In vitro corrosion degradation behaviour of Mg–Ca alloy in the presence of albumin

C.L. Liu a,b,*, Y.J. Wang c, R.C. Zeng a, X.M. Zhang a, W.J. Huang a, P.K. Chu b,***

a School of Materials Science and Engineering, Chongqing University of Technology, Chongqing 400050, China
b Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
c School of Applied Science and Technology, Chongqing Institute of Technology, Chongqing 400050, China

Abstract

The in vitro degradation behaviour of Mg–Ca alloy was studied in the presence of albumin by in-situ observation, hydrogen evolution method and various electrochemical techniques. The corrosion and hydrogen evolution rates decreased and the formation of filiform corrosion induced by Cl− was also significantly inhibited due to the adsorption of albumin molecule. Moreover, the higher the concentration of albumin, the higher is the inhibitive effect. The EIS results further show that addition of albumin significantly improved the charge transfer resistance and film resistance at the open-circuit potential. The synergistic effect of the negatively charged adsorbed albumin molecule and OH− has been discussed.

Article history:
Received 25 March 2010
Accepted 4 June 2010
Available online 15 June 2010

Keywords:
A. Magnesium
B. EIS
C. Corrosion
C. Passive films

1. Introduction

Magnesium alloys produced with a minimal amount of impurities by new casting techniques have better properties than many currently approved and commonly used inert metallic biomaterials. As an essential element in the human body, magnesium degrades spontaneously in body fluids via corrosion to remove the stress shielding effect and avoid repeated surgeries [1–3]. In order to apply magnesium alloys with moderate degradation characteristics to biomedical implants, it is important to evaluate their degradability and to understand the degradation mechanisms. In this respect, Mg–Al [4], Mg–RE [5], Mg–Ca [6], Mg–Mn–Zn [7], Mg–Zn [8] and pure Mg [9,10] have been investigated and in vivo and in vitro corrosion tests have been performed.

In vivo studies have been performed in small animals such as rats (subcutaneously), guinea pigs, and rabbits [11]. In vitro corrosion and/or electrochemical tests have been predominantly carried out in simulated body fluids such as 0.9 wt.% NaCl aqueous solution, phosphate buffered solution (PBS, pH 7.4), Hank’s solution, simulated body fluids (SBF) [12–14]. Witte et al. have explored the in vivo degradation of AZ91D, and LAE42 rods in the femur of guinea pigs. Their results show that the in vivo corrosion rates of AZ91D and LAE442 after 18 weeks of implantation obtained are approximately 3.516 × 10−4 mm/yr and 1.205 × 10−4 mm/yr through the SRμCT analysis, respectively, which are about four orders of magnitude smaller than those achieved form in vitro tests in simulated fluids [3]. Similar results have also been obtained from Mg–Ca and Mg–Mn–Zn alloys [6,7]. It has been mentioned that the absence of organic ingredients such as proteins and amino acids may be one reason for the variation in the corrosion rates between in vitro and in vivo corrosion tests [5,6,15].

The influence of albumin or serum proteins on the corrosion rates of magnesium alloys has been studied under different experimental conditions. Yamamoto and Hiromoto [12] have investigated the corrosion rate of pure magnesium in NaCl, E-MEM and E-MEM with fetal bovine serum (FBS), and found that the average degradation rate in NaCl aqueous solutions after 8–14 days exposure was about 100 times larger than that in E-MEM + FBS, which was also found by Kirkland [15]. This result is very similar to that in human blood plasma. The decreased corrosion rate is attributed to protein adsorption and precipitation of insoluble salts. Liu [16] has found that addition of 1 g/l albumin in the simulated body solution shifts the open-circuit potentials of AZ91 towards a more positive value. The corrosion resistance under the open-circuit conditions in SBF + 1 g/l albumin (Ab) is approximately twice that in SBF. Rettig [17,18] have investigated the time-dependent electrochemical behaviour of WE43 magnesium alloy in simulated body fluids (m-SBF) with and without 40 g/l albumin. They have observed that albumin may form a blocking layer on the surface during the initial hours of exposure, and the formed corrosion layers consisting of amorphous apatite have only a low protective ability. Although the above results show the inhibitive effect of protein, the interface reaction between magnesium alloy and protein has not been elucidated in detail at the early stage of immersion.
In the present study, three kinds of solution (NaCl, NaCl + albumin and distilled water + albumin) were adopted to measure the corrosion behaviour of Mg–Ca alloy by continuously monitoring the interface reaction at the early stage of immersion. Li [6] has explored the feasibility of Mg–Ca alloys for use as biodegradable materials. However, the reasons for the retarded corrosion rate are not clear. Hence, this work aims to investigate the influence of albumin on the corrosion behaviour of binary Mg–Ca alloy during the early stage of immersion, especially in the first hour. In addition, the synergistic effects of negatively charged albumin, Cl⁻, and OH⁻ ions during the exposure period are evaluated and a mechanism explaining the reduced corrosion rate is proposed.

2. Materials and methods

2.1. Materials and solutions

The extruded Mg–xCa alloy with nominal 1.5 wt.% calcium was machined into 10 mm × 10 mm × 4 mm disks for microstructure characterization, corrosion experiments, and electrochemical tests. The samples used in the corrosion and degradation tests were prepared by the standard technique of grinding with SiC abrasive paper up to 1200 grit, followed by ultrasonic cleaning in acetone, absolute ethanol, and distilled water sequentially.

In order to reduce the influence of other aggressive ions, we chose four different solutions which were distilled water (DW) + bovine serum albumin (Ab), 0.9 wt.% NaCl and 0.9 wt.% NaCl + Ab. The albumin-containing solution had albumin concentrations of 1 and 10 g/l.

2.2. Immersion tests

The volume of emitted hydrogen during immersion is related to the dissolution of magnesium. This technique has the advantage that variations in the degradation rates can be monitored by the hydrogen evolution rates, thereby allowing the study of the degradation rate variation versus exposure time. The samples were soaked in 250 ml solutions for different periods of time at an ambient temperature of 37 ± 1 °C. It has been verified that the dissolved oxygen does not influence the measurement results and so our experiments were carried without aeration. The hydrogen evolution volumes were measured as a function of immersion time [19].

The immersion test was carried out at 37 ± 1 °C. The samples were ground and cleaned prior to the tests. The corrosion morphology of each alloy immersed in the electrolytes in a special electrolytic cell was observed and recorded at 20× magnification on a remote measurement system. The surface morphology of the corroded alloy sample was recorded and studied simultaneously. In situ observation was found to be very important because as soon as the samples were taken out from the solution and exposed to air, the corrosion products turned white and the morphology subsequently changed. During the experiment, the sample was vertically immersed in the solution in the cell with the working surface of the sample parallel to the quartz window on the cell side wall. The digital camera and microscopic head were perpendicular to the outside surface of the window [20]. The morphology was observed and recorded at time points of 3, 10, 30 and 60 min.

2.3. Electrochemical tests

The electrochemical corrosion behaviour was investigated by open-circuit potential evolution and potentiodynamic polarization using an EG&G Instrument Versat™. A three-electrode cell with the sample as the working electrode, saturated calomel electrode as the reference electrode, and platinum electrode as the counter electrode was employed. All the potentiodynamic polarization tests were carried out using a scan rate of 0.1 mV/s. The experiments were conducted at 37 ± 1 °C in triplicate without aeration with fresh solutions and newly polished electrodes. The electrochemical impedance spectra were measured at 37 ± 1 °C from a solution volume of 250 ml. A frequency range from 10 mHz to 10 kHz was selected. Before the impedance measurement, the sample was kept floating at the open-circuit potential (OCP) and for each impedance spectrum, the potential was set to the actual value of the OCP. The disturbing voltage amplitude chosen was 10 mV. The period of one measurement series was 5, 30 and 60 min. The EIS spectra were fitted with the ZSimpWin software.

2.4. Fourier transfer infrared (FTIR) spectroscopy

The structure and compositions of the sample surfaces were determined by Fourier transform infrared spectroscopy (FTIR) after immersion in 10 g/l Ab containing 0.9 wt.% NaCl for different durations of time.

3. Results

Fig. 1 shows the metallographic microstructure of the extruded Mg1.5Ca alloy. The typical α(Mg) primary grains with the Mg2Ca precipitating phase [6] can be observed and the Mg2Ca phase exists along the grain boundaries or in the α(Mg) primary grains. Fig. 2 indicates the open-circuit potential (OCP) measured from Mg1.5Ca alloy in the solutions. The variations of the OCP values were similar during 1 h immersion in the different solutions. The OCP value was very low at the beginning of all experiments. It afterwards shifted rapidly to the positive direction after approximate 500 s of exposure, finally becoming nearly constant indicating establishment of the equilibrium. However, the final OCP values measured from all the solutions were different. In the NaCl aqueous solution, the OCP rose fast to a value of about −1.38 V(SCE) and it was more negative than that in NaCl + 1 g/l Ab or DW + 10 g/l Ab. Comparing the electrolytes NaCl solution with NaCl + 10 g/l Ab solution, the OCP value in the latter was significantly higher than that in the NaCl solution, which was about −1.34 V(SCE) after 1 h immersion. Another interesting phenomenon can be observed from the OCP curves for 0.9 wt.% NaCl and DW + 10 g/l Ab solutions. The increase in the OCP values in both electrolytes was similar during immersion, but it was followed by a slight increase in DW + 10 g/l Ab. In addition, the similar variation and slight increase in the OCP value in NaCl solution including 1 g/l Ab suggest that the lower concentration of albumin in NaCl may play a limited role in inhibiting the corrosion attack of Mg–Ca alloy.

Fig. 1. Optical micrograph of the extruded Mg1.5Ca alloy (500×).
In order to characterize the early corrosion stages of Mg–Ca alloy in all used electrolytes, the corrosion morphology and hydrogen evolution process were monitored in-situ by an optical microscope with a digital camera. Fig. 3 provides selected illustrations from the in-situ observations of the details of the corrosion morphologies for Mg1.5Ca in all used electrolytes. Comparing the electrolytes distilled water and DW + 10 g/l Ab, two main differences can be observed from the corrosion morphologies. One is that addition of albumin resulted in an increase of the amount and density of hydrogen bubbles compared with distilled water at the same exposure time. The other is that corrosion became visible on the surface in the form of pitting corrosion in both solutions. Also visible were a number of vertical streams composed of a larger number of small hydrogen bubbles and subsequently the formation of corrosion pits. It is concluded that addition of albumin in distilled water enhances the corrosion of Mg–Ca alloy. In every case illustrated in Fig. 3c, the diameter of hydrogen bubbles are larger, meaning that Mg1.5Ca sample suffers aggressive corrosion attack in 0.9 wt.% NaCl. It appears that corrosion pits agglomerated into an irregular array from which there was a dramatic hydrogen evolution. In addition, filiform corrosion also appeared. After 1 h immersion, filiform corrosion which developed with hydrogen evolution was concentrated exclusively at the growing tips. At the filiform corrosion area, the evolution of hydrogen may be inhibited by the corrosion products [20]. Comparing the electrolytes 0.9 wt.% NaCl and 0.9 wt.% NaCl + 10 g/l Ab, filiform corrosion may be inhibited by the adsorption of albumin. Also observed was the decrease in the amount and diameter of hydrogen bubbles in the same exposure time. Moreover, the size of the hydrogen bubbles increased very slowly in the same exposure time. Furthermore, when albumin was added to the NaCl solution, hydrogen evolution took place uniformly over the sample surfaces. Otherwise, hydrogen evolution was concentrated at the corroding sites. The results further suggest that albumin affects the corrosion process of Mg–Ca alloy significantly.

The potentiodynamic polarization curves of Mg1.5Ca obtained after open-circuit exposure to different test electrolytes for about 10 min are exhibited in Fig. 4. Generally, the cathodic polarization curves are assumed to represent the cathodic hydrogen evolution through water reduction, while the anodic polarization curves represent the dissolution of magnesium [6,21]. It can be seen that the
Fig. 5. Hydrogen evolution volumes of Mg1.5Ca alloy as a function of immersion time in different electrolytes.

Fig. 6 shows the EIS of Mg1.5Ca alloy immersed in different electrolytes for different time. The plots show three time constants in 0.9 wt.% NaCl with and without albumin, including one high frequency capacitance loop, one medium frequency capacitance loop, and one low frequency inductance loop. The diameter of the high frequency capacitance loop increases in the albumin solution. The influence on the degradation process of Mg1.5Ca in the solution with and without albumin is analyzed based on the EIS results. Three time constants correspond to the characteristics of the electric double layer, surface film, and existence of the metastable Mg$^{2+}$, respectively [21–23]. The plots can be explained by the equivalent circuit shown in Fig. 7. Herein, $R_s$ is the solution resistance, $R_t$ refers to the charge transfer resistance, $C_R$ represents the electric double layer capacity at the interface of the Mg–Ca alloy substrate and electrolyte, and $R_l$ is the film (consisting of the corrosion product and albumin adsorption layer) resistance. The film capacity is described by a constant phase element (CPEf). $CPE_f$ is defined by two values, $Y_0$ and $n$. If $n$ is equal to 1, $CPE_f$ is identical to a capacitor. Often a constant phase element is used in a model in place of a capacitor to compensate for the nonhomogeneity in the system [22,23]. $R_l$ and $L$ indicate the existence of metastable Mg$^{2+}$ during dissolution of the Mg–Ca alloy. The data are fitted using the ZsimpWin 3.20 software and the errors are less than 10%. The fitted results are shown in Table 1. Comparing the EIS in 0.9% NaCl with and without albumin, the existence of albumin caused a gradual decrease in the diameter of the medium frequency capacitance loop and finally it was replaced by an inductance loop. The EIS implies that the film layer formed on the Mg1.5Ca alloy surface were different in 0.9% NaCl with and without albumin, thereby suggesting different influence on the corrosion process of Mg1.5Ca alloy.

4. Discussion

Mg–Ca alloy has been shown to be suitable candidate as orthopedic biodegradable materials [6]. However, the in vitro and in vivo corrosion rates show great differences, and Gu et al. [3,6] have suggested that protein may play a significant role in retarding the corrosion. Our results here showed that addition of albumin into a NaCl solution retarded the corrosion of Mg–Ca alloy, which is similar to Kirkland’s results [15].

The OCP results in Fig. 2 showed similar variations in the different electrolytes, where the initial increase was followed by a relatively steady state. In the presence of 10 g/l albumin in the solution, the OCP value increased gradually with the prolonged immersion, which is different from that in 0.9 wt.% NaCl. The difference can probably be ascribed to the surface being accessible to the formation of corrosion product and adsorption of albumin. Gu et al. have pointed out that when the fresh Mg–Ca alloy surface was exposed to the aqueous solution, the internal second phase (Mg$_2$Ca) acted as an efficient cathode for hydrogen evolution, and anodic dissolution of magnesium occurs. In this process, a magnesium hydroxide film formed on the surface of the Mg–Ca alloy due to significant alkalization near the surface [6]. However, in the presence of Cl$^-$ ions, the Cl$^-$ ions are small enough to displace water molecules in the hydrogen sheath and then Cl$^-$ preferentially combines with Mg$^{2+}$ to transform magnesium hydroxide into...
soluble MgCl₂. Therefore, the variations of the OCP values should be attributed to the dissolution–precipitation process of Mg(OH)₂ film layer in NaCl solution [6,24,25]. In the presence of albumin, at the initial stage of immersion, the OCP values showed little difference before about 600 s immersion, which was probably ascribed to the quick formation of magnesium hydroxide. However, with longer exposure period, the OCP values showed obvious difference in different electrolytes. Addition of 10 g/l albumin into the NaCl solution resulted in a positive shift in the potential. This suggests that albumin might interact with the surface impeding further dissolution–precipitation process of Mg₁.₅Ca controlled by Cl⁻. Similarly, the in-situ observation results at 10, 30, and 60 min in Fig. 3c also indicate that aggressive corrosion took place in 0.9 wt.% NaCl. In comparison, the Mg₁.₅Ca alloy just suffers slight corrosion attack and no filiform corrosion in 0.9 wt.% NaCl + 10 g/l Ab, as shown in Fig. 3d. The potentiodynamic curves in Fig. 4 after 10 min open-circuit immersion also show that the corrosion potential in 0.9 wt.% NaCl + 10 g/l Ab is around −1.35 V(SCE), which is about 140 mV(SCE) higher than that in 0.9 wt.% NaCl. The above results indicate the synergistic effect of NaCl and bovine serum albumin could play a key role in the corrosion process of Mg₁.₅Ca alloy.

It has been reported that the bovine serum albumin molecule mainly consists of amino acid joined by peptide bonds. The basic structure of an amino acid consists of four parts: an amino group (A NH₂), a carboxyl group (A COOH), a central carbon (C) and a side chain. At physiological pH of 7.4, albumin undergoes a neutral–acidic transition and becomes negatively charged (isoelectric pH 4.7–4.9). Divalent cations such as Ca²⁺ or Mg²⁺ can serve as bridging agents to enhance adsorption of albumin molecules through electrostatic interaction [16,26]. In order to examine the adsorption of Ab on the Mg₁.₅Ca alloy surface, FTIR spectra were taken before and after immersion in 0.9 wt.% NaCl + 10 g/l Ab for different time durations and the results are displayed in Fig. 8. The strong amide I (1650 cm⁻¹), amide II (1545 cm⁻¹) and a weak

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Time (min)</th>
<th>Rₛ (Ω cm²)</th>
<th>Cₛ (µF cm⁻²)</th>
<th>Rₓ (Ω cm²)</th>
<th>Y₀ (Ω⁻¹ cm² s⁻¹/²)</th>
<th>n</th>
<th>Rₑ (Ω cm²)</th>
<th>L (mH cm⁻²)</th>
<th>Rₗ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9 wt.% NaCl</td>
<td>5</td>
<td>27.6</td>
<td>131.5</td>
<td>246.1</td>
<td>7.9 × 10⁻⁴</td>
<td></td>
<td>847.2</td>
<td>19.2</td>
<td>1363</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>27.8</td>
<td>142.7</td>
<td>253.5</td>
<td>6.3 × 10⁻⁴</td>
<td></td>
<td>790.6</td>
<td>43.7</td>
<td>1435</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>27.2</td>
<td>161.4</td>
<td>280.1</td>
<td>4.7 × 10⁻⁴</td>
<td></td>
<td>554.1</td>
<td>78.3</td>
<td>1813</td>
</tr>
<tr>
<td>0.9 wt.% NaCl + 10 g/l Ab</td>
<td>5</td>
<td>27.4</td>
<td>168.2</td>
<td>296.3</td>
<td>4.6 × 10⁻⁴</td>
<td></td>
<td>784</td>
<td>23.8</td>
<td>1029</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>27.7</td>
<td>181.5</td>
<td>319.5</td>
<td>3.9 × 10⁻⁴</td>
<td></td>
<td>931</td>
<td>35.4</td>
<td>1083</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>27.6</td>
<td>184.7</td>
<td>330.2</td>
<td>3.6 × 10⁻⁴</td>
<td></td>
<td>1057</td>
<td>60.6</td>
<td>1656</td>
</tr>
</tbody>
</table>

Fig. 6. EIS of Mg₁.₅Ca immersed in different electrolytes for different time: (a) 0.9 wt.% NaCl and (b) 0.9 wt.% NaCl + 10 g/l Ab.

Fig. 7. Equivalent circuit of Mg₁.₅Ca immersed in 0.9 wt.% NaCl with and without 10 g/l Ab for different period.
The corrosion process of Mg–Ca alloy in the aqueous solution includes the following chemical reactions.

\[
\text{Mg(s)} \rightarrow \text{Mg}^{2+} (aq) + 2e^- \quad \text{(anodic reaction)} \tag{1}
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(cathodic reaction)} \tag{2}
\]

\[
\text{Mg}^{2+} (aq) + 2\text{OH}^- (aq) \rightarrow \text{Mg(OH)}_2 (\text{product formation}) \tag{3}
\]

The Mg\(^{2+}\) cations may bridge the negatively charged albumin molecule and Mg–Ca alloy surface. During initial immersion, the collective effect of H\(_2\)O and Cl\(^-\) creates a large amount of Mg\(^{2+}\) [6], which may result in rapid adsorption of albumin. According to hydrodynamic studies, the highly helical molecule of albumin is described as three domains within the shell of a prolate ellipsoid (6–12 nm\(^2\)) or three spheres (diameters of 3.8, 5.3, and 3.8 nm) positioned adjacent to each other. The different shapes arise from the flexibility of the helical molecule allowing rapid expansion and contraction as ligands bind with ions. On the surface, the triangular albumin molecule with equilateral 8 nm sides and a 2.9 nm average thickness transforms to a flattened triangular shape with 13 nm sides and a 1.2 nm average thickness. The albumin with its marked size can easily inhibit the transfer of ions from the solution to the sample surface [28,29]. Therefore, the albumin adsorption layer may inhibit the dissolution of Mg(OH)\(_2\) under the effect of Cl\(^-\), leading to the gradual positive shift in the OCP value in 0.9 wt.% NaCl + 10 g/l Ab.

In order to further explain the \textit{in-situ} observation results, hydrogen evolution measurement was performed. It is known that the degradation rate of magnesium can be measured by the evolved hydrogen volume [19]. For all the electrolytes, the hydrogen evolution volume increased monotonously as a function of immersion time, but if the immersion time approaches infinity, the hydrogen evolution volume becomes a constant value. Fig. 9 shows the variations in the hydrogen evolution volume per square centimeter every hour during 12 h immersion. Comparing the solutions 0.9 wt.% NaCl without and with 10 g/l Ab, the hydrogen evolution rate in 0.9 wt.% NaCl was higher than that in the latter, which indicates some inhibitive factors during the corrosion dissolution of Mg1.5Ca. Based on the chemical reaction (3), the formation of Mg(OH)\(_2\) film is beneficial to the retardation of corrosion. However, the aggressive Cl\(^-\) results in further dissolution of the Mg(OH)\(_2\) film [24]. Therefore, the competitive effect between Cl\(^-\) and OH\(^-\) could lead to the dissolution–precipitation process on the Mg1.5Ca surface. When albumin and NaCl coexist, negatively charged albumin molecule and OH\(^-\) can form a mixed protective layer composed of an albumin adsorption layer and Mg(OH)\(_2\). On the one hand, the albumin layer can easily inhibit the transfer of Cl\(^-\) from the solution to the sample surface [24]. On the other hand, the negatively charged albumin molecule and hydroxyl may inhibit the penetration of Cl\(^-\) from the solution through electrostatic repulsive effects. Therefore, the protective effect from the combination of the albumin adsorption layer and Mg(OH)\(_2\) film may restrain the aggressive effect from Cl\(^-\).

If the albumin molecules absorb onto the sample surface, the interface between the sample and test electrolytes could be changed, which must result in the variation of some electrochemical corrosion parameters [17,18]. Based on the fitted results in Table 1 from the EIS test, the competitive effect between Cl\(^-\) and the protective layer composed of the albumin adsorption layer and Mg(OH)\(_2\) can be investigated better. In 0.9 wt.% NaCl, the \(R_\text{ct}\) value shows smaller increase with immersion. The change was from 246.1 to 280.1 \(\Omega\) cm\(^2\), indicating that the transfer of charge at the interface of the Mg1.5Ca/solution was retarded slightly. It is interesting to note that higher \(R_\text{ct}\) values were measured from 0.9 wt.% NaCl + 10 g/l Ab than 0.9 wt.% NaCl. It may result from the negatively charged albumin molecule, and the adsorption of albumin could increase the integrity of the film layer covering the Mg1.5Ca surface, changing the interfacial behaviour of charge transfer in high frequency range and hinders the diffusion of ions [10,23]. It’s interesting to note that the difference of hydrogen evolution rate was bigger than that of \(R_\text{ct}\) values in both solutions. The reason may be that the \(R_\text{ct}\) values referred to the charge transfer resistance at the interface of sample and test solution at a special potential during immersion time [23], however, the volume of hydrogen evolution is related to the average dissolution rate of magnesium alloy during immersion [19], which is not synchronous with the result of EIS. The increase of \(R_\text{ct}\) value indicates the hard charge transfer process. In addition, the \(R_\text{ct}\) values in 0.9 wt.% NaCl showed greater changes than those in 0.9 wt.% NaCl + 10 g/l Ab after the same immersion period. In 0.9 wt.% NaCl solution, there was gradual decrease in the \(R_\text{ct}\) values and it could be ascribed to the gradual corrosion attack of the original MgO and Mg(OH)\(_2\) by Cl\(^-\). The \textit{in-situ} observation results indicate that the corrosion attack on the Mg1.5Ca alloy becomes greater with increasing immersion time. In contrast, the \(R_\text{ct}\) values of the Mg1.5Ca alloy increased from 784.3 to 1057.4 \(\Omega\) cm\(^2\) and the associated CPE\(_\text{f}\) values decreased only slightly with immersion in 0.9 wt.% NaCl + 10 g/l Ab. This
may be evidence of the improvement in the integrity for the albumin adsorption and Mg(OH)₂ mixed layer covering the Mg₁.₅Ca surface during the exposure period [23,27], and a competition between albumin adsorption molecule, OH⁻, and Cl⁻ for sites on the surface could inhibit the in-leakage of Cl⁻ and its corrosion attack on Mg₁.₅Ca substrate under the layer.

These results demonstrate that albumin can act as an inhibitor in the presence of aggressive Cl⁻ ion. Its adsorption on the Mg₁.₅Ca surface impedes further dissolution of this alloy and increases the resistance by the cooperative effect of the adsorbed albumin layer and Mg(OH)₂. However, until now we have no verification of the reaction process of a protein layer on the sample surface and in future studies, the reaction process must be analyzed in more details.

5. Conclusion

The corrosion degradation behaviour of Mg–Ca alloy was investigated by electrochemical techniques, hydrogen evolution tests, and in-situ observation. Three test electrolytes simulating body fluids: NaCl, DW + Ab and NaCl + Ab were used in this study. The results indicate that the solution chemistry modified the corrosion behaviour on Mg₁.₅Ca at the early stage of immersion. According to the in-situ observation and hydrogen evolution results, Mg₁.₅Ca alloy suffered greater corrosion attack in 0.9 wt.% NaCl than in 0.9 wt.% NaCl + Ab. Albumin acted as a corrosion inhibitor on Mg₁.₅Ca and gave rise to diminished hydrogen evolution rates and cathodic corrosion current densities. Moreover, the higher the concentration of albumin, the greater is the inhibitive effect. The EIS plots show that addition of albumin enhanced the charge transfer resistance and the resistance of the surface film layer at the open-circuit potential. The synergistic effect of the negatively charged adsorbed albumin molecule and OH⁻ appeared to retard further corrosive effect from the aggressive Cl⁻ and to decrease the corrosion rate of Mg₁.₅Ca in solutions including Cl⁻ to some extent.

Acknowledgements

This work was financially supported by Natural Science Foundation Project of Chongqing CSTC (2008BB4062; 2008BB0063; KJ080615) and Hong Kong Research Grants Council (RGC) General Research Fund (GRF) No. CityU 112307. The authors would like to thank Prof. Chen RS for his assistance in MgCa alloy.

References


