The Preparation and Corrosion Performance of Self-Assembled Monolayers of Stearic Acid and MgO Layer on Pure Magnesium

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Self-assembled monolayers (SAMs) of stearic acid (SA) film were developed on pure magnesium with heat-pretreatment in order to improve both the corrosion resistance and the bioactivity of pure magnesium. A new method using a high concentration of SA solution (10⁻¹ mol/L) is proposed to reduce the process time of the conventional SAMs methods. The effect of ultrasonic cleaning treatment on SAMs was investigated. Contact angle measurements were employed to evaluate the hydrophobic properties of the SAMs. The corrosion resistance and the bioactivity of the specimens were evaluated under biological conditions (simulated body fluid, 37°C) using potentiodynamic polarization method and long term immersion test. Surface morphology, composition and structure analysis of samples were characterized by the scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS) and attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) after immersion test. The results showed the corrosion resistance of pure Mg was improved by stearic acid-SAMs and the MgO layer made by heat-pretreatment, the SAMs made in high concentration (10⁻¹ mol/L) of stearic acid solution just for 1.5 h showed better properties than conventional SAMs. Furthermore, ultrasonic cleaning treatment led to the formation of more dense and orderly SAMs and improved the anticorrosion property of SAMs prepared in high concentration of SA solution. Moreover, SAMs-Mg had better bioactivity than untreated magnesium. [doi:10.2320/matertrans.M2014117]

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1. Introduction

In recent years, the use of magnesium and its alloys as degradable implant biomaterials has caused great interest because of their excellent biocompatibility and similar mechanical properties to human bones.¹⁻³ However, the high reactivity and poor corrosion resistance of Mg and its alloys in chloride-containing biological environment have limited their practical applications in orthopedics and more efforts are needed to control their corrosion process in order to keep their mechanical integrity before the tissue has healed sufficiently.¹⁻⁶ Besides, although the biocompatibility of magnesium alloys is good, their bioactivity needs to be improved for promoting the early tissue healing.⁷⁻⁹ For these problems, surface modification/coatings is supposed to be one of the most effective approaches of both controlling magnesium degradation and endowing them with other functional properties including bioactivity. Extensive investigations have been focused on this field.⁷⁻¹² Among them, SAMs is a promising way to improve the anticorrosion and the bioactivity of magnesium in one process. It is well known that one of the characteristics of the bioactivity of a metallic implant for bone reconstruction is its apatite-forming ability in simulated body fluid, and it has been demonstrated that SAMs are able to induce the deposition of apatite on the metal substrate.¹³⁻¹⁷ In the supersaturated Ca-P solution, the end-group of SAMs reacts with inorganic ion, which induces the heterogeneous nucleation of hydroxyapatite and the apatite can grow up subsequently. SAMs used in this field are mainly thiols, silanes, carboxylic acids and organic-phosphate,¹³⁻¹⁸ and researches on metal are basically limited to the matrix of Au and Ti.

Regarding to the corrosion protection, most of the studies about aliphatic acid-SAMs have been done on Ag,²⁰ Fe,²¹⁻²³ Cu,²⁰ and Al¹⁹,²⁰ and their oxides in early days. Recently, a few studies have been reported about the application of SAMs to improve the corrosion properties of Mg alloys.²⁴⁻²⁸ Most of these researches are focused on carboxylic and phosphonic acids SAMs, especially aliphatic acid-SAMs²⁵⁻²⁸ as they are environmental friendly and can be assembled on the metallic oxide directly, unlike the thiolate-SAMs which just have strong bonding with noble metal. Ishizaki²⁶ prepared alkanolic and phosphonic acids derived SAMs on AZ31 magnesium alloy by vapor-phase method, and Szillies²⁷ studied the adsorption and orientation of carboxylic and phosphonic acids SAMs with different aliphatic chain lengths. These two papers reported phosphonic acids SAMs show better anticorrosion than carboxylic acids SAMs. Nge²⁸ prepared the stearic acid film having good bonding force on hydroxide magnesium formed by hydrothermal treatment. Salman²⁹ built oleic and stearic acid SAMs with various solvents on AZ31 Mg alloy, and SAMs of oleic acid in ethanol solution obtained the best anti-corrosion property. Actually, there are just few studies about these thin monolayers on magnesium at present, moreover, the research of improving both their anticorrosive and bioactive properties are not yet optimized. In this paper, the stearic acid (SA) with 18 carbons was selected to form SAMs on surface of pure Mg because of the better properties of the long carbon chain SAMs.²⁵ And as the conventional SAMs methods always treat samples in low concentration (10⁻³, 10⁻⁴ mol/L) organic solution for tens of hours, a new method using high concentration of 10⁻¹ mol/L SA solution is proposed to reduce the process time. And the interesting
effects of ultrasonic cleaning treatment on SAMs were also investigated. The effectiveness of this method is evaluated in terms of corrosion behavior and bioactivity.

2. Experiments

2.1 Preparation of stearic acid SAMs on Mg substrate

4N-magnesium (99.99% pure) samples with size of 20 m × 10 m × 5 mm were polished with SiC paper up to 1000 grit, and ultrasonically cleaned for 10 min in ethanol and distilled water respectively. The samples were heat-treated at 773 K for 10 h in air to form an MgO layer on their surface, so that the substrate can be combined with the molecule of SA.

Three different solutions containing $5 \times 10^{-1}$, $5 \times 10^{-3}$ and $5 \times 10^{-4}$ mol/L SA/ethanol were used to form SAMs for different immersion time (1.5 h, 24 h, 48 h). These parameters were selected according to other studies of the author.29

2.2 Effect of ultrasonic cleaning

After the SAMs treatment, specimens were ultrasonically cleaned in pure ethanol for 2 min to study the effect of ultrasonic cleaning (UC).

2.3 Contact angle measurement

The water contact angles of samples with SAMs forming time 1.5 h, 5 h, 10 h, 15 h, 20 h, 24 h, 48 h were measured in air to analyze the film formation process using a Contact Angle Meter (Future Digital Sicetic Ascia Inc) with 5 parallel samples.

2.4 Potentiodynamic scan tests

The potentiodynamic scan tests were carried out using a LKII98B electrochemical workstation (Tianjin Lanlike chemical and electron high technology Co., LTD.) in naturally aerated simulated body fluid solution (SBF, Table 1) at 37°C. A typical three electrode system was used, which consists of platinum working as a counter electrode, saturated calomel electrode (SCE) as a reference electrode and samples (exposed area < 1 cm²) as a working electrode. The potential was scanned at a rate of 1 mV/s.

Table 1 Concentration of the ions in SBF.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>142.0</td>
</tr>
<tr>
<td>Na⁺</td>
<td>5.0</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.5</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2.5</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>147.8</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>4.2</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>1.0</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>0.5</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td></td>
</tr>
</tbody>
</table>

2.5 Immersing in SBF

SAMs-samples which showed the best corrosion resistance prepared in each concentration of SA solutions were soaked in SBF at 37 ± 0.2°C for 30 days, with the SBF volume to sample area ratio of 1 mL/10 mm². The pH variation of SBF was monitored by pH meter (PHS-3C, Bei Jing weixin yiao Science and Technology Development Co., LTD.). SEM and EDS (Amray-X2000, 20 kV, XL30-TMP, 20 kV) were used to observe surface composition and morphology of the samples, and the sample immersed in SBF for 30 days was examined by ATR-FTIR (Perkin-Elmer, Spectrum GX) to compare with the samples before immersion.

3. Results and Discussion

3.1 Contact angle

The results that contact angles (Fig. 1, Fig. 2) showed a significantly increase after the SAMs treatment for all the specimens might be related to a hydrophobic SA-SAMs formed on the Mg substrate coated with MgO film. The highest value of the contact angle was obtained on the SAMs made in $5 \times 10^{-1}$ mol/L SA/ethanol solution for 1.5 h with ultrasonic cleaning treatment, which indicates that under these parameters the SAMs have a good coverage on the surface of Mg.

The contact angles plotted as a function of assembly time is shown in Fig. 2. The assembly time had an obvious effect on the contact angles on SAMs made in $5 \times 10^{-3}$ and $5 \times 10^{-4}$ mol/L SA solution for 1.5 h with ultrasonic cleaning treatment, which indicates that under these parameters the SAMs have a good coverage on the surface of Mg.

The contact angles plotted as a function of assembly time is shown in Fig. 2. The assembly time had an obvious effect on the contact angles on SAMs made in $5 \times 10^{-3}$ and $5 \times 10^{-4}$ mol/L SA solution in the first 20 and 24 h respectively, and the effect got less after that, while in those low concentration of SA solution, around 20 h of assembly time of ASMs was needed. However, the effect on SAMs made in $5 \times 10^{-1}$ mol/L SA were relatively smaller, assembly time which was longer than 1.5 h won’t improve the hydrophobicity of SAMs. We speculate that the film
The ultrasonic cleaning treatment increased the contact angles on SAMs made in $10^{-1}$ mol/L SA, while the contact angles on SAMs made in $10^{-3}$ and $10^{-4}$ mol/L SA solution decreased after ultrasonic cleaning, as shown in Fig. 3. The fact that the contact angles on SAMs increased after ultrasonic cleaning implies that the monolayer are more densely and orderly packed. The chemical reaction between head-group of molecule and substrate causes molecules to occupy active sites of substrate in the process of forming the SAMs. It can be inferred that the ultrasonic cleaning treatment can remove the molecules connecting with the substrate by physical absorption, then the other molecules can take active site more sufficiently, and more orderly fill up the vacancy after physical absorbed molecules were removed, the hydrophobicity was degraded consequently by the ultrasonic cleaning.

### 3.2 Potentiodynamic scan measurement

The results of polarization curve are exhibited in Table 2. The corrosion current density of samples decreased after the oxide layer and SAMs formed on pure Mg. From the results of Table 2, the corrosion current density of heat-treated Mg was nearly $1/2$ of untreated Mg, owing to the fact that a thickness of 15 µm dense MgO layer was formed (Fig. 4). And the corrosion resistance of pure Mg was further improved by the SAMs. As assembly time of SAMs increased, the current density of samples treated in $10^{-1}$ and $10^{-3}$ mol/L SA solution decreased, while the current density of samples treated in $10^{-4}$ mol/L solution increased. The ultrasonic cleaning treatment has reverse effect on the current density of samples made in high and low concentration of SA solution, which is similar to its effect on contact angles; it reduced corrosion current density of samples treated in $10^{-1}$ mol/L SA, however, increased corrosion current density of samples treated in $10^{-3}$ and $10^{-4}$ mol/L solution. The sample treated in $5 \times 10^{-4}$ mol/L for 1.5 h with ultrasonic cleaning presented the lowest current density, i.e., 17.2 µA/cm², which approximately equaled to $1/6$ of the current density of untreated-Mg (111.9 µA/cm²), and showed the best corrosion resistance. From the polarization curves of samples (Fig. 5), the self-corrosion potential of SAMs-Mg rose indicating that SAMs increase the anodic polarization and restrain the anodic corrosion process.
Corrosion inhibition efficiency of SAMs can be calculated by following formula which can be used to evaluate the effect of corrosion resistance of SAMs:31)

\[ \eta = \left( \frac{I_{corr}}{C_0} - \frac{I_{corr}}{C_0}^{0} \right) \]

where \( I_{corr} \) and \( I_{corr}^{0} \) indicate the current density of samples with and without SAMs.

Corrosion inhibition efficiency of samples treated in 5 \( \times \) 10\(^{-1}\) mol/L solution for 1.5 h with ultrasonic cleaning was 84.6%, corresponding to the lowest current density.

In our experiments, SA-SAMs absorb well on Mg substrate. On one hand, this absorption changes the structure of electric double layer and increases the active energy of corrosion. On the other hand, chain-alkyl group of SAMs is arranged orderly, forming a hydrophobic protective layer, hindering the spread of substances related to corrosion reactions, which reduce the corrosion speed of magnesium.

3.3 Immersing in SBF

3.3.1 The pH value of SBF

Figure 6 shows the evolution of pH as a function of immersion time in SBF at 37°C. All the specimens showed an increase of the pH with time, which is associated with the cathodic reaction in the corrosion process because of the formation of OH\(^-\), and high pH values suggest high corrosion rate of the specimens.

In concordance with the electrochemical results, the heat-treatment obviously decreased the corrosion rate of pure Mg and SAMs further reduced the corrosion rate. The specimens treated for 1.5 h in 5 \( \times \) 10\(^{-1}\) mol/L solution with ultrasonic cleaning showed the least value after 7 days of immersion, which indicates the best anti-corrosion performance, better than that of SAMs-Mg treated with low SA concentration. While, the highest value of the pH is found for the untreated magnesium.

3.3.2 Surface morphology

Figure 7 illustrates the surface morphology of samples after immersing different time in SBF at 37°C. After immersing in SBF for 3 days, on the surface of untreated-Mg (Fig. 7(a1)), corrosion pits with different diameters and shallow reticular cracks were distributed, and white particles were non-uniformly scattered. Compared with the untreated-Mg, reticular cracks that formed by heat pretreatment and some white hemispheres were regularly distributed on the
surface of SAMs-Mg (which were treated in 10^{-1} mol/L SA solution for 1.5 h with ultrasonic cleaning), and pits were not found yet (Fig. 7(b1)). According to Fig. 7(a3), 30 days later, wide cracks and deep pits formed on the surface of untreated-Mg, however, the surface of SAMs-Mg was covered with white precipitates, and there were no deep pits and wide corrosion cracks on it. In a word, SAMs-Mg showed more uniform and slower corrosion performance (Fig. 7(b3)).

### 3.3.3 Composition analysis

Table 3 shows the surface composition of samples after immersed in SBF for 30 days. The elements detected on the surface were the same as all the specimens with and without SAMs. However, their amount depended on the treatment. The element contents of weight percentage of P, Ca were much higher and Ca/P ratio was closer to HA on SAMs-Mg than those of untreated-Mg, especially within the first 15 days. Element content of P, Ca increased to 15 and 24% (mass%) respectively and Mg decreased to 3% on SAMs-Mg after the samples were immersed in SBF for 15 days, which indicates that the P-Ca deposition-layer has formed on surface of SAMs-Mg, and the coverings were also clear from Fig. 3(b2). Therefore, SAMs-Mg show better bioactivity than untreated-Mg during immersing in SBF.

### 3.3.4 ATR-FTIR

The ATR-FTIR spectrums of SAMs-Mg before and after being immersed in SBF for 30 days are showed in Fig. 8.
Compared with the spectrum of sample before immersion, for the sample after immersion test, the anisomorous absorption peaks of PO$_4^{3-}$ at 1141 and 990 cm$^{-1}$ were attributed to the Ca-P deposition, and some characteristic absorption peaks of SA-SAMs still existed after immersed for 30d, such as the C-H vibration peaks of SA at 3014 and 721 cm$^{-1}$ and the carboxylic acid (C=O) vibration peaks of SA at 1695 cm$^{-1}$, which showed that SA-SAMs still on the samples. For all spectrums, the C-O vibration peaks at 1557, 1445 cm$^{-1}$ (SAM-Mg) and 1457, 1576 cm$^{-1}$ (SAM-Mg(SBF30d)) and O-H vibration peaks took great change compared with SA, which indicates that SA-SAMs assemble on the substrate by ionic links between $\text{-COO}^-$ and Mg$^{2+}$, and then hydrophobic alkyl ($\text{-CH}_3$) is the end group of SA-SAMs.

Our immersion test indicates that SAMs-Mg have better bioactivity than untreated-Mg. While some researches report that the Ca-P deposition can be induced by the group of $\text{-COOH}$ rather than $\text{-CH}_3$. How can SA-SAMs improve the bioactivity of the samples? It can be speculated that SA-SAMs enhance the corrosion resistance of Mg, therefore hinder the release of Mg$^{2+}$, consequently reduce the negative effect of Mg$^{2+}$ on the deposition of Ca-P and improve the bioactivity of the samples. Since some reports suggest that the influence of Mg$^{2+}$ on Ca-P depends on the ratio of Ca/Mg$^{2+}$ is beneficial for Ca-P nucleation at low concentration, but blocks the growing up of Ca-P at high concentration.

### 4. Conclusions

1. Hydrophobic SAMs of stearic acid were successfully prepared on pure magnesium covering with MgO, and this SAMs of stearic acid and MgO layer effectively improved the corrosion resistance of pure Mg.

2. The preparation method of SAMs by dipping samples in high concentration (10$^{-1}$ mol/L) of stearic acid solution just for 1.5 h and with ultrasonic cleaning treatment showed better properties than conventional SAMs method, and the anti-corrosion efficiency is 84.6%.

3. The ultrasonic cleaning treatment led to the formation of a more densely and orderly SAMs.

4. All samples with SAMs showed a faster deposition of Ca-P layer with similar Ca/P ratio to HA compared with the untreated Mg, and they presented better bioactivity.

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### REFERENCES


