Influence of Tris in simulated body fluid on degradation behavior of pure magnesium

Yunchang Xin a,∗, Paul K. Chu b

a School of Materials Science and Engineering, Chongqing University, Chongqing 400030, China
b Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China

Article history:
Received 4 November 2009
Received in revised form 5 January 2010
Accepted 8 July 2010

Keywords:
Biomedical magnesium alloys
Degradation behavior
Simulated body fluids
Tris-hydroxymethyl-aminomethane

Abstract

In current paper, influence of tris-hydroxymethyl-aminomethane (tris) in simulated body fluid (SBF) on degradation behavior of pure magnesium is investigated using electrochemical tests as well as degradation measurement. Our results shows that tris mainly affects earlier degradation behavior of pure magnesium alloy. Tris and HCl used in preparation of SBF will form Tris–HCl which only lowers corrosion potential of magnesium slightly but accelerates degradation rates of pure magnesium by tens times. Consumption of OH− generated during magnesium dissolution by Tris–HCl progressively promotes transformation from Mg to Mg2+, which is the main reason for quite high degradation rate of pure magnesium in SBF. Pure magnesium is also more sensitive to pitting corrosion due to inclusion of Tris–HCl in SBF. This study deepens the understanding on degradation mechanism of biomedical magnesium alloys.

1. Introduction

The biodegradability of magnesium and its alloys in physiological environment make them desirable biodegradable biomaterials especially in loading bearing applications. Good biocompatibility has been demonstrated by many in vivo and in vitro experiments [1−4]. Unfortunately, the inherent poor corrosion resistance of magnesium-based implants and attack by aggressive components in body fluids give rise to fast degradation rates and hence, the materials can lose mechanical integrity before tissues have sufficient time to heal [2,5]. Many in vitro experiments have been conducted in simulated body fluid (SBF) to understand the degradation process and corresponding mechanism of biomedical magnesium alloys in physiological environment [6−13]. SBF was first proposed by Kokubo and widely utilized to evaluate the bioactivity or bone conductivity of biomedical implants in vitro [14]. The concentrations of inorganic ions in SBF mimic those in the human plasma. Thus, SBF is often adopted as a simulated physiological system to study the degradation behavior of biomedical magnesium alloys. Our recent studies find that magnesium alloys exhibit dramatically different degradation performance in solutions in SBF and Hank’s solution [5,12]. There are similar concentrations of inorganic ions in SBF and Hank’s solution. Tris is often used in preparation of SBF while not present in Hank’s solution. Thus, the difference in degradation behavior probably stems from the inclusion of Tris in SBF. It is crucial to determine the exact influence and corresponding mechanism of Tris–HCl in SBF on the degradation behavior of biomedical alloys.

The work described here focuses on the influence and corresponding mechanism of Tris in SBF on the corrosion behavior of pure magnesium and deepens the understanding on the degradation mechanism of biomedical magnesium alloys.

2. Experimental details

Commercially available pure magnesium was cut into 10 mm × 10 mm × 4 mm specimens which were ground with #4000 water proof diamond paper followed by polishing and ultrasonic cleaning in alcohol.

Three test solutions were prepared by dissolving reagent grade chemicals in doubly distilled water and finally buffered at a pH of around 7.42. The detailed procedures to prepare SBF (solution #1) refer to Ref. [14]. In solution #2, the concentrations of inorganic ions equals to those in solution #1 while absence of Tris–HCl. This allowed us to study the influence of Tris–HCl on the degradation behavior of magnesium. The pH value of solution #2 was finally adjusted to around 7.42 using HCl and NaOH. In addition, another test solution, solution #3, was prepared as the control. In solution #3, the same amount of tris used in preparation of solution #1 was dissolved in doubly distilled water and buffered at a pH of about 7.42 using HCl. The degradation behavior in solution #3 could further confirm the influence by Tris–HCl. The ion concentrations in the three test solutions are listed in Table 1.

Electrochemical tests in the three test solutions were carried out using a three electrode cell with the sample serving as the working electrode, calomel electrode as the reference electrode, and platinum sheet as the counter electrode. Potentiodynamic polarization tests were performed at a scanning rate 2 mV s−1. When the sample was soaked in the test solution, drastic corrosion will take place on the specimen. Therefore, potential scanning commenced right after the sample was exposed to the test solution. Open circuit potential was recorded per 5 s for a total time of 10 ks. All electrochemical tests were performed at ambient temperature 37 ± 0.5 °C.
3. Results and discussion

Potentiodynamic polarization curves in the three test solutions are shown in Fig. 1. Pure magnesium exhibits the most negative corrosion potential (−1.983 V) in solution #1. The corrosion potential determined from solution #2 (−1.932 V) is about 50 mV more positive than that from solution #1. It can be noted that corrosion potential observed from solution #3 is about 200 mV positive than that determined from solution #1. These results show that Tris–HCl only lowers the corrosion potential of pure magnesium slightly.

Open circuit potentials as a function of exposure duration in the three test solutions are shown in Fig. 2. Initially, the corrosion potential determined from solution #2 increases quickly followed by gradual enhancement of the corrosion potential from about 0.75 ks. In the early stage, the corrosion potential obtained from solution #1 moves to the positive direction quickly and from about 0.7 ks, the corrosion potential increases gradually and smoothly. It is observed that sharp drops (denoted by arrows) in the corrosion potential appear subsequently and the corrosion potential is enhanced gradually and smoothly again, suggesting that the corrosion pits are self-limited. The above results imply that Tris–HCl in the SBF raises the local pH, thereby promoting precipitation of the corrosion products. Formation of the corrosion products decreases the fresh surface area and suppresses further corrosion of the substrate leading to enhanced corrosion potentials. Corrosion potential in solution #3 does not enhanced obviously throughout the test duration, which probably implies that it is difficult to form effective protective corrosion products layer on the surface. During preparation of the solution #1 and solution #3, the used Tris and HCl will form Tris–HCl as illustrated in reaction (2). The generated OH− in reaction (1) can be quickly consumed by the bonded H+ in Tris–HCl, thereby suppressing precipitation of the corrosion products. Hence, in solution #3, the corrosion potential does not increase obviously even after exposure for a long time. It is known that the hydroxides will precipitate on the surface in the SBF can also react with OH− and protective corrosion products such as insoluble phosphates and carbonates will precipitate on the surface [17]. Therefore, the corrosion potentials determined from solution #1 and solution #2 are enhanced with prolonged immersion duration.

Fig. 3 presents the degradation rates of pure magnesium in the three test solutions as a function of immersion time. The degradation rates observed from all three test solutions are nearly stable. However, the corrosion rates obtained from solution #3 still drop gradually after immersion for 24 h. The degradation rate determined from solution #1 is about 30 times higher than that from solution #2 during the first 2 h. With longer exposure time, the gap between degradation rates in solution #1 and solution #2 gets smaller. At the end measurement, the degradation rates in the two test solutions do not increase obviously even after 10 ks immersion. As seen from reaction (1), magnesium dissolution will generate OH− which raises the local pH, thereby promoting precipitation of the corrosion products. Formation of the corrosion products decreases the fresh surface area and suppresses further corrosion of the substrate leading to enhanced corrosion potentials.

Table 1

<table>
<thead>
<tr>
<th>Ion concentration in the three test solutions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mmolL−1)</td>
</tr>
<tr>
<td>#1</td>
</tr>
<tr>
<td>#2</td>
</tr>
<tr>
<td>#3</td>
</tr>
</tbody>
</table>

![Fig. 1](image1.png)

**Fig. 1.** Potentiodynamic polarization curves obtained from magnesium immersed in the three test solutions (Ecorr: corrosion potential).

![Fig. 2](image2.png)

**Fig. 2.** Open circuit potential evolution of magnesium as a function of exposure duration in the three test solutions.
Phosphates and carbonates [17]. This is the reason why the degradation of protective corrosion products including magnesium/calcium phosphates in solution #1 also react with OH$^-$ significantly. However, the pH values in solution #2 are all higher than those in solution #1. The results reveal the much higher buffering capability of solution #1 compared to that of solution #2. Although hydrocarbonates and hydrophosphates ions in solution #1 and solution #2 are both buffers, the comparison of pH value in solutions #1 and solution #2 disclose the much higher buffering capability of Tris–HCl in solution #1 than that of hydrocarbonates and hydrophosphates in solution #1. The degradation in solution #3 are many times higher than these in solution #2 before 12 h, while the pH values in solution #3 are similar to those in solution #2. This result also confirms the good buffering capability of Tris–HCl. It also tells us that the progressively enhanced degradation rate in solution #1 compared to that in solution #2 mainly stem from the consumption of OH$^-$ by Tris–HCl.

4. Conclusion

To conclude, Tris–HCl in SBF lowers the corrosion potential of pure magnesium slightly, while enhance degradation rates of pure magnesium by teens times during earlier stage exposure. Tris–HCl can quickly consume the generated OH$^-$ during magnesium dissolution progressively accelerating the transformation from Mg to Mg$^{2+}$. The presence of Tris–HCl in SBF also induces more sensitive pitting corrosion behavior on pure magnesium. The good buffering capability of SBF is mainly ascribed to the inclusion of Tris–HCl. It is also found that tris mainly affects earlier degradation behavior of pure magnesium alloy.

Acknowledgements

The authors acknowledge the support from Hong Kong Research Grants Council (RGC) General Research Funds (GRF) No. CityU 112307. This project is also supported by Natural Science Foundation Project of CQ, CSTC 2010BB4053.

References


Fig. 3. Degradation rates of pure magnesium as function of exposure duration in the three test solutions.

Fig. 4. pH values in the three test solutions with immersed magnesium as a function of immersion time; inset is the pH values in the four test solutions during the first 4 h.