

PEO layers on Mg-based metallic glass to control hydrogen evolution rate

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Abstract. The amorphous Mg-based alloys may be used as metallic biomaterials for resorbable orthopedic implants. The Mg-Zn-Ca metallic glasses demonstrate variable in time degradation rate in simulated body fluid. In this work the $Mg_{66}Zn_{30}Ca_4$ alloy was chosen as a substrate for coatings. This paper reports on the surface modification of a $Mg_{66}Zn_{30}Ca_4$ metallic glass by plasma electrolytic oxidation (PEO). The structure characterization of uncoated $Mg_{66}Zn_{30}Ca_4$ alloy was performed by using TEM and XRD method. The immersion tests of coated and uncoated $Mg_{66}Zn_{30}Ca_4$ alloy were carried out in Ringer's solution at 37°C. The volume of released hydrogen by immersion tests was determined. The coatings structure and chemical composition after immersion tests by SEM/EDS were studied. Based on SEM images of surface structure samples, immersion tests results and hydrogen evolution measurement was proposed the course of corrosion process in Ringer's solution for Mg-based metallic glasses with PEO coating. Results of immersion tests in Ringer's solution allowed to determine the amount of evolved hydrogen in a function of time for $Mg_{66}Zn_{30}Ca_4$ metallic glass and sample with PEO coating. In comparison to the non-coated $Mg_{66}Zn_{30}Ca_4$ alloy, the sample with PEO layer showed a significantly decreased hydrogen evolution volume.

Key words: amorphous magnesium alloys, corrosion rate, plasma electrolytic oxidation, hydrogen evolution.

1. Introduction

According to previous studies [1], the $Mg_{66}Zn_{30}Ca_4$ metallic glass was characterized by good mechanical strength and high glass forming ability. Today, Mg based alloys are used mainly in automotive and aerospace materials [2]. Recently, Mg alloys have been considered in new areas of industry as materials absorbing hydrogen [3] and also as potential biomaterials in medicine. Magnesium alloys are of interest as materials for biomedical applications due to their good biocompatibility and biodegradability. Thanks to their chemical composition, Mg-Zn-Ca alloys especially could be considered as biomimetic materials [4]. Magnesium, zinc and calcium are macro- and microelements in human body. However, Mg alloys have limited application because of their too fast degradation rate, which is also variable in time, including hydrogen release rate in physiological body fluids. The major problem connected with the concept of bioresorbable Mg implants is high quantity and intensity of released hydrogen produced during corrosion process of magnesium alloys, which is too high and harmful for human body. The mechanism of released hydrogen depends among others on the solution's pH, chemical composition of alloy and solution, and the structure of implant's surface. An oxide layer forms spontaneously on surface of magnesium

alloys. It should be noted that an oxide layer on magnesium alloys surface is porous and discontinuous. The Pilling-Bedworth's coefficient for oxide magnesium is 0.81, which means that the spontaneous oxide layer on magnesium alloy is leaky [5]. Consequently, the spontaneous oxide layer cannot provide an effective barrier against corrosion. There are several approaches to slowing down the degradation rate of magnesium alloys, including changes in chemical composition or surface modification.

The ways to decrease dissolution rate include, among others, a change in composition of the Mg-based alloy and tailoring its microstructure or adopting surface modification (e.g. coatings). For biomedical purposes, pure Mg and new crystalline and amorphous Mg-based alloys, including biocompatible alloying elements: Mg-Zn [6], and Mg-Zn-Ca [7-9] and low toxic or rare earth elements: Mg-Zn-Ca-Gd [10], Mg-Zn-Ca-Sr [11], Mg-Zn-Ca-Mn-(Sr) [12], Mg-Zn-Mn-(Ca/Sn) [13] were examined. Surface modification methods in Mg alloys are based on thermal treatment [14], chemical conversion [15, 16], sol-gel process [17] or plasma electrolytic anodization (PEO) [18, 19]. In this work, the PEO coating on magnesium based metallic glass was prepared. The PEO layer shows a characteristic morphology (porous oxide layer, or porous layer with needle-flake microstructure), which depends on the anodizing conditions and substrate composition. The coatings obtained by PEO are usually multilayers. They are composed with three sublayers. The first sublayer is barrier layer with a thickness of several nanometers. The second sublayer is an adhesive layer with open and close pores. The third sublayer is a typical

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outer layer with open pores, and sometimes with some parts of melted layers. However, the porosity of the third sublayer (outer layer) could prove very helpful for osseointegration orthopedic implants.

2. Material and methods

The $Mg_{66}Zn_{30}Ca_4$ metallic glass in the form of plate was successfully fabricated by copper-mold casting. The production of the metallic glasses samples consisted of two stages: preparation of a crystalline master alloy and casting of metallic glasses samples in the form of plates. The preparation of the master alloy was carried out by the induction melting of pure components: zinc (99.98%), magnesium (99.95%) and calcium (99.99%) in the argon. In the second step amorphous plates with 2 mm in diameter were casted to the copper mould. The obtained plates were used for structural and corrosion studies.

Surface of the Mg alloy was anodized in solutions of 0.1 M Na_2SiO_3 with 0.1 M NaOH up to 250 V (power supply, KIKUSUI, Japan). Current density was 50 mA/cm^2 , and the process was carried out for 3 min. The structure characterization of uncoated $Mg_{66}Zn_{30}Ca_4$ alloy was performed by transmission electron microscopy (TEM) Tecnai TF 20 X-TWIN at an accelerating voltage of 120 kV. Observations were made on thin foils (lamellas) made of plate with 2 mm thickness. Thin films were made using a FEI QUANTA 3D 200i with a scanning microscope and an ion column (FIB). The structure characterization of uncoated $Mg_{66}Zn_{30}Ca_4$ alloy was performed also by X-ray diffraction method using PANalytical X'Pert Pro X-ray diffractometer with the $Co \text{ K}\alpha$ radiation source (wavelength = 1.7902 \AA). The immersion tests of coated and uncoated $Mg_{66}Zn_{30}Ca_4$ alloy were carried out in Ringer's solution ($8,6 \text{ g/dm}^3 \text{ NaCl}$, $0,3 \text{ g/dm}^3 \text{ KCl}$, $0,48 \text{ g/dm}^3 \text{ CaCl}_2 \cdot 6H_2O$) at 37°C . Measurements of released hydrogen volume were performed in Ringer's solution during 168 hours. Measurements of the released hydrogen volume were made using the burette. The volume of released hydrogen by immersion tests was determined. The coatings structure and chemical composition after immersion tests by scanning electron microscopy Supra 35 Carl Zeiss with energy-dispersive x-ray spectroscopy (EDS / EDX) were studied.

3. Results

The surface of sample with coating prepared by PEO method was shown in Fig. 1. The coating prepared by PEO method is porous in the outermost part.

The fracture of sample with coating prepared by PEO method was presented in Fig. 2. The PEO layer consist of three sublayers. The diffusion layer with a thickness of approx. 319 nm and adhesive layer with a thickness of 1.97 μm and porous layer (outermost part of layer).

Figure 3 presents structural studies results of substrate ($Mg_{66}Zn_{30}Ca_4$ metallic glasses). Figure 3a shows TEM image and electron diffraction pattern of $Mg_{66}Zn_{30}Ca_4$ metallic

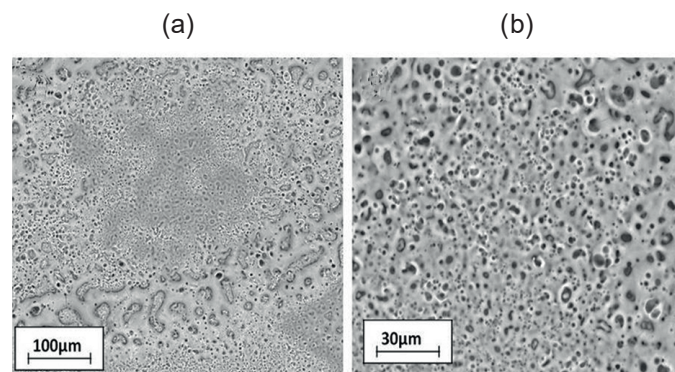


Fig. 1. SEM images (a, b) of the surface $Mg_{66}Zn_{30}Ca_4$ metallic glasses with PEO coating

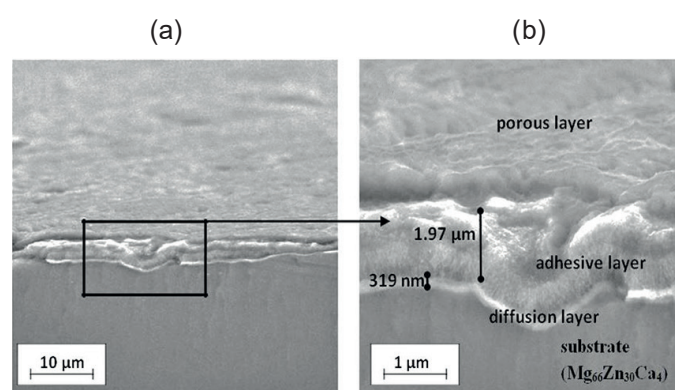


Fig. 2. SEM images (a, b) of the fracture $Mg_{66}Zn_{30}Ca_4$ metallic glasses with PEO coating

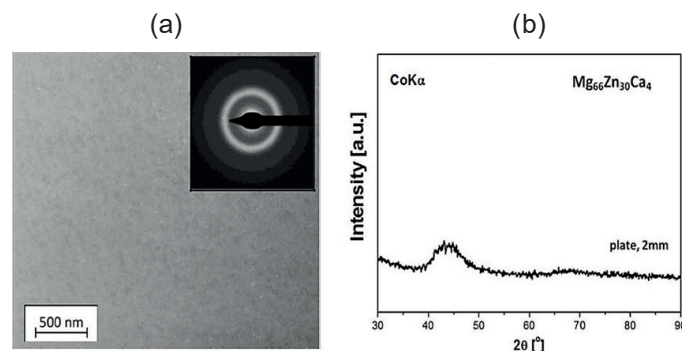


Fig. 3. TEM image, electron diffraction pattern (a) and X-ray diffraction patterns of $Mg_{66}Zn_{30}Ca_4$ metallic glass (b) in the form of plates with a thickness of 2 mm

glasses in as-cast state. The electron diffraction patterns include broad diffraction halo, indicating the formation of a single glassy phase. X-ray diffraction studies (Fig. 3b) confirmed that the investigated $Mg_{66}Zn_{30}Ca_4$ sample had an amorphous structure. The fuzzy spectrum in the range 38–52 was found, which is a typical pattern on X-ray for amorphous structure (Fig. 3b).

Results of immersion tests allowed to determine the hydrogen evolution rate in time and amount of released hydrogen

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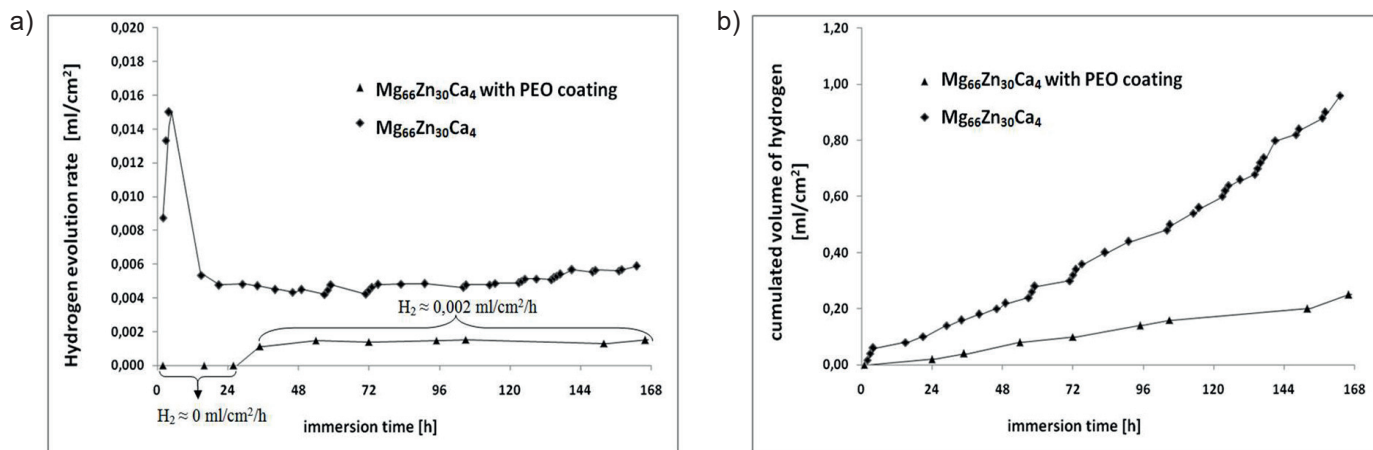


Fig. 4. Results of immersion tests: a) hydrogen evolution rate, b) cumulated volume of released hydrogen of studied Mg₆₆Zn₃₀Ca₄ alloy and sample with PEO coating immersed in the Ringer's solution at 37°C

for Mg₆₆Zn₃₀Ca₄ metallic glass and sample with PEO coating (Fig. 4a, 4b).

The structure of corrosion products formed during immersion tests on studied samples surface were examined by scanning electron microscopy (SEM). After 24 h immersion in Ringer's solution, the surface structure of sample with PEO coating (Fig. 5) is almost unchanged compared to surface images before immersion (Fig. 1). Analysis of PEO coating chemical composition indicated to present O, Si, Mg, Zn, Ca (Fig. 5c). Magnesium, zinc and calcium are components of amorphous substrate. Silicon and oxide are components of solution to prepare the PEO coating.

The SEM images of corrosion products structure and their chemical composition on the surface sample with PEO coating after 168 h immersion in Ringer's solution presented in Fig. 6.

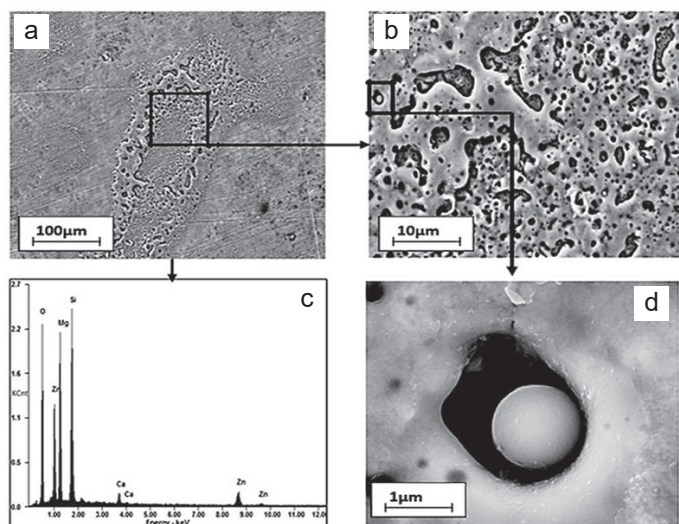


Fig. 5. SEM images (a, b, d) and EDX chemical composition (c) analysis of the surface Mg₆₆Zn₃₀Ca₄ metallic glasses with PEO coating after 24 h immersion in Ringer's solution at 37°C

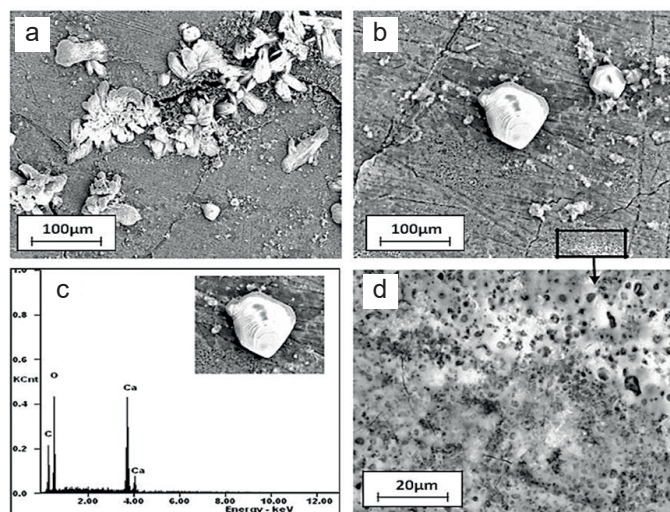


Fig. 6. SEM images of the surface Mg₆₆Zn₃₀Ca₄ metallic glasses with PEO coating (a, b, d) and EDX analysis of spherical element chemical composition (c) after 168 hours immersion in Ringer's solution at 37°C

The surface of sample is irregularly covered by corrosion products (Fig. 6a, 6b, 6d). On the surface microcracks are visible (Fig. 6a, 6b). The corrosion products on the edges of microcracks were crystallized (Fig. 6a). The chemical composition analysis of crystallized corrosion products showed that they consisted mainly of O, C, Ca (Fig. 6c). In Fig. 6b two types of surface morphology after immersion in Ringer's solution are visible. There are areas with PEO coating (Fig. 6d) and areas with crystallized corrosion products (Fig. 6b).

In case of Mg₆₆Zn₃₀Ca₄ surface after 168 h immersion in Ringer's solution (Fig. 7) a corrosion products layer was formed. This layer was non-continuous and included microcracks (Fig. 7b). There were areas with visible corrosion products and areas with lesser density of corrosion products (Fig. 7a, 7b, 7c). The chemical composition analysis of Mg₆₆Zn₃₀Ca₄ sample surface showed the presence of O, Zn, Mg, Ca (Fig. 7d).

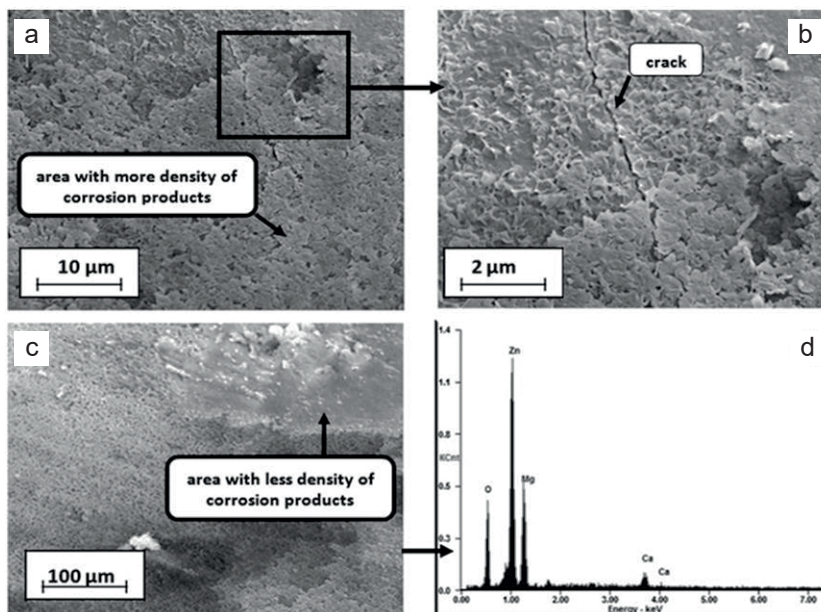


Fig. 7. SEM images (a, b, c) and EDX chemical composition (c) analysis of the surface $Mg_{66}Zn_{30}Ca_4$ metallic glasses after 168 hours immersion in Ringer's solution at $37^{\circ}C$

4. Discussion

In this work, the plasma electrolytic oxidation coating on magnesium based metallic glass substrate was successfully performed. SEM images of a PEO coating surface fracture (Fig. 2) show that PEO layer include the outer porous layer, the fairly compact layer in the middle and the thin and compact layer (barrier layer). The authors of [19] suggest that the compact middle layer is responsible for good mechanical properties (wear resistance) and improves corrosion resistance of substrate [10]. The PEO coating is visible on the surface sample on SEM images after 168 hours immersion in Ringer's solution (Fig. 6d). It could be the porous part or middle compact layer of PEO coating.

The $Mg_{66}Zn_{30}Ca_4$ alloy with PEO coating shows a reduction of hydrogen evolution in comparison to the substrate ($Mg_{66}Zn_{30}Ca_4$ alloy). In the case of substrate, in $Mg_{66}Zn_{30}Ca_4$ alloy the process of dissolution starts from the surface. Therefore, in the first 24 hours of immersion, hydrogen evolution is the highest for the substrate. The surface of substrate like Mg-based alloys is coated by spontaneous oxide layer before immersion. This spontaneous oxide layer does not have protection properties against dissolution process. Protection properties against dissolution of substrate has PEO coating during the 24 h hydrogen evolution rate is near to zero (Fig. 4a, 4b). In addition, after 24 h immersion in Ringer's solution, SEM images show that the surface structure of sample with PEO coating (Fig. 5) is almost unchanged as compared to surface images before immersion (Fig. 1). SEM images in Fig. 5 correlate with immersion tests results. However, the hydrogen evolution rate of both samples decreased during the following immersion time (Fig. 4a). The possible reason of this phenomena is formation of corrosion products layers on surface samples, which act as

protection layer. Unfortunately, corrosion product layers are created spontaneously and protection properties are temporary. In the case of sample with PEO coating, corrosion products are located near to damage of coating and prevent the penetration of chlorides into the sample. The chemical composition analysis indicates that corrosion products could be calcium carbonates, because EDS results included mainly C, O, Ca. Calcium carbonate (Fig. 6a, 6c) compounds were deposited on the samples, forming a new local protective layer, and reduced the hydrogen evolution rate. The calcium carbonate found on the surface of the studied samples (Fig. 6a, 6b) may precipitate as result of reaction of calcium ions from metal dissolution with carbon dioxide from the atmosphere. The calcium has high solubility in aqueous solutions and is very reactive. Therefore, it dissolves quickly among the elements that are components of the substrate. The calcium carbonate from particles in solution drops out from the solution on the surface of samples, creating an anticorrosive layer.

Based on SEM images of surface structure samples, immersion tests results and hydrogen evolution measurement, a course of corrosion process in Ringer's solution for Mg-based metallic glasses with PEO coating was proposed (Fig. 8). The pores of the outer layer of PEO coating caused partial damage of the adhesive layer. As a consequence, hydrogen releases and partial damage of layers (e.g. microcracks) occurred (Fig. 8a). The edges of microcracks were covered with Ca, C and O compounds (Fig. 8b). Calcium is the most active component of Mg based metallic glass. As a consequence, it easily reacts with the electrolyte components and creates corrosion products. The layers of corrosion products provide temporary protection against the progress of corrosion into the sample.

The volume of hydrogen evolution of the sample with PEO coating was less than in Mg-Zn-Ca sample with PEO

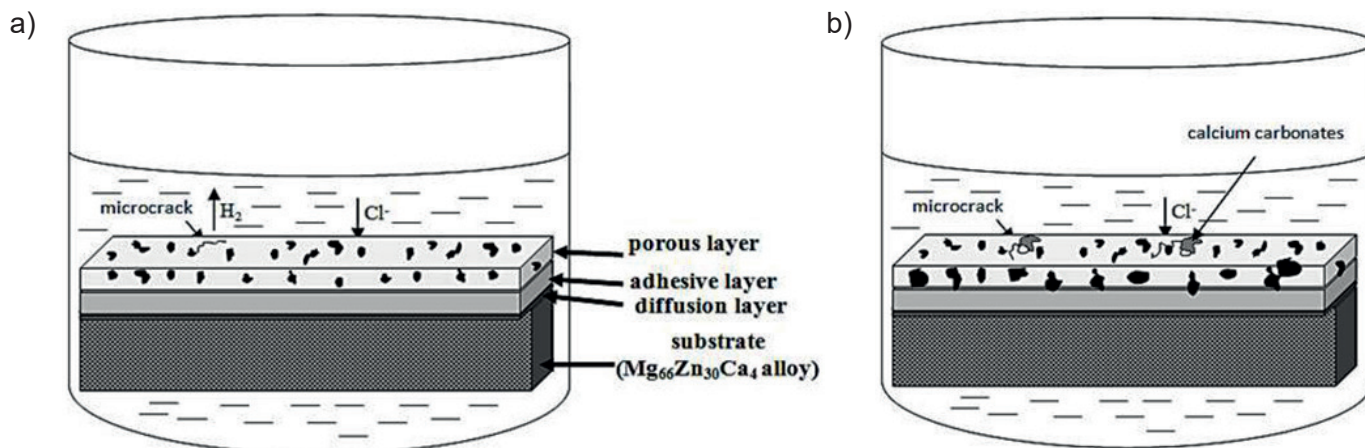


Fig. 8. The schematic drawing (two main phases) of corrosion process of Mg based metallic glasses with PEO coating in Ringer's solution at 37°C: a) hydrogen releases and partial damage of layers (e.g. microcracks), b) the edges of microcracks are covered with Ca, C and O compounds

coating from work [20] during 168 h immersion. In [20], the Mg–2Zn–0.2Ca (wt.%) developed about 2 ml/cm² hydrogen after one week immersion. In addition, in [21] the PEO-treated the WE43 alloy displayed less hydrogen evolution in comparison to the native ones immersed in SBF solution. In [21], the WE43 alloy developed about 10 ml/cm² hydrogen after one week immersion. In this work, the sample with PEO coating developed about 0.25 ml/cm² hydrogen. This very large hydrogen reduction is probably associated not only with various immersion test solutions, but also with the structure of substrate. The substrate in works [20, 21] are crystalline magnesium alloys, and in this work the substrate is an amorphous magnesium alloy. In present work amorphous Mg-based alloys were chosen for research due to their single-phase structure, which is characterizes by reduced susceptibility to local corrosion (pitting) [22, 23].

5. Conclusion

In this work, a PEO coating on amorphous Mg₆₆Zn₃₀Ca₄ alloy was successfully prepared, which may be used to control hydrogen evolution rate. In comparison to the non-coated Mg₆₆Zn₃₀Ca₄ alloy, the sample with PEO layer showed a significantly decreased hydrogen evolution volume.

Since the pores of the outer layer of PEO coating allow for partial damaging of the adhesive layer, hydrogen releases and partial damage of layers (e.g. microcracks) was occurred. Therefore, technologies for the production of the PEO coatings on Mg alloys should be developed and the pores should be reduced. Another way is to fill the pores of the outer PEO layer and consequently use them as drug carriers.

After immersion in Ringer's solution, the surface of sample was irregularly covered with corrosion products. The majority of crystallized corrosion products was located on the edges of microcracks. Around microcracks there may be a higher (faster) release of calcium ions from inside of sample (Ca is the most active element in the examined alloy), which allows for the

growth of corrosion products in the form of (crystallized) aggregates.

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