



Characteristic features of fine-grained coatings deposited on magnesium alloys

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ABSTRACT

Purpose: This work presents the research results on the structure of gradient/monolithic coatings (Ti/Ti(C,N)/CrN, Cr/CrN/TiN) deposited onto the magnesium alloy substrate by cathodic arc evaporation method.

Design/methodology/approach: The investigations were performed using scanning and transmission electron microscopy (with different image techniques) for the microstructure determination. The morphology was studied as well as the lattice parameters for the layer matrix and substrate phase identification using diffraction methods.

Findings: A thin metallic layer (Ti and Cr) was deposited prior to deposition of gradient coatings to improve adhesion. It was found out that the microstructure of the PVD coatings deposited by the cathodic arc evaporation method is composed of fine crystallites and that their average size is in the range of 15-200 nm, depending on the coating type. SEM micrographs showed that the deposited coatings are characterized by compact structure without delamination or defects and they closely adhere to each other. Investigations confirm also that the Ti(C,N)/CrN and CrN/TiN coatings reveal a clearly visible transition zone between the gradient Ti(C,N) and CrN layers and the wear resistant CrN and TiN layers, obtained as a result of the separately applied metal vapour sources.

Practical implications: Achieved coatings with good adhesion and without the disadvantage of delamination was made possible by cathodic arc evaporation method. Obtained properties of gradient/monolithic coatings (Ti/Ti(C,N)/CrN, Cr/CrN/TiN) deposited onto the magnesium alloy substrate and the study of them can contribute to development in a given group of materials used for different surface engineering processes.

Originality/value: The original value of the work is that it applied the PVD method for a common material like magnesium alloy.

Keywords: Magnesium alloys; Coating deposition; PVD method; Electron microscope

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MATERIALS

1. Introduction

Magnesium and its alloys have excellent physical and mechanical properties for a number of applications. In particular, its high strength-weight ratio makes it an ideal metal for automotive applications, where weight reduction is of significant concern. Due to limited fossil fuel resources and environmental problems associated with fuel emission products, there is a push in the automotive industry to make cars lighter in order to decrease fuel consumption. The use of magnesium alloys can significantly decrease the weight of automobiles without sacrificing their structural strength [1-3].

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 [4-11]. Selection of the substrate material onto which the investigated coatings were deposited by PVD technique in the presented project was not incidental either. Traditionally, automotive components products used in the construction and power industries should have – apart from their special aesthetic features – a high corrosion-, erosion- and wear resistance. Thin, hard PVD coatings on a soft substrate, turn out to be an advantageous material combination from the material point of view [4-11].

The aim of this innovative work was to obtain best possible hybrid coatings, consisting of – a gradient transition layer, with a continuous change of one or more components reaching from the substrate to the surface top – as well as an outer coating using the cathodic arc evaporation process on the surface of the cast AZ61 magnesium alloys to increase the low stiffness of the substrate material. This article focuses only on the structure analysis in order to evaluate the quality of the obtained coating and provides a reference for future work concerning the structure influence on the properties of the investigated coating.

2. Experimental procedure

The chemical compositions of the investigated alloy are presented in Table 1.

In order to determine the relationship between structure and properties of the achieved hybrid coatings, – a system composed of a soft substrate – transition gradient layer, with a continuous change of one or more components from the substrate to the outer surface – and the outer layer, independent coatings were produced by means of the cathodic arc evaporation PVD CAE (called: Cathodic Arc

Evaporation) on a substrate of magnesium cast alloys, Mg-Al-Zn. PVD CAE method was implemented using the device DREVA ARC400 supplied by Vakuumtechnik by the cathodic arc evaporation method. The device is equipped with three pairs of independent sources of metals vapour. Prior to the coating process the substrate was cleaned chemically by washing and rinsing in a ultrasonic cleaner and dried in a stream of hot air. Moreover, the samples were ion-cleaned using Ar ions at a polarisation voltage of 800/200 V for 20 min. For the PVD coating process it were used water cooled discs with a diameter of 65 mm and containing pure metals (Cr, Ti). The samples were coated in an inert Ar atmosphere as well in reactive gases atmosphere N₂ to obtain nitrides. Achieving of a right balance of elements concentration in the phase significantly improves the control of the coating properties. A gradient change of the chemical composition on the coating cross-section was achieved by changing the proportion of reactive gas dose or target evaporation current change on the arc sources. The determined coating process conditions are presented in Table 2. During the PVD coating process the substrates – made of cast magnesium alloys – move relative to the vapour sources, by performing of rotational movements in order to obtain uniform thickness of the layer, and preventing at the same time the phenomenon of so-called “shadow on the coated surfaces”. The distance between each of the cathodes and the deposited substrates was 120 mm. To improve the adhesion of coatings, a transition Cr or Ti interlayer was deposited.

The examinations of thin foils microstructure and phase identification were made on the JEOL 3010CX transmission electron microscope (TEM), at the accelerating voltage of 300 kV using the selected area diffraction method (SAD) for phase investigations. Microstructure investigation was performed using scanning electron microscope (SEM) ZEISS Supra 35 with a magnification between 10000 and 35000 times. For microstructure evaluation the Secondary Electrons (SE) detection was used, with the accelerating voltage of 5-25 KV. Qualitative and quantitative chemical composition analysis in micro-areas of the investigated coatings was performed using the X-ray microanalysis (EDS) by means of the spectrometer EDS LINK ISIS supplied by Oxford. The analysis of phase composition of the substrates and of the obtained coatings was carried out using the X-ray diffraction method (XRD) on the X-ray apparatus X'Pert of the Panalytical Company using the filtered radiation of a cobalt lamp. In order to obtain more accurate information from the surface layer of the investigated materials, we applied in our further investigation studies the grazing incident X-ray diffraction technique (GIXRD method).

Table 1.
Chemical compositions of the investigated magnesium alloy

Type of material	Mass concentration of the elements, %					
	Al	Zn	Mn	Si	Mg	Rest
AZ61	5.92	0.49	0.15	0.04	93.3	0.1

Table 2.
Deposition parameters of the investigated coatings

Parameters	Coating	
	Ti/Ti(C,N)-gradient/CrN	Cr/CrN-gradient/TiN
Base pressure, Pa	5×10^{-3}	5×10^{-3}
	80*	80*
Argon flow rate, sccm	10**	80**
	10***	20***
Nitrogen flow rate, sccm	225→0**	0→250**
	250***	250***
Acetylene flow rate, sccm	0→170**	-
	70*	60*
Substrate bias voltage, V	70**	60**
	60***	100***
Target current, A	60	60
Process temperature, °C	<150	<150

*during metallic layers deposition, **during gradient layers deposition, *** during ceramic layers deposition

3. Results and discussion

Results of diffraction measurements achieved by the high resolution transmission electron microscope (Figs. 1-4) made it possible to identify the CrN and TiN phases which occurred in the Ti/Ti(C,N)/CrN surface layer and Cr/CrN/TiN surface layer respectively. For both cases of the investigated bilayer coatings produced on magnesium light alloys had the nanocrystalline character (Figs. 1, 3). The CrN phase was determined as a cubic phase of the 225-Fm3m space group with the lattice constant of $a=b=c=0.414$ nm. The TiN phase as a cubic phase of the Fm3m (225) space group with the lattice constant of $a=b=c=0.424173$ nm (Figs. 3, 4). Investigations performed using particularly the dark field technique on the transmission electron microscope have confirmed, that the size of the TiN crystallites, of which the Cr/CrN/TiN coating consists, is in the range of up to 200 nm. CrN crystallites are several times smaller (Fig. 3) compared to TiN crystallites. Whereas the area of the Ti/Ti(C,N)/CrN coating based on the CrN phase, in the majority of the cases does not exceed the limit of ~15 nm (Figs. 1, 3). Also

a globular bulk shaped morphology and homogeneity of these crystallites was found, as well a low statistical dispersion in the range between 15 to 20 nm.

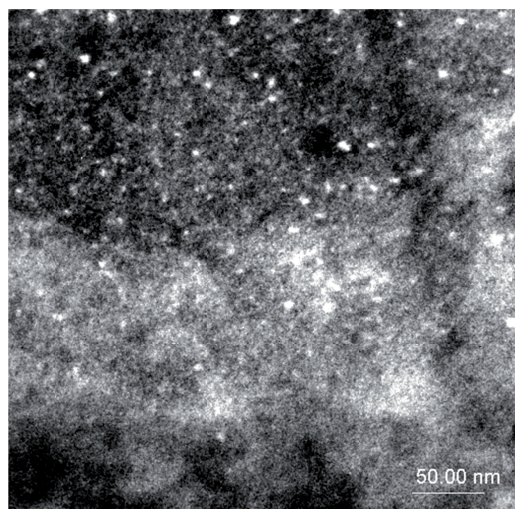


Fig. 1. Structure of the thin foil from CrN surface layer (Ti/Ti(C,N)/CrN coating), dark field, TEM

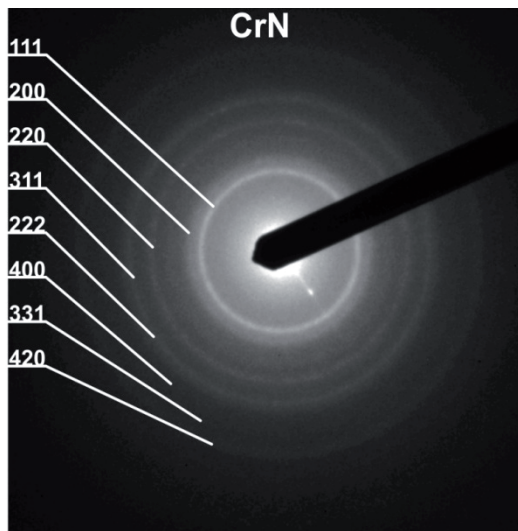


Fig. 2. Structure of the thin foil from CrN surface layer (Ti/Ti(C,N)/CrN coating) solution of the diffraction pattern presented in Fig. 1

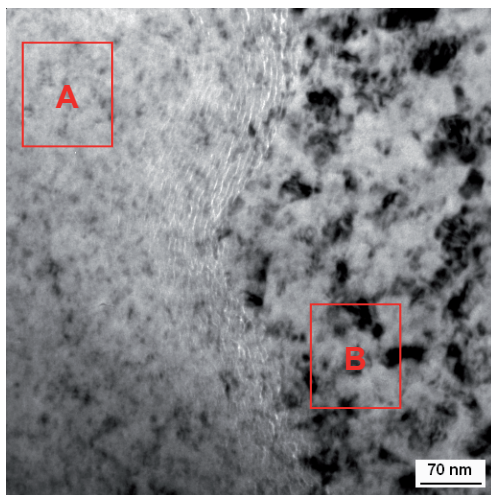


Fig. 3. Structure of the thin foil from CrN and TiN surface layer (Cr/CrN/TiN coating) fracture, bright field, TEM

It was found out, as a result of the microstructure investigations on scanning electron microscope, that there are no pores or cracks in the produced coating and no defects and failures occurring spontaneously in this single layer are of significant importance for the properties of the whole layer (Figs. 5,6). Occasionally occurring discontinuity of the layer can be seen as a product of the deposition process and may be neutralised or “masked” by the properly adjusted deposition process. The thickness of the Ti/Ti(C,N)/CrN layer is in the range from 3.2 to 3.5 μm and Cr/CrN/TiN is in the range from 1.6 to 2 μm .

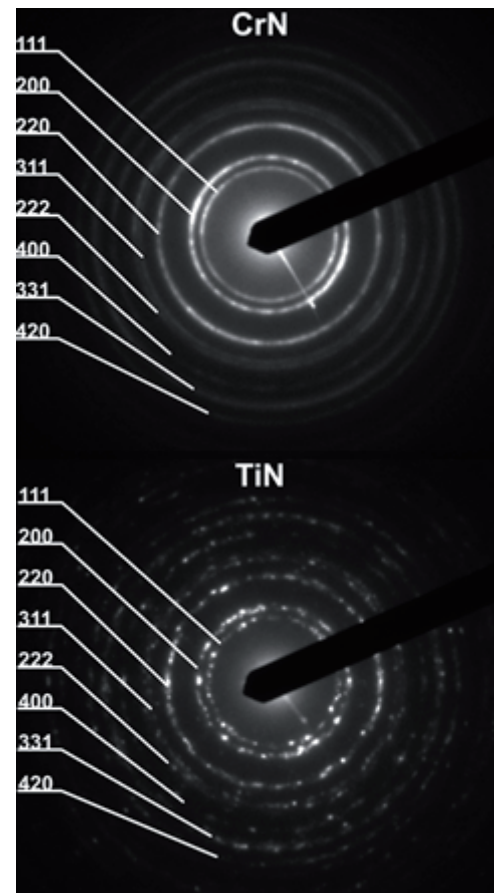


Fig. 4. Structure of the thin foil from area A- CrN coating and area B-TiN coating fracture, solution of the diffraction pattern

It was also found that the examined layers were not uniform and consisted of three sub-layers, where the upper one had a thickness of ca. 0.6 μm (Figs. 5, 6). Coating thickness was measured using a scanning electron microscope. Further investigations revealed the exact morphology and nature of these sub-layers. In the investigated coatings the negative (compressive) internal stresses occur. Depending on their value, internal stresses can affect the substrate – coating arrangement unfavourably or positively. Compressive stresses increase crack resistance and to some degree, dependent on thickness, phase and chemical composition as well as material, at which they have been reached, minimize a coating chipping increasing their adhesion to substrate. In case of our investigation it can be observed that the stress increases as the coating's thickness increases. Fracture image evaluations of the investigated magnesium alloy samples with the deposited layers onto the surface of the Ti/Ti(C,N)/CrN and

Cr/CrN/TiN type show a sharp transition zone between the coating and the substrate material. Moreover there can be recognised, that the obtained layers are uniformly deposited and closely adhere to the substrate without any breaks or defects (Figs. 5, 6).

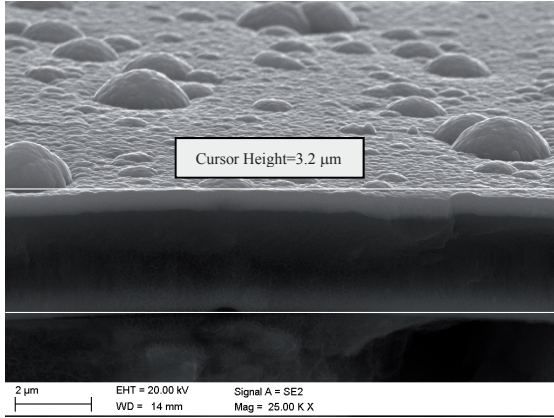


Fig. 5. Cross-section SEM images of the Ti/Ti(C,N)/CrN coating deposited onto the AZ61 substrate

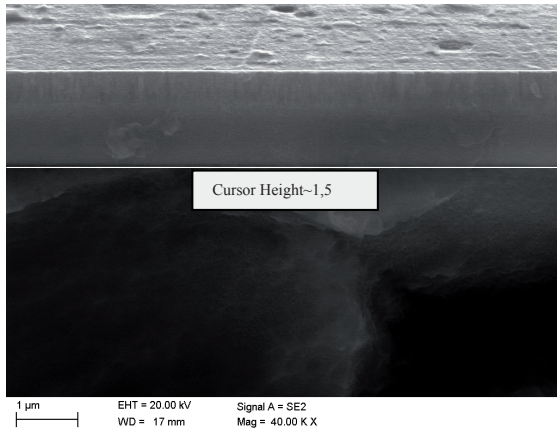


Fig. 6. Cross-section SEM images of the Cr/CrN/TiN coating deposited onto the AZ61 substrate

Fracture morphology of the Ti/Ti(C,N)/CrN coating is characterised by a lack of columnar structure (Fig. 5). Whereas in case of the Cr/CrN/TiN coating the top wear resistant layer clearly shows a character similar to the column one structure (Fig. 6). Fracture investigations confirm also, that the Ti/Ti(C,N)/CrN and Cr/CrN/TiN layers has a layered structure, with a clearly visible transition zone between the gradient layer and the wear resistant coating achieved using separate metals

evaporation sources. On the basis of the performed observations on scanning electron microscope the coating of the Ti/Ti(C,N)/CrN type show an increasing non-homogeneity compared to the Cr/CrN/TiN coating what is connected with the presence of numerous droplet-shaped microparticles and should that fore significantly influence mechanical properties and resistance of the investigated surfaces (Figs. 7, 8). The droplets observed in SEM are noticeably different in terms of size and shape (regular and irregular shape, slightly flat). There were also some hollows formed probably when the solidified droplets break off after the PVD process has been completed (Figs. 7, 8). The occurrence of such morphology defects is connected to the nature of the cathodic process of the electric arc evaporation.

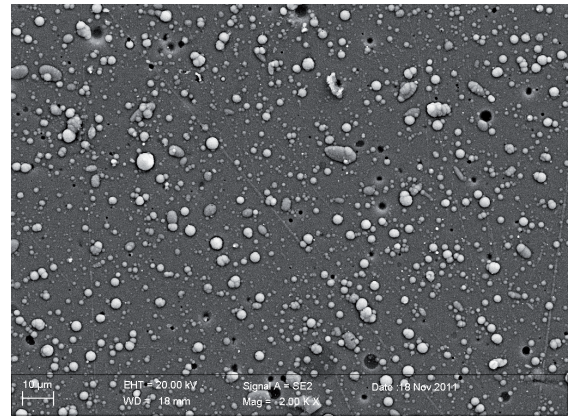


Fig. 7. Surface topography of the Ti/Ti(C,N)/CrN coating deposited onto AZ61 substrate

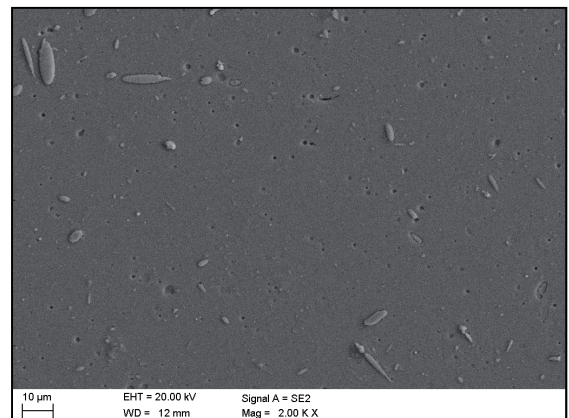


Fig. 8. Surface topography of the Cr/CrN/TiN coating deposited onto AZ61 substrate

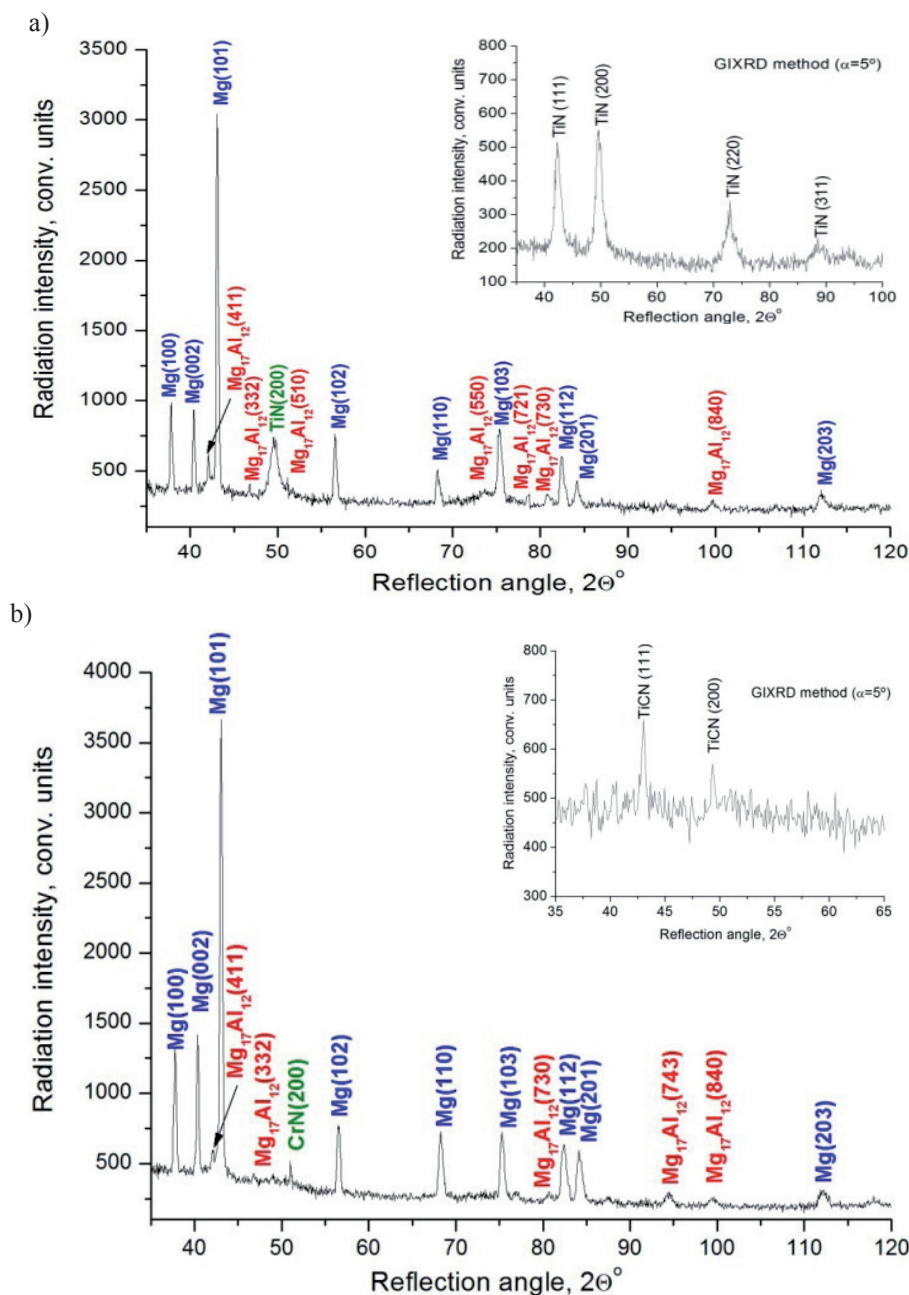


Fig. 9. X-ray diffraction pattern of: a) Ti(Ti,C,N)/CrN coating deposited on the AZ61 magnesium alloys, b) Cr/CrN/TiN coating deposited on the AZ61 magnesium alloys obtained by Bragg-Brentano method and GIXRD method

Qualitative phase composition analysis carried out using the X-ray diffraction method has allowed it to evaluate the quality of the achieved Ti(C,N), CrN coatings based on the resulting X-ray diagrams, collecting by the application of the Bragg-Brentano technique (Fig. 9). Because of the overlapping reflections of the substrate and the coating

material, as well the relatively small thickness of each layer, there were difficulties with identification of the phases. It was also confirmed the presence of reflexes coming from the phases present in the substrate, e.g. Mg and Mg₁₇Al₁₂ (Fig. 9). Very small volume fraction of other phases present in the substrate does not allow it to

perform an unambiguous identification of the recorded X-ray spectrum. The presence of substrate reflexes was confirmed on every achieved X-ray diffraction collected from the coating, due to the thickness of the obtained coatings $< 3.5 \mu\text{m}$, smaller than the X-ray penetration depth. Using the technique of fixed incidence angle (GIXRD method) there are collected only reflexes from the thin surface layers (Fig. 9). A lack of reflexes from the CrN

phase – present in the Ti/Ti(C,N)/CrN coating – in the GIXRD method results from the specific identification of this phase by this method.

Based on the results obtained by the quantitative X-ray microanalysis using the energy dispersed X-ray EDS spectrometer it was confirmed the presence of Mg, Al, Ti, Cr, N, as major alloying elements of the cast of magnesium alloys as well the obtained coatings (Fig. 10, Table 3).

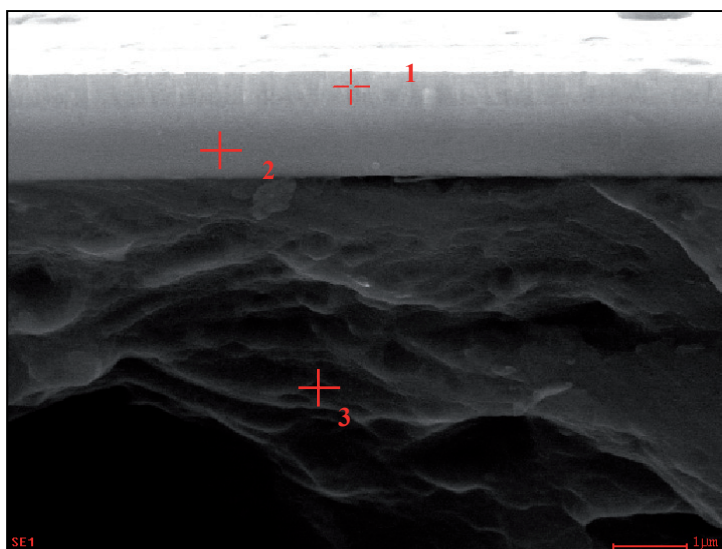


Fig. 10. Cross-section SEM images of the Cr/CrN/TiN coating deposited onto the AZ61 substrate

Table 3.

The results of quantitative chemical analysis from third 1, 2, 3 areas of coating Cr/CrN/TiN deposited onto substrate from AZ61 alloy marked in Fig. 10

Chemical element	The mass and atomic concentration of main elements, %	
	mass	atomic
Analysis 1 (point 1)		
N	26.07	55.06
Ti	59.12	36.51
Cr	14.81	08.43
Matrix	Correction	ZAF
Analysis 2 (point 2)		
N	13.03	31.60
Mg	14.59	20.38
Ti	12.80	09.08
Cr	59.59	38.94
Matrix	Correction	ZAF
Analysis 2 (point 3)		
Mg	95.27	95.72
Al	04.73	04.28
Matrix	Correction	ZAF

4. Summary

The metallographic examinations carried out give grounds to state that the coatings were deposited uniformly onto the investigated substrate materials and that they are characteristic of the depending on the coating type employed, and that the particular layers adhere tightly to themselves and to the substrate. In general the following should be pointed out:

- Deposited coatings are characterized by compact structure without delamination or defects and they closely adhere to one,
- The surface layer has a polycrystalline structure consisting of nanoscale crystallites of ca 10 to 20 nm in size for CrN layer and ca. 200 nm for TiN layer,
- The CrN phase was determined as a cubic phase of the 225-Fm3m space group with the lattice constant of $a=b=c=0,414$ nm. The TiN phase as a Cubic phase of the Fm3m (225) space group with the lattice constant of $a=b=c=0.424173$ nm,
- The thickness of the Ti/Ti(C,N)/CrN layer is in the range from 3.2 to 3.5 μm and Cr/CrN/TiN is in the range from 1.6 to 2 μm ,
- The PVD process gives good results with high quality of the layer, which is better in case of the Cr/CrN/TiN variant.

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