Effects of cerium ion implantation on the corrosion behavior of magnesium in different biological media

Hao Wu, Guosong Wu, Paul K. Chu *

Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

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Cerium ion implantation is conducted to modify the surface properties of magnesium. Electrochemical polarization and immersion tests show that the corrosion resistance of the Mg samples is improved in artificial hand sweat, Ringer's solution, and complete cell culture medium (cDMEM) after Ce ion implantation with the most significant improvement observed from cDMEM. The retardation effect is attributed to the formation of a robust cerium-rich oxide layer formed by energetic ion bombardment and implantation.

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1. Introduction

Magnesium and its alloys are considered revolutionary metallic materials in biomedical applications due to their natural degradability in the physiological environment. However, the degradation rate of most common magnesium-based materials is too high to meet clinical requirements [1]. Problems arising from fast degradation of magnesium include hydrogen evolution and inflammatory response [2,3] and it is thus crucial to control the corrosion rate of magnesium and magnesium alloys.

Ion implantation is an effective technique to modify the surface of metals by providing the possibility to energetically inject different elements with specific fluences into pre-designed depths into the host materials [4,5]. In recent years, metal ion implantation has been employed to improve the corrosion resistance and biological functions of Mg and Mg alloys [6–8]. However, the high reactivity of magnesium makes it difficult to retard the corrosion rate because many implanted metallic elements such as Cr and Ti can cause severe galvanic corrosion. To achieve better corrosion resistance, additional treatment such as oxygen ion implantation [9,10] has been applied after metal ion implantation. Obviously, it will be more convenient if ion implantation of a single element is sufficient to deliver the desirable corrosion-resistant performance.

Cerium is the most abundant rare earth element with an abundance similar to that of copper. Because of its high affinity to oxygen and sulfur, cerium has been incorporated into a myriad of aluminum and iron alloys [11]. Wang et al. [12,13] performed Ce ion implantation into magnesium alloys and observed improved oxidation resistance in oxygen as well as enhanced corrosion resistance in a 3.5 wt.% NaCl solution. Nonetheless, there have been few studies on the effects of Ce ion implantation on the corrosion behavior of magnesium alloys in the physiological environment. In this work, cerium ion implantation is conducted using a MEVVA source to modify pure magnesium and the electrochemical corrosion behavior is investigated in three different biological solutions: artificial hand sweat, Ringer’s solution, and complete cell culture medium (cDMEM).

2. Experimental details

The specimens with dimensions of 10 mm × 10 mm × 5 mm were cut from a piece of commercial pure magnesium. They were mechanically polished with SiC paper up to # 4000, ultrasonically cleaned in ethanol, and dried prior to ion implantation. Ion implantation was carried out on the HEMII-80 ion-implanter equipped with a metal vapor vacuum arc (MEVVA) source in the Plasma Laboratory at City University of Hong Kong. Cerium was the cathodic target in the implantation process and the implantation process was conducted at 20 kV for 2 h at a pressure of 1 × 10⁻³ Pa.

X-ray photoelectron spectroscopy (XPS, PHI 5802, Physical Electronics, Inc., USA) with Al Kα irradiation was performed to obtain the elemental depth profiles. The sputtering rate was estimated to be 16 nm/min based on a reference standard and the binding energies were referenced to the Au 4f line at 84.0 eV. Atomic force microscopy (AFM, Auto Probe CP, Park Scientific Instruments, USA) was conducted to examine the surface topography before and after ion implantation.

The corrosion behavior of the untreated and implanted samples was evaluated in artificial hand sweat, Ringer’s solution, and complete cell culture medium (cDMEM, Dulbecco Modified Eagle Medium, Gibco) at 37 °C. The artificial hand sweat was prepared with 0.5% NaCl, 0.1% lactic acid, 0.5% glucose, and 0.5% 

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* Corresponding author.
E-mail address: paul.chu@cityu.edu.hk (P.K. Chu).

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acid, and 0.1% urea with a pH adjusted to 6.5 with ammonia [14]. Ringer’s solution was prepared from the following reagent grade chemicals: 154 mM NaCl, 5.8 mM KCl, 2.4 mM NaHCO3, and 2.2 mM CaCl2 [15]. The complete cell culture medium (cDMEM) was prepared by Dulbecco’s Modified Eagle Medium (DMEM, Gibco, Life Technologies, USA) and 10% fetal bovine serum (FBS, Gibco, Life Technologies, USA) at 37 °C [16]. Electrochemical potentiodynamic polarization was conducted on a Zahner electrochemical workstation to evaluate the corrosion resistance. The three-electrode technique was adopted with the potential referenced to a saturated calomel electrode (SCE) and the counter electrode being a platinum sheet. Polarization was performed at a scanning rate of 1 mV s⁻¹ from −250 mV in the cathodic direction to +500 mV in the anodic direction relative to the open circuit potentials (OCPs). The corrosion potential (Ecorr) and corrosion current density were estimated.

Fig. 1. AFM images of: (a) Pure magnesium and (b) Ce ion implanted magnesium.

Fig. 2. XPS depth profiles: (a) Pure magnesium and (b) Ce ion implanted magnesium samples; high-resolution XPS spectra acquired at different sputtering times, with the numbers denoting the sputtering time: (c) Pure magnesium and (d and e) Ce ion implanted magnesium.
were calculated according to the Tafel extrapolation method. In addition, immersion tests were carried out to evaluate the corrosion resistance in the three solutions and scanning electron microscopy (SEM) was performed to examine the surface morphology afterwards.

3. Result and discussion

The AFM images of the untreated and Ce ion implanted Mg samples are depicted in Fig. 1. The untreated sample has a relatively rough morphology with many bud-like protrusions (Fig. 1a) but the surface becomes smoother after Ce ion implantation (Fig. 1b). It has been observed that the corrosion rate increases with larger surface roughness [17,18] and so a smoother surface is expected to give rise to better corrosion resistance.

The XPS elemental depth profiles are exhibited in Fig. 2. After ion implantation for 2 h, the Ce implanted layer is about 70 nm thick showing a typical Gaussian distribution. In both the untreated and ion implanted Mg samples, the O concentration decreases gradually with sputtering time indicating natural surface oxidation. Specifically, the oxygen-rich layer on the Ce ion implanted Mg sample is about 96 nm thick compared to 80 nm on the untreated Mg sample. This may be due to the enhanced affinity of Ce to oxygen. The high resolution XPS spectra of the untreated and ion implanted samples are displayed in Fig. 2(c) and (d). In the pure magnesium sample, the Mg 2p peak shifts from the oxidized state to metallic state with sputtering time and a similar peak shift can be observed from the Mg 2p spectra of the Ce ion implantation sample. The cerium 3d photoelectron can be assigned to the 3d_{3/2} spin orbit state (ranging from 890 – 910 eV) and 3d_{5/2} spin orbit state (ranging from 880 – 890 eV) [19,20]. As shown in Fig. 2(e), both the Ce 3d_{3/2} and Ce 3d_{5/2} spectra show the oxidized state in the outer layer and shift to metallic state with depth, indicating that a film composed of cerium oxide and magnesium oxide is formed on the surface after Ce ion implantation.

The corrosion behavior of the untreated and ion implanted samples in different physiological media is evaluated by potentiodynamic polarization and the polarization curves are presented in Fig. 3. In the polarization curve, the anodic branch describes dissolution of the sample at an elevated potential and the cathodic branch represents hydrogen evolution from the reduction reaction [21]. As shown in Fig. 3, the polarization curves shift towards higher potentials and exhibit smaller current densities after Ce ion implantation in all three solutions. The corrosion potential (E_{corr}), corrosion current density (I_{corr}), and Tafel slope (β_c) are calculated by Tafel extrapolation from the linear cathodic polarization region and the results are shown in Table 1. In corrosion analysis, the corrosion current density is one of the most important parameters which can be used to determine the corrosion rate. As shown in Table 1, the corrosion currents decrease in artificial hand sweat (from 106.1 ± 9.4 to 39.9 ± 3.4 μA/cm²), Ringer’s solution (from 41.8 ± 8.9 to 26.8 ± 4.3 μA/cm²), and cDMEM (from 20.4 ± 3.4 to 5.2 ± 1.4 μA/cm²) after Ce ion implantation. The polarization results indicate that the Ce-implanted sample has better corrosion resistance.

Different psychological environments with various pH values and chloride ion concentrations can affect the corrosion rates of magnesium. According to the larger I_{corr} values of both the untreated and implanted samples, the artificial hand sweat is more corrosive to magnesium than the other two solutions. In spite of its slightly lower chloride ion concentration, the more corrosive nature of artificial hand sweat may

<table>
<thead>
<tr>
<th>Solution</th>
<th>Sample</th>
<th>E_{corr} (V)</th>
<th>I_{corr} (μA/cm²)</th>
<th>β_c (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artifical hand</td>
<td>Mg</td>
<td>−1.878 ± 0.001</td>
<td>106.1 ± 9.4</td>
<td>401 ± 33</td>
</tr>
<tr>
<td>sweat</td>
<td>Ce ion implanted</td>
<td>−1.789 ± 0.017</td>
<td>39.9 ± 3.4</td>
<td>301 ± 25</td>
</tr>
<tr>
<td></td>
<td>Ce ion implanted</td>
<td>−1.748 ± 0.051</td>
<td>41.8 ± 8.9</td>
<td>333 ± 7</td>
</tr>
<tr>
<td>Ringer’s solution</td>
<td>Mg</td>
<td>−1.514 ± 0.056</td>
<td>26.8 ± 4.3</td>
<td>319 ± 8</td>
</tr>
<tr>
<td></td>
<td>Ce ion implanted</td>
<td>−1.532 ± 0.027</td>
<td>5.2 ± 1.4</td>
<td>309 ± 39</td>
</tr>
<tr>
<td>cDMEM solution</td>
<td>Mg</td>
<td>−1.731 ± 0.030</td>
<td>20.4 ± 3.4</td>
<td>342 ± 36</td>
</tr>
<tr>
<td></td>
<td>Ce ion implanted</td>
<td>−1.552 ± 0.027</td>
<td>5.2 ± 1.4</td>
<td>309 ± 39</td>
</tr>
</tbody>
</table>
derive from the presence of lactic acid which can lower the pH of the solution, expedite the cathodic hydrogen reaction, and increase the corrosion rate [22]. H⁺ in the solution can also cause damage and dissolution of the generated corrosion products to accelerate corrosion. In Ringer’s solution, the sodium chloride concentration is 0.9% and weakly alkaline. However, HCO₃⁻ in the solution may contribute to the production of H⁺ to facilitate degradation of the corrosion product layer leading to further corrosion. In contrast, cDMEM consists of 10% serum and a considerable amount of protein. The serum protein can absorb onto the materials and act as a corrosion inhibitor [23] thereby making cDMEM less corrosive than Ringer’s solution. In artificial hand sweat, Ringer’s solution, and cDMEM solution, the reduction in the corrosion current densities after Ce ion implantation are 62.3%, 35.9%, and 74.5%, respectively, supplying strong evidence that Ce ion implantation can mitigate surface corrosion in different types of biological media and pH conditions.

The SEM micrographs of the untreated and Ce ion implanted Mg samples after immersion in the solutions for 12 h in Fig. 4 show different surface morphologies. As shown in Fig. 4(a), after immersion in artificial hand sweat, severe cracks with a web-like morphology are observed from the untreated sample but only a few pits and small cracks are observed from the Ce ion implanted samples, indicating that the corrosion damage is much less after Ce ion implantation. Fig. 4(c) reveals cracks and block-like corrosion product on the untreated sample after immersion in Ringer’s solution. In contrast, no cracks and only some particle-like corrosion products are present on the Ce ion implanted sample after immersion (Fig. 4d). Similar results are observed after immersion in cDMEM (Fig. 4e and f). With regard to the pure Mg samples after immersion, cracks are formed due to quick localized corrosion and dehydration of the corrosion product indicative of a high corrosion rate and poor corrosion resistance [24,25]. Our results provide clear evidence that Ce ion implantation improves the corrosion resistance of Mg under different physiological conditions.

4. Conclusion

Ce ion implantation is conducted to modify pure magnesium and electrochemical polarization and immersion tests are conducted in artificial hand sweat, Ringer’s solution, and complete cell culture medium (cDMEM) to investigate the corrosion resistance in different biological media. The formation of a cerium-rich surface oxide layer plays an important role in mitigating surface corrosion in these aggressive media. Our results provide evidence that Ce ion implantation improves the corrosion resistance of Mg in all the tested physiological media with different acidity and alkalinity.

Acknowledgments

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