Degradation behaviour of pure magnesium in simulated body fluids with different concentrations of HCO$_3^-$

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ABSTRACT

Corrosion behaviour of pure magnesium in simulated body fluids (SBF) with HCO$_3^-$ concentrations of 4, 15 and 27 m mol/L is studied. Magnesium is not sensitive to pitting corrosion in all the SBFs. Higher HCO$_3^-$ concentration effectively slow down the corrosion rates. Uniform and compact corrosion product layer preferentially forms in SBF with HCO$_3^-$ of 27 m mol/L. Potentiodynamic polarization test indicates that HCO$_3^-$ of 27 m mol/L dramatically enhance corrosion potential and induce passivation. EIS results further confirm that higher concentration of HCO$_3^-$ induce more effective protection layer, especially in SBF with HCO$_3^-$ of 27 m mol/L.

The HCO$_3^-$ in SBF can react with OH$^-$ generated during magnesium dissolution, which dramatically promote transformation from Mg to Mg$^{2+}$. On the other hand, the reaction between HCO$_3^-$ and OH$^-$ also results in formation of insoluble carbonates. Precipitation of insoluble carbonates will suppress the dissolution of magnesium and affect subsequent corrosion processes too. Thus, the concentration of HCO$_3^-$ in SBF is suspected to pose great influence on in vitro corrosion performance of biomedical magnesium alloys. Therefore, it is important to carry out systematical investigation to disclose the exact influence and find out the most suitable one for in vitro studies.

In current paper, corrosion performances of pure magnesium in SBFs with HCO$_3^-$ concentrations of 4, 15 and 27 m mol/L, respectively are systematically studied. The exact influence and associated mechanism are disclosed. This study benefits the selection of suitable test solution for in vitro corrosion studies of biomedical magnesium alloys.

2. Experimental details

2.1. Sample preparation

Commercially available pure magnesium was used in current experiments. The as-received materials were cut into blocks with dimensions of 15 × 15 × 3 mm. The samples were ground with 4000# water proof diamond paper and polished followed by ultrasonically cleaning in alcohol.

Three types of SBFs with different concentrations of HCO$_3^-$ (named as SBF-1, SBF-2 and SBF-3, respectively) were prepared.
by dissolving reagent grade chemicals in double distilled water and finally buffered at pH of around 7.42. Ion concentrations in the three SBF were listed in Table 2. Body fluid was a buffering system. The good buffering capability mainly came from HCO\textsubscript{3}/CO\textsubscript{3} (about 27 m mol/L), HPO\textsubscript{4}/CO\textsubscript{3} (about 1 m mol/L) and plasma protein buffers (HPr/Pr/CO\textsubscript{3}, about 17 m mol/L) [17]. The buffering agents in SBF were composed of HPO\textsubscript{4}/CO\textsubscript{3}, HCO\textsubscript{3}/CO\textsubscript{3} and Tris–HCl. There were the same concentrations of HPO\textsubscript{4}/CO\textsubscript{3} in SBF-1, SBF-2 and SBF-3. The three SBFs were prepared with equal concentration of buffering agents, while different contents of HCO\textsubscript{3}/CO\textsubscript{3}, by balancing the concentrations of Tris–HCl and HCO\textsubscript{3}/CO\textsubscript{3} as demonstrated in Table 2.

2.2. Corrosion morphology and corrosion products analysis

The samples after 24 h exposure in SBFs were fully rinsed in double distilled water and dried subsequently. The corroded surfaces were monitored by scanning electron microscopy (SEM, TESCAN VEGA2). Elemental mapping from the corroded surfaces were acquired using energy dispersive X-ray spectrometry (EDS). The phase constituents in the corrosion product layers were determined by X-ray diffraction (XRD, Cu K\textalpha\textalpha irradiation, 40 k V and 30 mA).

2.3. Corrosion rate measurement

As demonstrated in reaction (1), magnesium dissolution was related to evolution of hydrogen. Thus, the dissolved magnesium can be calculated from the volume of generated hydrogen. This method (usually called hydrogen evolution method) was reliable, easy to implement, and not prone to errors inherent to the weight loss method [17]. In addition, the hydrogen evolution method allowed studying the variation of corrosion rates versus exposure time. It had been reported that the dissolved oxygen in test solution does not affect the evolution of hydrogen [17] and therefore, the experiments were carried out without deaeration. Fig. 1 schematically illustrates the hydrogen evolution method. In order to obtain better statistical results, three groups of samples were measured in each test. Three samples were soaked in 200 ml test solution and then put into incubator for 24 h at an ambient temperature 37 ± 0.5°C. The emitted hydrogen volumes were measured as a function of immersion time. Studies demonstrated that the initial corrosion behavior of the Mg-based implant played the most important role in cell response [7]. Therefore, in current study, only corrosion performance during the first 24 h exposure was studied.

3. Results and discussion

3.1. Corrosion morphology and corrosion products

Corrosion morphologies of samples after exposure in different SBFs for 24 h are monitored by SEM and the results are given in

<table>
<thead>
<tr>
<th>Ion concentration (mmol/L)</th>
<th>Na\textsuperscript{+}</th>
<th>K\textsuperscript{+}</th>
<th>Ca\textsuperscript{2+}</th>
<th>Mg\textsuperscript{2+}</th>
<th>HCO\textsubscript{3}</th>
<th>Cl\textsuperscript{−}</th>
<th>HPO\textsubscript{4}/CO\textsubscript{3}</th>
<th>SO\textsubscript{4}/CO\textsubscript{3}</th>
<th>Tris–HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>27.0</td>
<td>103.0</td>
<td>1.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>c-SBF</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>4.2</td>
<td>147.8</td>
<td>1.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>r-SBF</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>27.0</td>
<td>103.0</td>
<td>1.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>m-SBF</td>
<td>142.0</td>
<td>5.0</td>
<td>2.5</td>
<td>1.5</td>
<td>10.0</td>
<td>103.0</td>
<td>1.0</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 2

Ion concentrations in SBF-1, SBF-2 and SBF-3.
Fig. 2. No pitting corrosion is present on all the samples. A number of cracks appear on all the samples as shown in Fig. 2d–f. Generally, these cracks result from water loss in corrosion products by irradiation of electron beam [22]. The shrinkage of surfaces leads to presence of cracks. Non-uniform corrosion is noticeable on samples immersed in SBF-1 and SBF-2. The inhomogeneous structures are more obvious in high magnification views. Peeling of corrosion products seems to take place in denoted regions by the white arrows. Many white irregular areas are observed. Uniform and compact corrosion surface are observed on sample immersed in SBF-3. The above results suggest that pure magnesium is not sensitive to pitting corrosion in all the three SBFs. However, the concentration of HCO$_3$/$CO_3$ up to 27 mmol/L tends to induce more uniform and compact corrosion product layer.

Element mapping of Mg, O, P and Ca on samples exposed in the three test solutions for 24 h are shown in Fig. 3. On sample soaked in SBF-1, oxygen distributes uniformly. The white regions consist of high content P and Ca, while low content of Mg. The peeling-like regions (the grey regions) contain low content of P and Ca, while high content of Mg. This implies that calcium phosphates prefer aggregating at the white regions. There are similar distributions of Mg, O, P and Ca on sample exposed in SBF-2. The homogeneous corrosion morphology on sample immersed in SBF-3 also leads to uniform distribution of Mg, Ca, P and O in corrosion product layer.

XRD measurement is employed to identify the phase constituents in corrosion product layer and the result is present in Fig. 4. Only peaks from magnesium matrix are present in all XRD pattern. The absence of peaks from corrosion products probably implies the amorphous state of corrosion products. As demonstrated in reaction (1), in aqueous solutions, insoluble magnesium oxide and/or hydroxide will forms. The HCO$_3^-$ and HPO$_4^{2-}$ in SBF can react with OH$^-$ generated during magnesium dissolution, which induces precipitation of insoluble carbonates and phosphates in corrosion product layer. The reactions can be described as below:

\[ Mg^{2+} (or \ Ca^{2+}) + OH^- + HPO_4^{2-} + (n - 1)H_2O \rightarrow Mg_n(\ or \ Ca)(PO_4)_y \cdot nH_2O \]  \hspace{1cm} (2)

\[ Mg^{2+} (or \ Ca^{2+}) + OH^- + HCO_3^- + (n - 1)H_2O \rightarrow Mg_n(\ or \ Ca)(CO_3)_y \cdot nH_2O \]  \hspace{1cm} (3)

The presence of insoluble carbonates and phosphates on magnesium alloy exposed in SBF has been reported by many studies [1,13–15,22].

3.2. Corrosion Rates

Corrosion rates of sample as a function of immersion duration are demonstrated in Fig. 5. During the first hour, the corrosion rates in SBF-1 is the highest, 2 times higher than that in SBF-2 and 5 times higher than that in SBF-3, respectively. With prolonged immersion time, the corrosion rates in all the three test solutions drop quickly. Obviously, this can be ascribed to the constant precipitation of corrosion products such as MgO/Mg(OH)$_2$, magnesium/calcium phosphates and carbonates and so on [22]. Formation of corrosion products reduces active regions and suppresses further dissolution of substrate. From 12 to 24 h, the dissolution rate in SBF-3 is quite small (0.0024 mg cm$^{-2}$ h$^{-1}$), while, in SBF-1, the sample still exhibit a rapid corrosion (0.078 mg cm$^{-2}$ h$^{-1}$). As listed in Table 3, the average corrosion rate after 24 h exposure in SBF-1 is about 3 times higher than that in SBF-2, about 10 times higher than that in SBF-3. The as-measured degradation rate of commercial pure magnesium in current study (about 0.02–0.19 mg cm$^{-2}$ h$^{-1}$) is lower than that of commercial pure magnesium in [4], about 1.08 mg cm$^{-2}$ h$^{-1}$. Various factors contribute to the great gap in as-measured degradation rates. It is well known that purity of magnesium dramatically affects the degradation rates. Although the as-used materials are...
both commercial pure magnesium, the purities of as-used materials probably differ greatly with each other due to the supply from different companies. In fact, the as-used test solutions in these two studies are different too, with Hank’s solution in one study and SBF in the other. The high concentrations of hydrocarbontes in electrolytes of current study can greatly suppress the degradation. The inorganic compound of glucose in Hank’s solution may also accelerate degradation. In addition, other experimental parameters as the ratio of sample surface area to electrolyte volume, surface roughness of ground samples may also disturb the measurement. The above results suggest that higher concentration of HCO$_3^-$, especially concentration upto 27 m mol/L, can dramatically slow down corrosion rate of magnesium.

Magnesium dissolution generates OH$^-$ as demonstrated in reaction (1). The buffers in SBF including Tris–HCl, HCO$_3^-$, HPO$_4^{2-}$ can consume OH$^-$ rapidly, which will accelerate the forward reaction in reaction (1). Reaction of Tris–HCl and OH$^-$ dose not induce formation of corrosion products. Unlike Tris–HCl, consumption of OH$^-$ by HCO$_3^-$ also leads to precipitation of insoluble carbonates. The above two effects are balanced by HCO$_3^-$ concentration. In current study, it can be seen that suppress of corrosion is the domi-
nated effect when HCO₃⁻/CO₃ concentration in SBF rises from 4 m mol/L to 15 m mol/L and 27 m mol/L. It is also noted that HCO₃⁻/CO₃ up to 27 m mol/L can induce quite uniform and compact corrosion products layer compared to those in SBF-1 and SBF-2.

3.3. Electrochemical behavior

Polarization curves of samples in different SBFs are shown in Fig. 6. Tafel fitting of polarization curves is carried out. The derived corrosion potential and corrosion current density are listed in Table 4. There are similar corrosion potentials and corrosion current density.

<table>
<thead>
<tr>
<th></th>
<th>E&lt;sub&gt;corr&lt;/sub&gt; (V/SCE)</th>
<th>I&lt;sub&gt;corr&lt;/sub&gt; (A cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBF-1</td>
<td>-1.97</td>
<td>3.0 x 10⁻⁴</td>
</tr>
<tr>
<td>SBF-2</td>
<td>-1.96</td>
<td>3.98 x 10⁻⁴</td>
</tr>
<tr>
<td>SBF-3</td>
<td>-1.71</td>
<td>2.88 x 10⁻⁵</td>
</tr>
</tbody>
</table>

Fig. 6. Potentiodynamic polarization curves of pure magnesium in SBF-1, SBF-2 and SBF-3.

Fig. 7. EIS spectra of pure magnesium as function of immersion time in SBF-1, SBF-2 and SBF-3.
densities in SBF-1 (−1.97 V/Saturated Calomel Electrode, SCE) and SBF-2 (−1.96 V/SCE). However, corrosion potential in SBF-3 (−1.71 V/SCE) is about 0.25 V/SCE positive than those in both SBF-1 and SBF-2. The corrosion current density in SBF-3 is one magnitude lower than those in SBF-1 and SBF-2 too. It is noted that obvious passivation region (as denoted by rectangular) is present in polarization curves of sample in SBF-3. Similar passivation behavior of AZ91 magnesium alloy in solution containing high concentration of hydrocarbonates is observed in [23] too. This passivation behavior of pure magnesium in SBF is closely related with the rapid formation of insoluble carbonates. However, this passivation behavior is highly dependent on the concentration of HCO₃⁻. Obvious passivation behavior only occurs in SBF with a concentration of HCO₃⁻ of 27 m mol/L. The passivation behavior in SBF-3 is suspected to be the main reason for the much lower corrosion rates and formation of compact corrosion product layer on sample in SBF-3.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to study the electrochemical corrosion process on metals. When an excitation signal with small amplitude is applied to the system, the response depends on the electrode controlled kinetics. It usually consists of several different sub-processes including mass transfer, charge transfer and so on. By analyzing these responses, the individual sub-process can be deduced [24]. EIS spectra of samples in the three test solutions as function of immersion time are harvested and shown in Fig. 7. For sample exposed in SBF-3 for 0.5 h, two time constants are observed: one capacitive arc in high frequency region and one capacitive arc in low frequency region. However, before 6 h, the capacitive arc in low frequency region of sample in both SBF-1 and SBF-2 are not obvious. Obvious capacitive arcs in low frequency in both SBF-1 and SBF-2 appear from 6 h. In all the test solutions, both capacitive arcs in high frequency regions and low frequency regions are enlarged with increased exposure duration. The capacitive arc in high frequency generally results from charge transfer, film effects [25]. Usually, the low frequency region in EIS contains important information on the electrode controlled process together with the contribution from localized defects to the overall impedance [24]. The capacitive arc in low frequency is probably attributed to the mass transportation relaxation in solid phase, for example, in the aggregating layer [26].

Considering the physical structure of the electrode system and its impedance response, equivalent circuit (EC) that not only matches the physical structure, but also creates similar spectra as test spectra is proposed and given in Fig. 8, C, one of the constant phase element (CPE) components, represents the capacitance of the corrosion products layer. Rₚ is the relevant resistance named after pore or ionic conducting defect resistance. Cᵦ, another component of CPE, corresponds to the capacitance of the double layer. Rₜ is the charge transfer resistance related to the electrochemical reaction. Rₛ is the solution resistance between the reference electrode and working electrode. Its value is determined by the conductivity of the test medium and the geometry of the cell [24]. Usually, Rₛ is placed in series with other elements of the circuit. The fitting result of EIS spectra is present in Table 5. After 0.5 h immersion, there are quite low Rₛ (105 Ω cm²) as well as Rₚ (28 Ω cm²) in SBF-1, Rₛ (401 Ω cm²) in SBF-2 are much higher than that in SBF-1, while Rₚ (63 Ω cm²) are still quite low. Both Rₛ (1509 Ω cm²) and Rₚ (292 Ω cm²) in SBF-3 are much higher compared to those both in SBF-1 and SBF-2. Higher Rₛ and Rₚ reveal the formation of more compact corrosion product layer on sample surface and higher resistance to magnesium dissolution. After 6 h immersion, the Rₛ in SBF-1 increases to some extent, while there is still no obvious enhancement in Rₛ. This probably implies the formation of partially covered corrosion products layer on sample surface. When the exposure prolongs to 18.5 and 24 h, much more effective protection layer is suspected to form on sample in SBF-1 due to the great increasing in both Rₛ and Rₚ. Higher Rₛ and Rₚ in SBF-2 and SBF-3 dramatically increase with elongated duration. Similarly, Rₛ and Rₚ in SBF-3 are also much higher than that in SBF-2. The values of Rₛ and Rₚ in SBF-2 are also quite higher than that in SBF-1. More rapid enhancement in Rₛ and Rₚ of sample in SBF-3 occurs compared to those in SBF-1 and SBF-2. The above results obviously demonstrate that high concentration of hydrocarbonate can induce more rapid formation of corrosion product and more effective protective layer tends to form in SBF with higher concentration of hydrocarbonates, especially in SBF with 27 m mol/L. Higher values of Rₛ and Rₚ also correspond to lower Cᵦ and Cᵦ respectively in current experiment. Here, m and n are indices of the dispersion effects of Cₛ and Cᵦ, respectively representing their deviations from the ideal capacitance due to the inhomogeneity and roughness of the electrode on the micro scale [24].

![Fig. 8. Equivalent circuit (EC) for analysis of EIS spectra.](image_url)

Table 5
Fitted results of EIS spectra in Fig 7 using EC in Fig 8.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Sample</th>
<th>Cₛ (10⁻⁶ F cm⁻²)</th>
<th>m</th>
<th>Rₛ (Ω cm²)</th>
<th>Cᵦ (10⁻⁴ F cm⁻²)</th>
<th>n</th>
<th>Rₚ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>SBF-1</td>
<td>46.2</td>
<td>0.84</td>
<td>105</td>
<td>8.4</td>
<td>0.69</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>SBF-2</td>
<td>28.2</td>
<td>0.85</td>
<td>401</td>
<td>7.0</td>
<td>0.74</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>SBF-3</td>
<td>7.3</td>
<td>0.72</td>
<td>1509</td>
<td>2.2</td>
<td>0.95</td>
<td>292</td>
</tr>
<tr>
<td>2</td>
<td>SBF-1</td>
<td>45.1</td>
<td>0.84</td>
<td>118</td>
<td>6.9</td>
<td>0.73</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>SBF-2</td>
<td>25.3</td>
<td>0.74</td>
<td>579</td>
<td>7.1</td>
<td>0.98</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>SBF-3</td>
<td>3.5</td>
<td>0.74</td>
<td>2134</td>
<td>1.3</td>
<td>0.99</td>
<td>374</td>
</tr>
<tr>
<td>6</td>
<td>SBF-1</td>
<td>34.7</td>
<td>0.80</td>
<td>265</td>
<td>7.4</td>
<td>0.95</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>SBF-2</td>
<td>22.2</td>
<td>0.73</td>
<td>909</td>
<td>5.6</td>
<td>0.96</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>SBF-3</td>
<td>2.6</td>
<td>0.68</td>
<td>2560</td>
<td>0.91</td>
<td>0.93</td>
<td>510</td>
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<tr>
<td>18</td>
<td>SBF-1</td>
<td>26.1</td>
<td>0.82</td>
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<td>0.85</td>
<td>0.79</td>
<td>495</td>
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<tr>
<td></td>
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<td>3.2</td>
<td>0.75</td>
<td>2125</td>
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<td>SBF-3</td>
<td>1.1</td>
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<td>5160</td>
<td>0.092</td>
<td>0.97</td>
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<td>24</td>
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<td>0.76</td>
<td>494</td>
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<tr>
<td></td>
<td>SBF-2</td>
<td>3.0</td>
<td>0.76</td>
<td>2403</td>
<td>0.65</td>
<td>0.95</td>
<td>636</td>
</tr>
<tr>
<td></td>
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<td>0.82</td>
<td>0.73</td>
<td>6178</td>
<td>0.085</td>
<td>0.99</td>
<td>1661</td>
</tr>
</tbody>
</table>
of m and n are always 0 < m, n < 1. It is obvious that the values of m and n in current experiments are all in this range.

The above results show that the concentration of HCO$_3^-$ in SBF dramatically influences the corrosion behaviour of pure magnesium during the first 24 h exposure. In fact, study has demonstrated that initial corrosion performance of Mg-based implant plays critical role on the cell response [9]. Fast corrosion rate lead to dynamic surface state and suppress the attachment of cell greatly. Hence, acquisition of accurate corrosion performance of magnesium alloy during early exposure duration is of great importance for in vivo experiments and further clinical trials. In fact, surface modification has become an important and necessary pre-treatment of Mg-based implants. Typical surface modification treatments are anodizing and electrochemical deposition of calcium phosphates coatings [4,27,28]. The as-anodized coatings with sealing treatment usually possess good corrosion resistance and excellent bonding strength with substrate [4,27]. Electrochemically deposited biocompatible Ca-phosphate coatings not only benefit suppression of fast degradation, but can also induce precipitation of hydroxyapatite leading to enhanced bone conductivity. These surface modifications can suppress the fast degradation and, therefore, contribute to the cell attachment and maintaining of mechanical integrity of implants. As the buffering agents in SBF can react with OH$^-$ generated during magnesium dissolution and promote dissolution of magnesium, the used SBF should possess similar buffering capability to that of body plasma. From current studies, it can be seen that the concentration of HCO$_3^-$ in different SBFs greatly affects corrosion behaviour of pure magnesium. Body plasma contains HCO$_3^-$ of around 27 m mol/L. Therefore, in corrosion measurement of biomedical magnesium alloys, the usage of SBF with similar HCO$_3^-$ concentration to that of body plasma is crucial to acquire more accurate corrosion performance.

4. Conclusion

In this paper, corrosion behavior of pure magnesium in three types of SBFs with different concentrations of HCO$_3^-$ (4, 15 and 27 m mol/L) is systematically investigated. Pure magnesium is not sensitive to pitting corrosion in all the three SBFs. Higher concentration of HCO$_3^-$ can effective slow down corrosion rate due to promoting precipitation of protective carbonates. HCO$_3^-$ up to 27 m mol/L can dramatically enhance corrosion potential and induce rapid surface passivation behavior. Therefore, in order to acquire more accurate corrosion performance of Mg-based implants, it is suggested to use SBF with HCO$_3^-$ concentration of 27 m mol/L.

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Reference