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Corrosion Protective Conversion Coatings on Magnesium Disks Using a Hydrothermal Technique

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A uniform, compact, and well adherent conversion coating of magnesium hydroxide has been formed on bioresorbable magnesium disks by means of a hydrothermal technique. Electrochemical results indicate that the coating brings about a significant reduction in magnesium corrosion in phosphate buffered saline (PBS) solution. It is also observed that corrosion resistance of the coating increases with an increase in treatment time, which in turn, increases the coating thickness. The protective behavior of magnesium hydroxide coating is attributed to its chemical inertness in PBS solution. The coatings are found to be free from pores that reduce the direct contact between corroding media and underlying magnesium.

KEY WORDS: Magnesium; Polarization; Electrochemical impedance spectroscopy (EIS); Scanning electron microscopy (SEM); Conversion coating; Corrosion

1. Introduction

Magnesium (Mg) and its alloys have attracted considerable research interest for biomedical and automobile applications because of their promising properties such as biocompatibility, low density, high specific strength, castability, and appropriate hardness[1−6]. However, the high corrosion rate of Mg severely limits its usage in almost all of these applications[7,8]. Therefore, in order to utilize Mg in these applications, the corrosion rate of Mg needs to be slowed down[9,10]. An effective way to reduce the corrosion rate of Mg and its alloys is surface modification[7,11,12]. Surface modification includes anodic oxidation[13], metal coating[14], chemical conversion coating[15], plasma electrolytic oxidation[16], and organic coating[17]. The surface modification by chemical conversion coating is widely used because of its easier operation, effectiveness, and lower cost[18]. Among the chemical conversion coatings, chromate conversion coating is one of the most effective and popular conversion coating to reduce the corrosion rate of Mg[19]. However, the use of chromate coating is being progressively restricted due to the high toxicity of the hexavalent chromium compounds; hence it is necessary to develop environment friendly replacements for chromate conversion coatings[11,20].

Different types of conversion coating such as phosphate[21], phosphate/permanganate[22], fluoride[23], stannate[24], phytic acid[25], rare earth element based conversion coatings[26,27] have been emerging as an alternative to chromate conversion coating to reduce the corrosion rate of the Mg and its alloys. Cui et al.[28] used neodymium-based conversion coating on Mg alloy as a substitute for toxic chromate conversion coating. They observed that post treatment of the phytic acid coating improves the corrosion resistance of the Mg alloy. Recently, we have also reported that post heat treatment of phytic acid conversion coated Mg shows improved corrosion resistance compared to non-heat treated phytic acid conversion coated Mg[29]. Cerium based conversion coatings have been used to decrease the corrosion rate of AZ31 magnesium alloy[30]. The effect of varying Ca^{2+} and PO_4^{3-} concentrations on the formation of calcium phosphate conversion coatings on Mg alloy was studied[31]. It was observed that low PO_4^{3-} concentration improves the corrosion resistance of Mg alloy.

Recently, Ishizaki et al.[32] used magnesium hydroxide/magnesium phosphate compound composite coating for corrosion protection of Mg alloy by a combination process of chemical conversion and steam curing. It was found that the corrosion current density for the coated sample decreased by more than four orders of magnitude as compared to uncoated sample. Zhu et al.[33,34] used hydrothermal technique to deposit a protective coating on the Mg alloy. They observed that the conversion coating fabricated using the hydrothermal method gives efficient

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corrosion protective layer on the Mg alloys. Guo et al.[35] fabricated zinc−aluminum layered double hydroxide bilayer films on aluminum substrates by one-step hydrothermal crystallization method. The advantage of the hydrothermal technique is that the coatings are uniform, compact, and have strong adhesion to substrates and thus, can effectively protect substrates from corrosion. As the hydrothermal crystallization occurs on a 3-dimensional structure, this method can also be used to coat 3-dimensional objects[33].

In the present work, a hydrothermal technique was used to obtain a corrosion protective conversion coating of magnesium hydroxide ($Mg(OH)_2$) on the surface of Mg disks. The idea of $Mg(OH)_2$ coating stems from the fact that if the Mg implant surfaces are already coated with $Mg(OH)_2$, Mg will not react with the fluid in the body and the release of Mg ions and thereby evolution of hydrogen will not take place. The structural and corrosion properties of the hydrothermally coated Mg disks and uncoated Mg disk (control) were studied. The results indicate that the hydrothermally coated Mg disks are corrosion protective compared to uncoated Mg disk which is due to low porosity of the coatings.

2. Experimental

Mg disks for the hydrothermal treatment were prepared by cutting Mg (99.9%, Good Fellow, Germany) rod (13 mm in diameter) with a thickness of ~1.5 mm. Each Mg disk was polished with SiC paper successively up to #1200 grit, followed by ultrasonic cleaning in acetone and isopropyl alcohol for 5 min, respectively. A hydrothermal technique was applied for conversion coatings on Mg disks using deionized water. The deionized water was poured into a hydrothermal reaction vessel, which was made of Teflon lined stainless steel, and filled upto 75% volume of reaction vessel. The Mg disk was kept in the reaction vessel and heated to 160 °C in a furnace. The hydrothermal treatment was carried out for 1, 3, 5, and 7 h. Hereafter, sample 1 represents uncoated Mg disk (control) whereas sample 2, 3, 4, and 5 represent hydrothermal coated Mg disks in deionized water for 1, 3, 5, and 7 h, respectively.

The structural characterizations were performed by X-ray diffraction (XRD) technique. The XRD spectra of the uncoated Mg disk and hydrothermally coated Mg disks were recorded with Bruker AXS (D8 Discover) X-ray diffractometer using the $2\theta-\theta$ scan with Cu$K\alpha$ ($\lambda = 0.15405$ nm) radiation. The microstructures of the samples were recorded before and after corrosion process by scanning electron microscopy (SEM, SU8000, Hitachi). The degradation rate of the uncoated and coated Mg disks was studied using hydrogen release rate. For this study, the disks were immersed and kept in the phosphate buffered saline (PBS) solution (137 mmol/L NaCl, 2.7 mmol/L KCl, 8 mmol/L Na_2HPO_4, and 2 mmol/L KH_2PO_4) and kept in the solution for 2 weeks at 37 °C in a water bath. Hydrogen gas released due to the corrosion of samples was collected into a burette. The reading of total volume of evolved hydrogen gas was recorded at regular time interval.

DC potentiodynamic polarization measurements were performed in 1× PBS solution using Gamry Potentiostat (R600, Gamry Instruments) with a standard three-electrode configuration. A saturated calomel electrode (SCE) and platinum wire were used as the reference and counter electrodes, respectively. Uncoated Mg disk and coated Mg disks were used as working electrode. The polarization measurements were carried out in the applied potential range of ±300 mV vs. SCE, at a scan rate of 5 mV/s. Corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were determined using the Echem Analyst software (Gamry Instruments). The electrochemical impedance spectroscopy (EIS) study was performed in the frequency range of $1-10^6$ Hz under 10 mV amplitude of the perturbation signal.

3. Results and Discussion

3.1. X-ray diffraction study

X-ray diffraction patterns for the uncoated Mg disk and hydrothermally treated Mg disks are shown in Fig. 1. As seen in Fig. 1, the observed diffraction patterns of the Mg disk showed polycrystalline nature. All the observed peak positions of the Mg disk were found to be in good agreement with the hexagonal phase of Mg (JCPDS file No. 035-0821). Besides the typical peaks corresponding to Mg, some other diffraction peaks were also observed in the hydrothermally treated Mg samples. The presence of other diffraction peaks in the XRD patterns of hydrothermal treated Mg samples indicates the existence of other phases. The extra diffraction peaks other than those arising from Mg plate were observed to be due to the formation of $Mg(OH)_2$ during the hydrothermal treatment of the Mg disks. The formation of $Mg(OH)_2$ on the surface of Mg disks during the hydrothermal reaction can be explained on the basis of following reactions:

$$H_2O(l) \rightarrow H^+(aq) + OH^-(aq) \quad (1)$$

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \quad (2)$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad (3)$$

$$Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s) \quad (4)$$

The observed extra peaks in the hydrothermally treated Mg samples were in good correlation with the hexagonal phase of $Mg(OH)_2$ (JCPDS file No. 075-1527). It is also evident from the XRD patterns that the intensity of magnesium hydroxide's

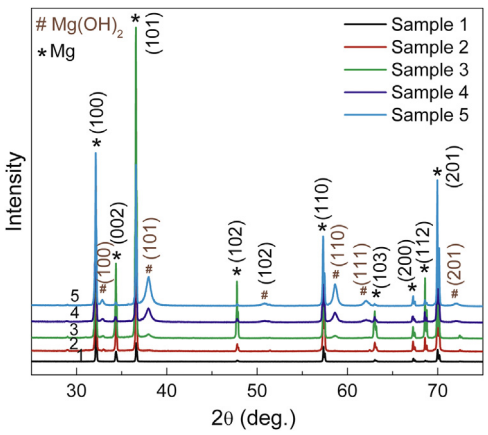

Fig. 1 XRD patterns of uncoated Mg disk (control) and hydrothermally coated Mg disks.