Study of oxide coated Mg-based bio-substrate for therapeutic purpose

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ABSTRACT

Porous modified Mg foam surface with functional properties is proposed as a platform for local drug release at the target. In particular, MgO coatings were prepared on the magnesium foams surfaces by an anodic electrodeposition process in concentrated 10M KOH solution followed by heat treatment in air. The corrosion behavior of the MgO-coated samples was evaluated by electrochemical measurements and immersion tests in 0.9 % NaCl solution. The experimental results show that the MgO-coated Mg foams show higher stability and lower corrosion rate, and thus enabled to improve the corrosion resistance, whereas the bare Mg foams suffered from severely localized corrosion attack.

CCS Concepts

• Applied computing → Physical sciences and engineering → Chemistry• Information systems → Information retrieval, interfaces and storage → Specialized information retrieval→ Chemical and biochemical retrieval.

Keywords

Metallic bio-materials, Mg-based implants, surface modification, human body

1. INTRODUCTION

Over the past few decades, a remarkable progress in the development of biomaterials occurred [1]-[4]. Medical implantation offers successfully solutions to unhealthy or damaged bones. Metallic biomaterials, i.e. stainless steel, Ti and its alloys, Co-based alloys have been widely used for such purpose. Because of their excellent combination of high mechanical strength and fracture toughness, good corrosion resistance their use offers some advantages over ceramics or polymeric materials. In case of permanent implants, some obstacles are present. Firstly, they cause stress shielding deriving by a different mechanical mismatch between their elastic modulus (above 100 GPa) and the adjacent bone (under 50 GPa). In such circumstances, the metallic implant-bone interface deteriorates and the regular bone healing and the following re-formation of healthy tissues can be compromised. On the other hand, even permanent biometals have to be removed from the body after a definite period through one more clinical intervention, causing less freedom and comfort for human being.

Over the years, biodegradable implants have extensively attracted the attention and a great progress in their design route and technology have been arises. Mg and its alloys, as biodegradable implants, can degrade naturally in the biological surroundings through corrosion and they have significant benefits over Fe-based or Zn-based ones. Mg alloy foams are definitely expected to be particularly advantageous due to low density of their metal matrix, which is approximately two thirds that of aluminum and due to their good mechanical properties. Mg alloys possess a density of about 1.7–2.0 g cm^{-3} that is close to that of natural bones (1.8–2.1 g cm^{-3}), the compressive strength and tensile strength are much higher than those of biodegradable polymers. Compared to Ti alloys (110–117 GPa), stainless steels (189–205 GPa), and Co-Cr alloys (230 GPa), the elastic modulus of Mg alloys (41–45 GPa) is the most closest one to that of natural bones. According to [4], Mg implants stimulate the formation of new bone. Mg^{2+} is the fourth most abundant cation in the human body and half of the total physical Mg is present in the bone tissue; additionally, it is key element in many human metabolic reactions, it is a cofactor in many enzymes and a crucial element of the ribosomal machinery that translates the genetic information encoded by mRNA into polypeptide structures [2]–[8]. Early clinical investigations and recent in vivo and in vitro studies have evidenced that Mg-based implants have good biocompatibility [9]–[11] and can encourage the development of a hard callous at fracture sites [9], [11].

However, Mg and its alloys are predisposed to corrosion: in particular in wet environment, principally related to the low electrode potential exhibited by Mg (-2.37 V) and it is sacrificial to all other engineering metals. Therefore, the principal weakness of their limited use is related to their low corrosion resistance. Two key factors contribute to the poor corrosion resistance of Mg alloys: (i) the presence of secondary phases or impurities and (ii) the formation of quasi-passive hydroxide layer on their surface, which is not as stable as those developed on Al or on stainless steel.

Corrosion is a surface effect, and the environment in which the material is situated has an important role in determining the level to which the corrosion occurs. In the presence of any chlorides with concentrations above 30 mmol/l, the developed hydroxide will evolve toward the production of magnesium chloride ($MgCl_2$) rather than magnesium hydroxide [12]. It was found that $Mg(OH)_2$ has protective action on the implant at pH>11.5, but the corrosion is accelerated when pH< 11.5. The pH of the human body fluid is about 7.4 or less, then the protective film dissolves and the surface of the metallic implant is unprotected and exposed always to the hazardous effect of Cl^- ions. When the environment

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is a biological fluid, with chloride concentrations of about 150 mmol/l, generally, surface pitting corrosion takes place [13]. Consequently, the Mg-based implants lose the basic mechanical integrity earlier than the necessary time for a fully reestablishment of the tissue.

For these reasons, over the years, many efforts have been dedicated to control the corrosion rate of Mg and Mg-based alloys and to improve their corrosion resistance. There are several ways to do this: (i) via alloying [5], [14], (ii) employing of composites [15], [13] or (iii) adopting an adequate surface treatment, i.e. protective coating on Mg and Mg-based alloys. [16], [17]. When alloying procedures have been adopted, special attention has to be observed in order to avoid elements which are harmful for the body, i.e. neurons [18], osteoblasts [19] or can be associated to Alzheimer disease [16]. Surface modification of Mg and Mg-based alloys constitutes an interesting task, because the corrosion rate is low in the early stage of the corrosion and thanks to the presence of the modified surface layer, the possibility to return to the normal value has been created. Such a degradation pattern is appropriate because the loss of strength of the implant would reflect the strengthening of the therapeutic [20].

In this research paper, MgO coating is proposed on Mg foams surface by a costless electrodeposition method. The results pointed out that the coated Mg foams show higher stability and lower corrosion rate, compared to the bare Mg foams, which suffer from severely localized corrosion attack, and also when compared to Mg-based alloys. Additionally, the porous surface can constitute a useful bio-network able to host some medicine allowing their local pre-programmed release at the target, promoting the repair of the bone and of the neighboring tissues.

2. EXPERIMENTAL

Samples of 10mm×10mm×10mm were cut from Mg metal or Mg metal foam (Mg, Mg-5% foam, Mg-10% foam, Mg-20% foam). The samples were used as working electrodes (anode), while a Pt plate was used as the counter electrode (cathode). Mg foam samples were prepared by melt foaming process. Prior to the electrochemical experiments, the samples were polished with alumina powder of 0.05 mm size, rinsed with distilled water, cleaned in ethanol in an ultrasonic bath and dried under an air pressure stream. Electrochemical measurements were performed on Zahner IM6 electrochemical workstation with a three-electrode system comprising the as-cleaned magnesium alloy slice as working electrode with an exposed geometric area of $6cm^2$, a platinum wire as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode.

The MgO coatings on Mg samples were produced by anodic electrodeposition in 10 M KOH alkaline solution at constant potential of 1.0V (SCE) for 2 h, and subsequent annealing treatment at 450 ^{o}C for 8 h in air. All treated samples are ultrasonically cleaned in deionized water and dried before further characterization.

In order to evaluate the corrosion protection behaviors, electrochemical measurements and immersion tests were carried out in a 0.9 % NaCl isotonic solution. Immersion tests were carried out in accordance with ASTMG31-72 [9] (the ratio of surface area to solution volume was 100 ml). The pH value of the solution was recorded during the immersion tests (Thermo Fisher Scientific pH meter, Orion). Samples were removed after 1 days of immersion, rinsed with distilled water and dried at room temperature. Potentiodynamic polarization curves were acquired at a scanning rate of 10 mV/s in 100 ml 0.9% NaCl isotonic solution. For the microstructural characterization of the samples Keyence VH-Z250R optical microscope was used.

3. RESULTS AND DISCUSSION

Prior to anodic electrodeposition, a linear potential sweep was carried out to check the anodic oxidation process of magnesium alloy in an alkaline solution. Fig. 1 shows the anodic polarization curve of the Mg and Mg-foams electrodes in 10 M KOH solution at a scan rate of 10 mV s−1. As could be observed, the anodic oxidation curve in 10M KOH solution shows that the Mg foams experienced four processes, which are active dissolution, passivation, secondary oxidation and transpassive processes, which is in good agreement with [8]. The first step was ascribed to the anodic dissolution of magnesium leading to the formation of Mg^{2+} [9[, [10]:

$$Mg \rightarrow Mg^{2+} + 2e^{-}$$

Therefore, when the potential applied was more positive than the open circuit potential (Eocp), the Mg and Mg foams behaved active dissolution and the anodic oxidation product of magnesium is Mg^{2+}. When the concentration of Mg^{2+} on the electrode surface reached its saturation, deposited $Mg(OH)_2$ was formed on the electrode surface, which thickened with anodization time and progressively hindered the oxidation rate, and thus magnesium became passivated. Accordingly, the reaction for the anodic oxidation of magnesium in the passive region was the direct oxidation of magnesium to magnesium hydroxide, in which the hydroxyl passed through the film from solution to the surface of magnesium:

$$Mg + 2OH^{-} \rightarrow Mg(OH)_2 + 2e^{-}$$

The oxidation of magnesium in the secondary oxidation region is confirmed to form MgO [21].

$$Mg + H_2O \rightarrow MgO + 2H^{+} + 2e^{-}$$

The trans-passive process was ascribed to oxygen evolution, which was confirmed by the observation of a large amount of bubbles on the Mg electrode surface. Consequently, when potential was controlled at oxidation region in 10M KOH solution for anodic oxidation of Mg and Mg foams, the formation of MgO coating was anticipated, on the other hand when the potential was controlled in passivation region, $Mg(OH)_2$ coating was produced, which could be converted into MgO by following calcination treatment in air at 450 °C, 8h [9], [21]. The corrosion resistance of the oxidized samples (MgO coating modified Mg and Mg foams) was determined in 0.9 % NaCl isotonic solution using potentiodynamic polarization tests as shown in Fig. 1. The corrosion potential (E_{corr}) and corrosion current density (j_{corr}) were derived directly from the polarization curves by Tafel region extrapolation (Tab. 1). In general, the cathodic polarization curve is attributed to hydrogen evolution reaction, due to the reduction of water, while the anodic polarization curve is associated with the dissolution of Mg, leading to the formation of Mg^{2+} [21], [22-24].

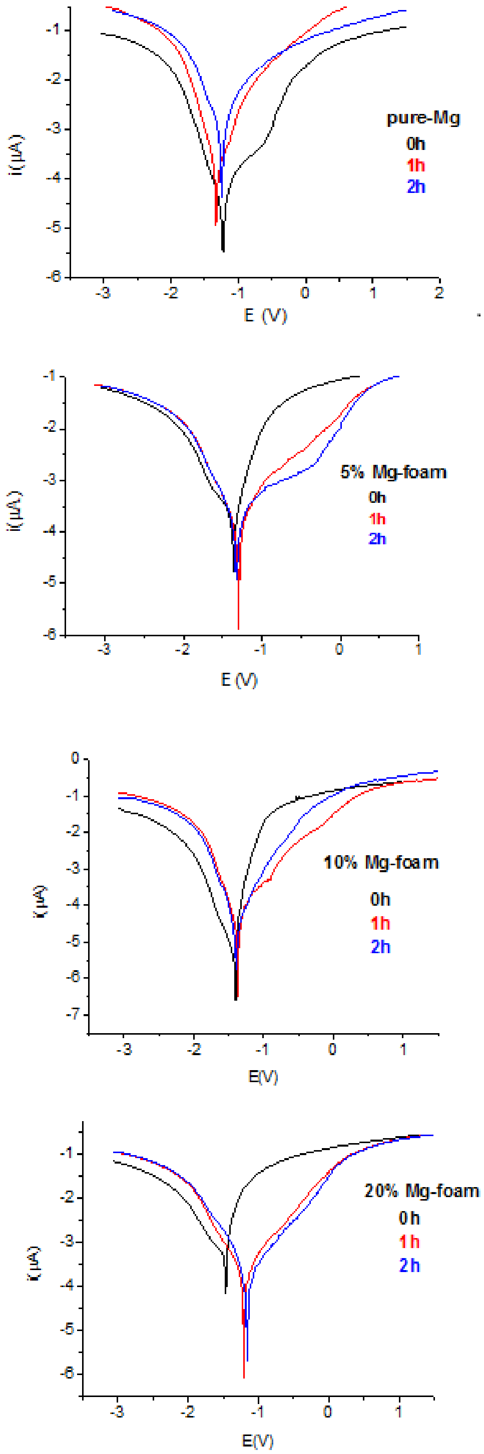

Figure 1. Potenciodynamic polarization curves of the pure Mg, 5% Mg-foam, 10% Mg-foam ad 20% Mg-foam samples in 0.9% NaCl solution.

Analysis of the polarization curves pointed out that the MgO-coated 20% Mg foam reveal weaker corrosion susceptibility than MgO-coated pure Mg, 5% Mg foam and 10% Mg foams and also compared to Mg based alloys too [20].

Table. 1: Corrosion parameters of pure-Mg and Mg foams modified by MgO coatings in 0.9% NaCl solution.

Samples	time (h)	E_{corr} (V)	j_{corr} ($\mu A/cm^2$)
pure-Mg	0	-1.24	1.62
	1	-1.16	1.19
	2	-1.32	1.15
5% Mg-foam	0	-1.63	1.34
	1	-1.22	1.67
	2	-1.24	1.76
10% Mg-foam	0	-1.66	1.54
	1	-1.36	1.51
	2	-1.38	1.27
20% Mg-foam	0	-1.8	1.09
	1	-1.03	1.33
	2	-1.1	1.4

Moreover, the pure-Mg with MgO coatings exhibits a corrosion potential at -1.24 V(SCE), the 20% Mg foam sample with MgO coatings shows a corrosion potential at -1.8 V(SCE), which is negatively shifted about 560 mV(SCE). Additionally, in the case of 20% Mg foam the corrosion potential after 2h was changed significantly, while in the case of pure-Mg almost the same demonstrating once again the higher corrosion tendency of this samples compared to the coated ones. Based on the polarization test results one can claim that MgO coating film could provide an adequate protection to the magnesium alloys in 0.9% NaCl corrosive mediums. Immersion behavior of MgO-coated Mg and Mg foams in 0.9% NaCl shows the variation of the pH value from 8.8 to 10.6 before and after immersion test respectively. When the bare pure-Mg and Mg foams substrate is immersed in NaCl solution, loose and porous $Mg(OH)_2$ formed quickly on samples surface. With increasing anodic potential during polarization, corrosive (Cl-) would be rapidly transferred trough the outer porous layer and reached the inner Mg matrix, which then resulted increasing polarization current. At the same time, thy chloride ions can transform $Mg(OH)_2$ to more soluble $MgCl_2$. Therefore, the pure-Mg showed rapid corrosion rate than the 20% Mg foam. In the case of 20% Mg foam the precipitation product, as ion, was less than the pure-Mg. Fig. 2 reports the surface morphology of the MgO coated samples before and after immersion test in 0.9% NaCl. The evolution of the microstructure confirm the highest corrosion tendency of the pure and MgO coated Mg sample (Fig.2a, b) compared to the MgO coated foam samples (Fig.2c-d).

). The surface, which does not present a compact protective oxide layer will undergo quickly to a localized corrosion attack.

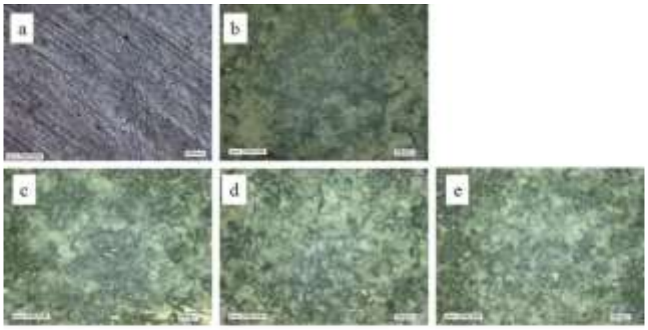

Figure 2. Surface morphology of the MgO coated samples: a) pure-Mg before and (b), (c), (d) after immersion test in 0.9% NaCl solution of 5% Mg-foam, 10% Mg-foam ad 20% Mg-foam respectively.

4. CONCLUSIONS

In this paper, MgO coatings were prepared on pure magnesium and magnesium foams surfaces by a low cost anodic electrodeposition process. The deposition was carried out in concentrated 10M KOH solution followed by heat treatment in air. The corrosion behavior of the MgO-coated samples was evaluated by electrochemical measurements and immersion tests in 0.9 % NaCl solution. The research carried out revealed that the MgO-coated Mg foams present higher stability and lower corrosion rate, leading to improve the corrosion resistance of such samples, while the un-modified Mg foams suffered from harshly localized corrosion attack. Additionally, the oxide layer protected Mg foam samples can be used as loading system for encapsulation of some medicine, which can be locally released contributing to the healing of the bone and eventually of the adjacent tissues.

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