to the substrate (Fig. 2).

Fractographic examinations of the coatings done on the scanning electron microscope confirm the above statement concerning the correctness of the deposition of coatings. The coatings reveal compact structure without visible delamination, discontinuities or defects. Monolayer coatings show columnar structure (Fig. 3). The observed columnar structure of the investigated coatings refers to I zone of the Thornton model.

The analysis of the texture of the examined coatings was made using the method of the inverse pole figures demonstrating the

distribution of the normal to coating surface in the base triangle (100)-(110)-(111) (Figs. 4÷10). Intensities were analyzed of the following diffraction lines: {111}, {200}, {220}, and {311}.

In case of the analyzed coatings one ought to judge that the preferred orientation should be {111}, as it is the plane with a dense packing of atoms. The examinations of the PVD coating textures indicate, in majority of cases, a binary texture {111} and {100} or {110} and {311}. The binary coating texture is not connected with the substrate texture and epitaxy phenomenon because the extent to which a brass substrate was textured and onto which the coatings were deposited was small. The changes of crystallographic orientations of the examined coatings result from their position in respect to the magnetron axis, temperature effect and unstable conditions during their deposition process. All these result from cyclic changes in delivering reactive gases in case of multi-layer coatings as well as slightly changing current-voltage conditions what consequently influences the change of the resulting energy vector, according to which the condensate is oriented.

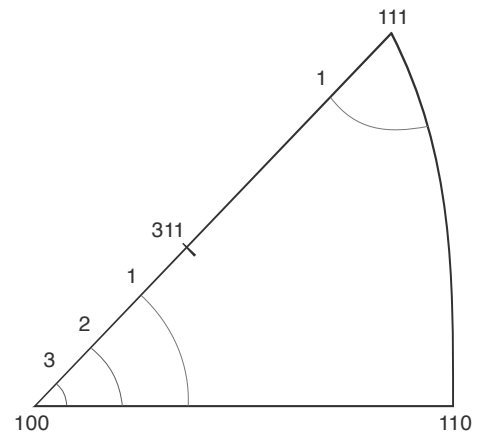


Fig. 4. Inverse pole figure representing the distribution of normal to the Ti/CrN coating surface in the (001)-(011)-(111) base triangle

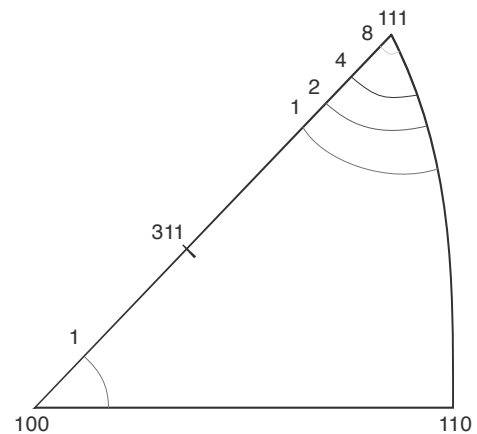


Fig. 5. Inverse pole figure representing the distribution of normal to the Ti/ZrN coating surface in the (001)-(011)-(111) base triangle

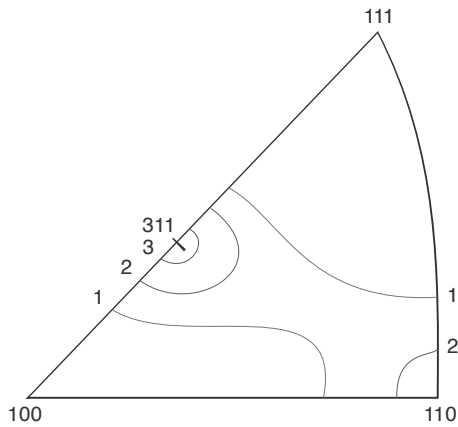


Fig. 6. Inverse pole figure representing the distribution of normal to the Ti/TiAlN coating surface in the (001)-(011)-(111) base triangle

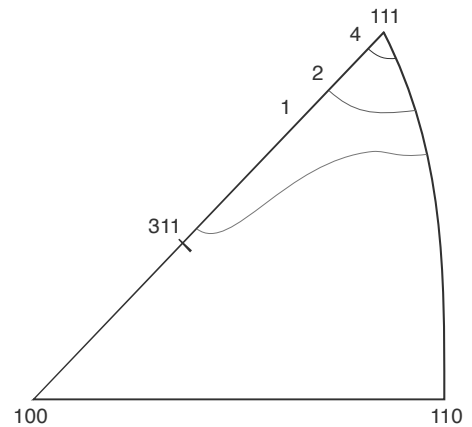


Fig. 9. Inverse pole figure representing the distribution of normal to the Ti/TiN coating surface in the (001)-(011)-(111) base triangle

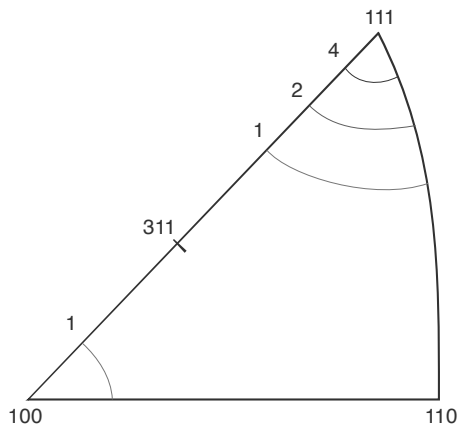


Fig. 7. Inverse pole figure representing the distribution of normal to the Zr/ZrN coating surface in the (001)-(011)-(111) base triangle

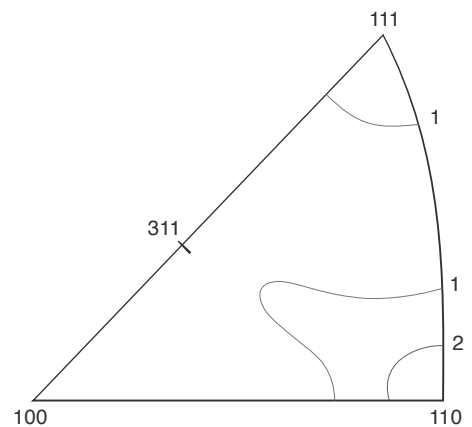


Fig. 10. Inverse pole figure representing the distribution of normal to the TiAl/TiAlN coating surface in the (001)-(011)-(111) base triangle

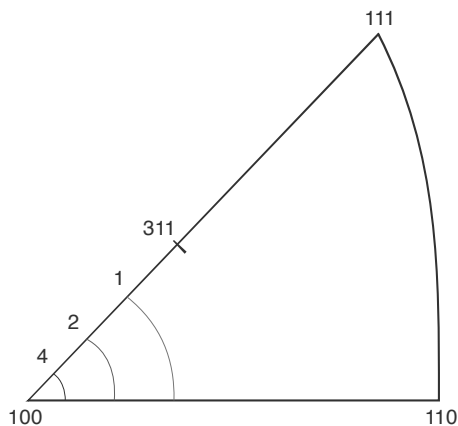


Fig. 8. Inverse pole figure representing the distribution of normal to the Cr/CrN coating surface in the (001)-(011)-(111) base triangle

In Figs 11-17 there are the concentration changes of the components of coatings shown as well as the substrate material depending on the number of deposited layers made in glow discharge optical spectrometer GDOS. The changing concentration of elements making a Ti/CrN coating tells about its chemical heterogeneity. Also the chemical composition of the Ti/ZrN coating differs from the equilibrium one. The nitrogen concentration systematically diminishes while the Zr concentration grows. A similar situation is in case of Ti/TiAlN coating where the changes of concentration of elements of the pure Ti and Al metals as well as nitrogen are considerable. In the Cr/CrN coating the chemical composition is close to the equilibrium one. However, in Ti/TiN, Zr/ZrN, TiAl/TiAlN coatings there are differences in the concentration of respective elements which may be caused by a formation of secondary solid solutions or heterogeneous material evaporation from the specimen surface during the examinations in GDOS spectrometer. It has been ascertained, on the basis of the analysis of the chemical composition of the coating micro-areas, that it is

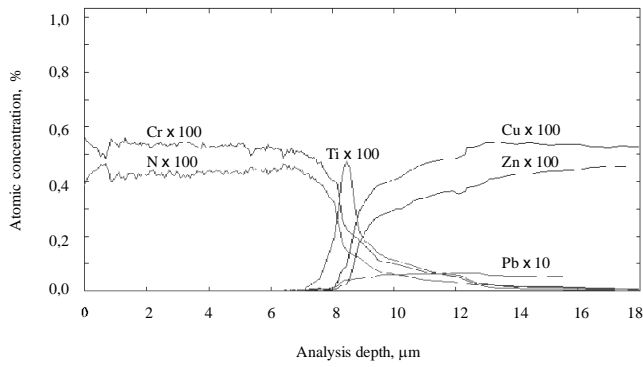


Fig. 11. Changes of concentrations of constituents of the Ti/CrN coating and of the substrate material

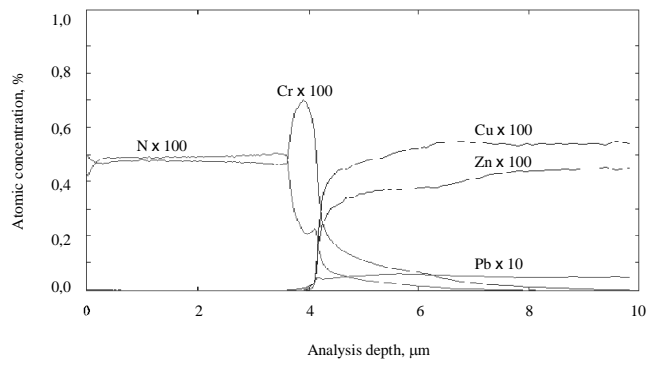


Fig. 14. Changes of concentrations of constituents of the Cr/CrN coating and of the substrate material

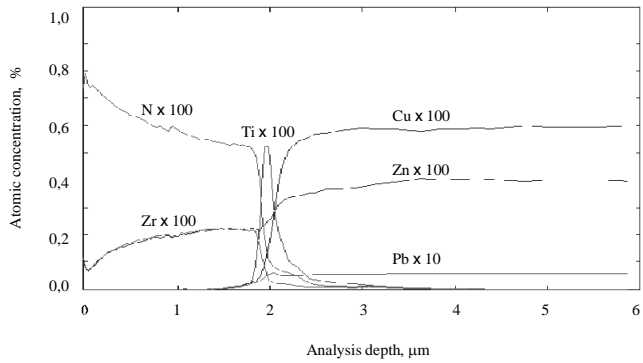


Fig. 12. Changes of concentrations of constituents of the Ti/ZrN coating and of the substrate material

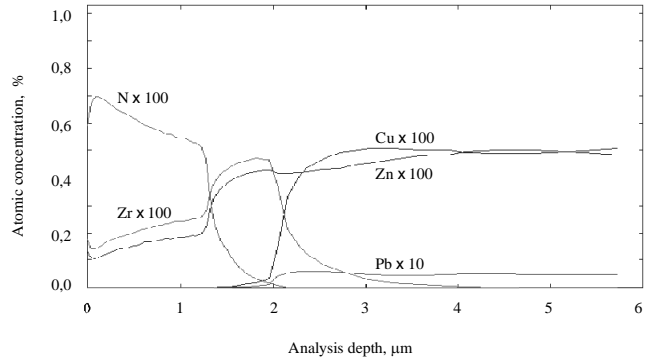


Fig. 15. Changes of concentrations of constituents of the Zr/ZrN coating and of the substrate material

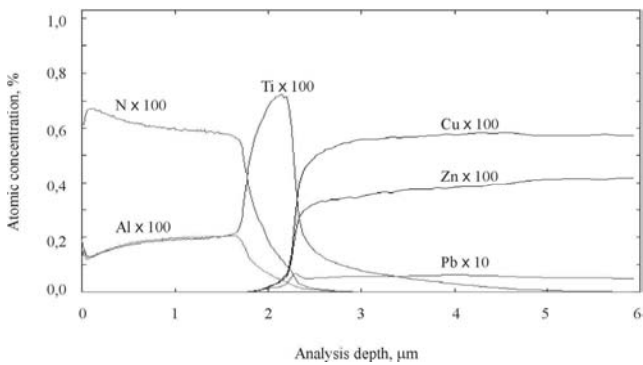


Fig. 13. Changes of concentrations of constituents of the Ti/TiAlN coating and of the substrate material

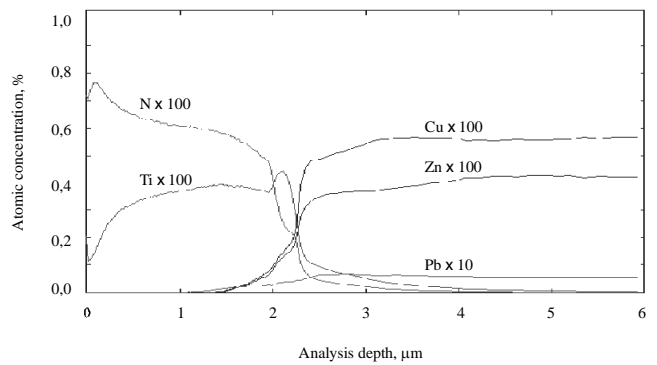


Fig. 16. Changes of concentrations of constituents of the Ti/TiN coating and of the substrate material



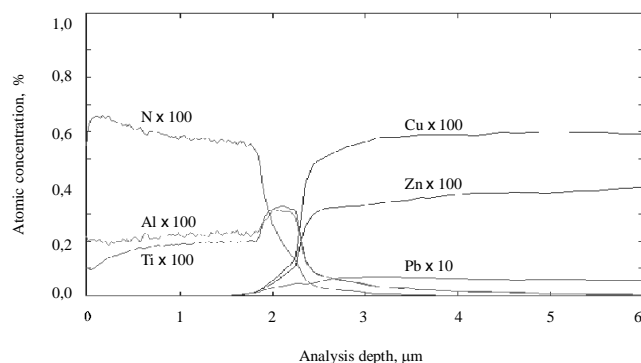


Fig. 17. Changes of concentrations of constituents of the TiAl/TiAlN coating and of the substrate material

similar to the equilibrium one. In case of investigation coatings one can clearly observe thin intermediate layers whose aim is to increase the adhesion to the substrate of the correct nitride coating.

The examinations with the use of Glow Discharge Optical Spectrometer GDOS show that in the connection zone of the analyzed cases there is the increase in the concentration of the elements that are parts of the substrate along with the rapidly decreasing concentration of elements of the coatings. This may prove the existence of the transitory layer between the material of the substrate and the coating that influences the adhesion of the deposited coating, although these results cannot be explicitly interpreted because of the heterogeneous material evaporation from the specimen surfaces. The existence of the transitory layer should be bound with the increase of desorption of the substrate surface and the defects in the substrate as well as translocation of the elements in the connection zone as a result of an interaction of great energy ions.

#### 4. Conclusions

The application of PVD techniques of coating deposition allows for the increase of mechanical and usable properties of the coated with them elements. Depending on the expected usable properties one can apply multilayer coatings that significantly increase the corrosive resistance or hard, monolayer coatings resistant to abrasive wear and erosion, as indicated in the papers [1, 7, 15]. Simultaneously, a great influence on the above mentioned properties possesses the structure of coatings itself (eg. a grain size or a columnar structure), which determines their use to particular needs. Thus the structural characteristics of the coatings seems to be particularly important to a constant improvement and increase of the process of making coatings that are supposed to fulfill specific usable requirements.

The hard PVD coatings deposited with the method of the reactive magnetron sputtering demonstrate a structure composed of fine crystallites, the effect of which is the increase of the strength and hardness of coatings. The chemical composition of monolayer coatings is close to the equilibrium one and there is a columnar structure that causes a deterioration of the corrosion

resistance of coatings resulting from the possibility of getting a corrosion factor into the material. As a result of the examinations of surface location of elements one cannot explicitly validate the fact that there is a transitory layer between the examined coatings and the brass substrate. Only the examinations with the use of glow discharge optical spectrometer GDOS indicate the existence of the transitory layer between the substrate material and the coating that influences the improvement of the adhesion of the coatings deposited onto substrate. The examined coatings demonstrate, in majority of cases, a binary texture. The binary texture that occurs in the coatings is not connected with the substrate texture and epitaxy phenomenon but is a result of a development of a new, independent texture in the constituted coating.

#### References

- [1] L.A. Dobrzanski, K. Lukaszewicz, Erosion resistance and tribological properties of coatings deposited by reactive magnetron sputtering method onto the brass substrate, *Journal of Materials Processing Technology* 157-158 (2004) 317-323.
- [2] L.A. Dobrzański, K. Lukaszewicz, K. Labisz, Structure monolayer coatings deposited by PVD techniques, *Journal of Achievements in Materials and Manufacturing Engineering* 18 (2006) 271-274.
- [3] A.A. Voevodin, J.S. Zabinski, C. Muratore, Recent Advanced in Hard, Tough, and Low Friction Nanocomposite Coatings, *Tsinghua Science and Technology* 10/6 (2005) 665-679.
- [4] C. Donnet, A. Erdemir, Historical developments and new trends in tribological and solid lubricant coatings *Surface and Coatings Technology* 180-181 (2004) 76-84.
- [5] V. Teixeira, M. Andritschky, W. Fischer, H. Buchkremer, D. Stover, Analysis of residual stresses in thermal barrier coatings. *Journal of Materials Processing Technology* 92-93 (1999) 209-216.
- [6] P.H. Mayrhofer, C. Mitterer, L. Hultman, H. Clemens, Microstructural design of hard coating, *Progress in Materials Science* 51 (2006) 1032-1114.
- [7] L.A. Dobrzanski, K. Lukaszewicz, A. Zarychta, L. Cunha, Corrosion resistance of multilayer coatings deposited by PVD techniques onto the brass substrate, *Journal of Materials Processing Technology* 164-165 (2005) 816-821.
- [8] C. Liu, Q. Bi, A. Leyland, A. Matthews, An electrochemical impedance spectroscopy study of the corrosion behaviour of PVD coated steels in 0.5 N NaCl aqueous solution, *Corrosion Science* 45 (2003) 1257-1273.
- [9] I. Dörfel, W. Österle, I. Urban, E. Bouzy, Microstructural characterization of binary and ternary hard coatings system for wear protection. Part I: PVD coatings, *Surface and Coatings Technology* 2-3 (1999) 199-209.
- [10] B. Skoric, D. Kakas, N. Bibic, M. Rakita, Microstructural studies of TiN coatings prepared by PVD and IBAD, *Surface Science* 566-568 (2004) 40-44.
- [11] K. Holmberg, A. Matthews, *Coating Tribology*, Elsevier Science Ltd, Amsterdam, 1994.

- [12] M. Ohring, *The Materials Science of Thin Films*, Academic Press, San Diego, 1992.
- [13] M. Parlinska-Wojtan, A. Karimi, T. Cselle, M. Morstein, Conventional and high resolution TEM investigation of the microstructure of compositionally graded TiAlSiN thin films, *Surface and Coatings Technology* 177-178 (2004) 376-381.
- [14] P. Panjan, M. Cekada, B. Navinsek, A new experimental method for studying the cracking behaviour of PVD multilayer coatings, *Surface and Coatings Technology* 174-175 (2003) 55-62.
- [15] L.A. Dobrzański, K. Lukaszewicz, A. Križ, Properties of the multi-layer Ti/CrN and Ti/TiAlN coatings deposited with the PVD technique onto the brass substrate, *Journal of Materials Processing Technology* 143-144 (2003) 823-837.