Magnesium and its alloys are interesting materials for biodegradable implant applications. Magnesium alloys have very good strength properties, they are lightweight, but their main disadvantage is a low corrosion resistance in the physiological environment. Various modifications of a Mg alloys surface by deposition of different coatings are used to prevent untimely dissolution. The article presents the investigation results of a thin ZnO coating deposited on a MgCa2Zn1Gd3 alloy by means of the magnetron sputtering method. The studies include: scanning electron microscope observation of the ZnO surface, X-ray phase analysis, surface roughness measurement in atomic force microscopy, the microhardness test and potentiodynamic corrosion resistance test in the Ringer solution at 37°C. It was found that the ZnO coating is compact and continuous. It increases the hardness of the MgCa2Zn1Gd3 alloy and also improves its corrosion resistance. The corrosion potential is shifted slightly towards the positive values from –1.52 V to –1.50 V for the alloy with the ZnO coating.

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1. Introduction

In recent years, a growing interest in biodegradable implants has been observed. Such materials should have an adequate bearing capacity and also exhibit high resistance to corrosion in the physiological environment.

Magnesium and its alloys are biocompatible with the body, they are characterized by low density and have a very good mechanical strength which makes them potential candidates for biomedical implants [1, 2]. Compared to other materials used for bone implants (e.g. biodegradable polymers), the tensile and compression strengths of magnesium alloys are significantly higher. Another advantage of magnesium is that its ions are vital to proper functioning of the body, so the implant could partially cover the human requirement for this element.

Despite many advantages, magnesium and its alloys also have a significant disadvantage, poor corrosion resistance in a physiological pH environment where the chloride ion concentration is high [3].

In order to slow down the corrosion process and further improve mechanical properties, alloy elements such as Ca, Zn, Cu or rare earth elements are added to Mg alloys [4]. An important role in the protection against corrosion is also performed by various types of surface modifications (e.g. biodegradable polymers), the tensile and compression strengths of magnesium alloys are significantly higher. Another advantage of magnesium is that its ions are vital to proper functioning of the body, so the implant could partially cover the human requirement for this element.

When choosing the chemical composition of Mg alloys and the applied coatings, it is important to remember that their dissolution products should be harmless to the human body.

The paper presents the results of structure, microhardness, topography and surface roughness analysis, as well as corrosion resistance studies of a single-layer ZnO coating applied on the MgCa2Zn1Gd3 alloy using the magnetron sputtering method.

The choice of ZnO layer as a modifier of MgCa2Zn1Gd3 alloy protecting the material from the surface digestion was determined by its proper characteristics associated with low toxicity, biocompatibility, corrosion resistance under physiological saline environment at 37°C [10, 11]. Moreover, ZnO layer significantly reduces proliferation of bacteria and has antithrombotic properties.

2. Experimental procedure

MgCa2Zn1Gd3 master alloy in the form of a 100 × 280 × 14 mm³ plate has been obtained by casting in an induction vacuum furnace under Ar atmosphere at the temperature of about 700°C. 99.978% pure magnesium in the form of goose, zinc rods (99.99% pure), 99.9% pure Gd granules and Ca granules (99.5% pure) have been the casting process feedstock.

Samples of the MgCa2Zn1Gd3 alloy in the form of cylinders with diameters of 13 mm and heights of 15 mm were the substrate material. A single layer of ZnO coating was applied onto an appropriately prepared alloy surface by magnetron sputtering using the Kurt J. Lesker PVD 75 device. The coating process was performed at the temperature of 100°C, with inert Ar gas shielding, over the time of 75 min.

The structure of the resulting coating was observed in the Zeiss SUPRA 25 scanning electron microscope.
equipped with the energy dispersive spectrometry (EDS) chemical analysis system.

Thickness of ZnO layer has been determined by observations of sample fracture images obtained by scanning electron microscopy (SEM). Adhesion of the studied layer to the substrate has been estimated based on SEM image only.

The analysis of the phase composition of the sample surface was carried out with the PANalytical X’Pert PRO X-ray diffractometer using the radiation of a Cu $K_\alpha$. Analysis was performed using the method of step registration in the angular range of $2\theta$ from 30° to 90°.

The X-ray qualitative analysis was performed using HighScore Plus software with a dedicated PAN-ICSD phase identification card database.

Observation of the topography of the applied coating and roughness measurement were performed using the Park Systems AFM XE-100 atomic force microscope in non-contact mode. The results of the studies were analysed using the XEI software.

The measurement of microhardness of the ZnO coating and the base alloy was conducted using the Future-Tech FM-ARS 9000 and the Vickers method, under the load of 0.05 N.

Electrochemical (potentiodynamic) corrosion resistance tests were performed using an Autolab PGSTAT302N Multi BA potentiostat. Where the reference electrode was a calomel electrode and the auxiliary electrode was a platinum electrode, a three-electrode electrochemical system was used. The working electrode was a MgCa$_2$Zn$_1$Gd$_3$ sample with the ZnO coating. The measurement was performed in the Ringer solution at 37°C, over the time of 1 h.

3. Results and discussion

The ZnO coating, obtained by magnetron sputtering in a vacuum furnace, is evenly distributed over the entire surface of the MgCa$_2$Zn$_1$Gd$_3$ alloy, tightly adhering to the substrate material (Fig. 1).

It is characterized by a homogeneous, fine grain structure with clearly defined grain boundaries. No defects were found in the form of pores or cracks on the surface of the coating.

The lines from O and Zn were observed on the EDS spectrum.

The presence of the ZnO phase confirms the results of X-ray studies (Fig. 2). Based on the obtained diffraction pattern, it can be assumed that the studied coating has a preferential orientation of crystals, which results in a change in the intensity ratio of the diffraction lines of the studied material with regard to the reference sample.

Images of the surface topography which define the surface morphology were made for the selected area of the sample ($5 \times 5 \, \mu m^2$) with the ZnO coating (Fig. 3).

Based on the image analysis it can be stated that the ZnO coating has a uniform granular structure, without visible cracks. The vast majority of surface roughness values do not exceed 25 nm (Fig. 4).
Based on the results of the tests, roughness parameters were determined — mean roughness (roughness average) Ra of 14.27 nm and root mean square RMS of 17.80 nm, as well as the maximum profile height of 70.56 nm.

The roughness parameters of the MgCa2Zn1Gd3 alloy — substrate material — were also determined. The mean roughness Ra is equal to 16.35 nm, RMS is 20.64 nm, and the maximum profile height is 120 nm.

Based on these values, it seems that the surface roughness of the ZnO coating is not so high. These results should have a positive influence on the corrosion resistance of tested material.

The microhardness test of the single-layer ZnO coating on a MgCa2Zn1Gd3 alloy was also performed. The measurement results indicate an increase in the hardness of the master alloy after applying the coating. The average hardness of the alloy with a ZnO coating was 80 HV (standard deviation (SD): ±6.2, 98% confidence interval (CI): ±5.53), while the average hardness of the master alloy was equal to 71 HV (±4.7 SD, ±4.2 CI). The average value of microhardness was calculated from 10 measurements.

Electrochemical studies of corrosion resistance were performed in the Ringer solution at 37°C.

A potentiodynamic curve for the master alloy and alloy coated with ZnO was determined (Fig. 5).

As a result of the analysis of the curve it can be stated that, compared to the uncoated alloy, the applied ZnO coating slightly improves corrosion resistance. There is a slight shift in the corrosion potential towards positive values from −1.52 V to −1.50 V.

4. Conclusions

Out of many resorbable materials, magnesium alloys deserve special attention. These materials have, however, a significant disadvantage — low corrosion resistance in the tissue environment. The key issue related to studied biomaterial for implants application is a control of corrosion process. This is associated with hydrogen evolution. Too high value of H2 can lead to inflammation in the body. This has led, among other things, to the search of the possibility to modify the surface of these alloys by applying a protective coating.

The presented results of the single-layer ZnO coating applied on the MgCa2Zn1Gd3 alloy using PVD technique suggest a slight improvement in corrosion resistance which confirms the corrosion potential shift toward positive values from −1.52 V to −1.50 V.

The resulting coating is characterized by a fine-grained structure, it is continuous with no clearly visible pores or cracks. Additionally, it increases the microhardness in comparison to the base alloy.

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