Corrosion Behavior of Magnesium with Hydroxyapatite Coatings Formed by Hydrothermal Treatment

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Corrosion resistance of magnesium alloys must be improved for their applications to orthopaedic bioabsorbable devices. Since hydroxyapatite (HAp) is chemically stable in the body and is the main component of bones, HAp coatings have been well studied to improve the corrosion resistance and osteoconductivity of magnesium alloys. In this study, highly crystallized HAp coatings were formed on pure magnesium with a single-step hydrothermal treatment using a CaCl2·2H2O·Ca(NO3)2·4H2O solution with various pH values. Morphology of the HAp coating varied depending on the pH value. Corrosion behavior of the HAp-coated magnesium was investigated by anodic polarization, impedance and immersion tests in a simulated body fluid. It was revealed that the corrosion resistance of pure magnesium was improved more than 10 times with the HAp coatings. Stable localized corrosion was prevented with the HAp coatings although the occurrence and moderation of unstable localized corrosion appeared to take place at the defects of the HAp coatings. The initial protectiveness of the HAp coating depended on the treatment condition. During 4-day immersion, the precipitated HAp sealed the defects of the HAp coatings, resulting in the negligible release of magnesium ions regardless of the treatment conditions. [doi:10.2320/matertrans.M2010192]

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1. Introduction

Magnesium alloys are potential bioabsorbable metals for orthopaedic devices such as mini/micro-plate systems because magnesium is one of the essential elements in the human body and their mechanical integrity to bones is high owing to the Young’s modulus equivalent to that of bones.1–6 Degradation of bioabsorbable metals should be arrested until the fractured bone is sufficiently repaired to bear the load. However, the existing magnesium alloys do not show enough corrosion resistance for bone fixation devices.8 Improvement of the corrosion resistance is essential for the promotion of the practical use of magnesium alloys. Surface modification is one of the methods to improve the corrosion resistance.9–19 Especially, coatings with hydroxyapatite (HAp) and its related calcium phosphate compounds attract attention1–19 because HAp is an essential element of bone and the calcium phosphate compounds precipitated from simulated body fluids improved the corrosion resistance of magnesium.9,20–22

A single-step process using aqueous solutions consisting of non-toxic compounds is desirable for the formation of HAp coating from the viewpoint of biocompatibility, production cost and environmental load. However, direct formation of well-crystallized HAp on the surface of magnesium and its alloys in aqueous solutions is thermodynamically difficult. Biomimetic process using a concentrated simulated body fluid was employed; however the crystallinity of HAp precipitated was relatively low.14 To promote the HAp formation, two-step processes with electrodeposition or ion beam deposition methods have been employed.11–13,18 In the two-step processes, either a pre-treatment or a post treatment is necessary. The pre-treatment is carried out to prevent the corrosion of magnesium substrate in the treatment solution. This is because corrosion of magnesium substrates in aqueous solutions with pH less than 11 is inevitable23 and because the released Mg ions prevent HAp crystallization with the substitution of Mg atom for the Ca atom in the HAp structure.24,25 On the other hand, the post treatment such as a heat treatment and an alkali heat treatment is carried out to transform the deposited calcium phosphate compounds to HAp. From the viewpoint of mechanical property of magnesium alloys, the temperature of the heat treatment should be lower than the recrystallization temperature of the alloys.

Recently, Hiromoto et al. succeeded in the single-step formation of highly-crystallized HAp coatings on pure magnesium and AZ series magnesium alloys with a hydrothermal treatment using an aqueous Ca-EDTA solution.26 The developed process enabled to shorten the treatment time and to increase the crystallinity of HAp in the coating comparing with the previously reported processes.11,13,18,19 Moreover, the shape of HAp crystals was varied from plate-like to needle-like with the pH of the treatment solution. Additionally, it was demonstrated that the HAp-coated pure magnesium showed high corrosion resistance under artificial sea environments.26 In this study, corrosion behavior of the HAp-coated pure magnesium treated at various pH values was examined in a simulated body fluid. Influence of the pH of the treatment solution on the corrosion behavior of the HAp-coated pure magnesium was investigated. Anodic polarization and impedance tests of the HAp-coated pure magnesium were carried out using a rotating disk electrode to elucidate the initial corrosion behavior. Immersion test was carried out to examine the corrosion behavior for a rather long time.

2. Materials and Methods

2.1 Formation of HAp coatings on pure magnesium

Disks of 8 mm diameter and 2 mm thickness were cut from a pure magnesium extruded rod. The surface of the disk

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substrates was finished with a 0.1 \mu m-alumina lapping film and rinsed ultrasonically in acetone. A treatment solution was prepared with ethylenediaminetetraacetic acid calcium disodium salt hydrate (C\textsubscript{10}H\textsubscript{12}Ca\textsubscript{2}Na\textsubscript{2}O\textsubscript{8}, aq.; Ca-EDTA), potassium dihydrogenphosphate (KH\textsubscript{2}PO\textsubscript{4}), and sodium hydroxide (NaOH). The concentration of both Ca-EDTA and KH\textsubscript{2}PO\textsubscript{4} was 50 mmol L\textsuperscript{-1}, and the pH was varied from 6.3 to 11.3 by the addition of various volumes of 1 mol L\textsuperscript{-1} NaOH solution. The substrate was immersed in the treatment solution at room temperature and then the temperature was elevated to 368 K and kept for 8 h or 24 h. The change in pH of the bulk solution after the treatment was negligible. The treated specimens were characterized using an X-ray diffraction (XRD) and a scanning electron microscope (SEM). The HAp-coated specimens prepared were listed in Table 1.

### Table 1: Specimen number and treatment conditions.

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Concentration of Ca-EDTA, C\textsubscript{1} (mol L\textsuperscript{-1})</th>
<th>Concentration of KH\textsubscript{2}PO\textsubscript{4}, C\textsubscript{2} (mol L\textsuperscript{-1})</th>
<th>pH</th>
<th>Treatment time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>50</td>
<td>50</td>
<td>6.3</td>
<td>8</td>
</tr>
<tr>
<td>A-2</td>
<td>50</td>
<td>50</td>
<td>7.3</td>
<td>8</td>
</tr>
<tr>
<td>A-3</td>
<td>50</td>
<td>50</td>
<td>11.3</td>
<td>8</td>
</tr>
<tr>
<td>B-1</td>
<td>50</td>
<td>50</td>
<td>6.3</td>
<td>24</td>
</tr>
<tr>
<td>B-2</td>
<td>50</td>
<td>50</td>
<td>7.3</td>
<td>24</td>
</tr>
</tbody>
</table>

#### 2.2 Polarization and impedance tests

Anodic polarization and impedance tests of the HAp-coated specimens (A-1, A-2, A-3 and B-2) and as-polished specimen were carried out in a modified Hanks’ solution (m-Hanks) in which the concentration of chloride ion was adjusted to that of blood plasma because the corrosion of Mg\textsuperscript{2+} ions in the m-Hanks was quantified by a colorimetric method using xylidyl blue-I.\textsuperscript{28,29} Then, the gross amount of Mg\textsuperscript{2+} ions in 150 ml of the m-Hanks after 4 days immersion was calculated. The surface after the immersion was characterized using the XRD and SEM. Cross-sections of the specimens immersed were observed using the SEM equipped with a backscattering electron image detector. Composition of the designated localized area on the cross-sections of the A-1 and A-2 was analyzed using an energy dispersive X-ray spectrometry (EDS).

### Table 2: Composition of the modified Hanks’ solution.

<table>
<thead>
<tr>
<th></th>
<th>Cl\textsuperscript{-}</th>
<th>Ca\textsuperscript{2+}</th>
<th>PO\textsubscript{4}\textsuperscript{2-}</th>
<th>Na\textsuperscript{+}</th>
<th>K\textsuperscript{+}</th>
<th>Mg\textsuperscript{2+}</th>
<th>SO\textsubscript{4}\textsuperscript{2-}</th>
<th>CO\textsubscript{3}\textsuperscript{2-}</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Hanks’ solution</td>
<td>1.0 × 10\textsuperscript{-1}</td>
<td>1.3 × 10\textsuperscript{-3}</td>
<td>7.8 × 10\textsuperscript{-4}</td>
<td>1.0 × 10\textsuperscript{-1}</td>
<td>5.8 × 10\textsuperscript{-3}</td>
<td>8.1 × 10\textsuperscript{-4}</td>
<td>8.1 × 10\textsuperscript{-4}</td>
<td>4.2 × 10\textsuperscript{-3}</td>
<td>8</td>
</tr>
<tr>
<td>Blood plasma</td>
<td>1.0 × 10\textsuperscript{-1}</td>
<td>2.5 × 10\textsuperscript{-3}</td>
<td>1 × 10\textsuperscript{-3}</td>
<td>1.4 × 10\textsuperscript{-1}</td>
<td>5 × 10\textsuperscript{-3}</td>
<td>1.5 × 10\textsuperscript{-3}</td>
<td>5 × 10\textsuperscript{-4}</td>
<td>2.7 × 10\textsuperscript{-2}</td>
<td>7.2–7.4</td>
</tr>
</tbody>
</table>

#### 2.3 Immersion test

The rim of the A-1, A-2 and B-1 was covered with silicone and the surface area of 1 cm\textsuperscript{2} was exposed to the test solution. Two samples from each specimen were used for the immersion test. The specimens were immersed in the m-Hanks of 150 ml at 310 K for 4 days. The concentration of Mg\textsuperscript{2+} ions in the m-Hanks was varied from 10–25 \mu m in size deposited over the dense and uniform coating consisting of small crystals with a few \mu m in size. The coatings of the A-1, A-2 and A-3 consisted of HAp.\textsuperscript{26}

The ocp transient curves and anodic polarization curves of the A-1, A-2, A-3 and B-2 and the as-polished specimen are shown in Fig. 1.\textsuperscript{26} As reported in Ref. 26, the A-1, A-2 and A-3 were covered with plate-like, needle-like and rod-like HAp crystals, respectively. In case of the A-1 and A-3, relatively large crystals with 10–25 \mu m in size deposited over the dense and uniform coating consisting of small crystals with a few \mu m in size. The coatings of the A-1, A-2 and A-3 consisted of HAp.\textsuperscript{26}

3. Results and Discussion

#### 3.1 Anodic polarization behavior

SEM images of the A-1, A-2 and A-3 are shown in Fig. 1.\textsuperscript{26} As reported in Ref. 26, the A-1, A-2 and A-3 were covered with plate-like, needle-like and rod-like HAp crystals, respectively. In case of the A-1 and A-3, relatively large crystals with 10–25 \mu m in size deposited over the dense and uniform coating consisting of small crystals with a few \mu m in size. The coatings of the A-1, A-2 and A-3 consisted of HAp.\textsuperscript{26}

The ocp transient curves and anodic polarization curves of the A-1, A-2, A-3 and B-2 and the as-polished specimen are shown in Fig. 2. The ocp of the HAp-coated specimens increased in the initial 5 min and showed almost constant values which were higher than that of the as-polished specimen. Although the anodic polarization curve of the as-polished specimen showed an abrupt increase in current density following to a quasi-passive region with 10–5 A·cm\textsuperscript{-2}, the curves of the HAp-coated specimens did not show such an abrupt increase in the anodic current. The HAp-coated specimens showed a wide quasi-passive region with a lot of fluctuations. After the polarization test, pits were observed on the surface of the as-polished specimen by the optical observation. No apparent pit was observed on the surface of the HAp-coated specimens. These results proved that the HAp coatings prevented the growth of stable pitting corrosion in the simulated body fluid.

The current density near corrosion potential of the A-2 was lower than that of the A-1 and A-3 though the quasi-passive current density of the HAp-coated specimens did not clearly depend on the pH of the treatment solution. This result...
suggests that the corrosion resistance of the A-2 was the highest between the A-1, A-2 and A-3. The A-2 was treated at pH 7.3 that was equivalent to pH 8 of the m-Hanks. It is suggested that the pH of the treatment solution should be near the pH of body fluids to obtain highly protective HAp coatings.

The quasi-passive current density drastically decreased with an increase in the treatment time from 8 h to 24 h (A-2 and B-2). Noticeably, the quasi-passive current density of the B-2, ca. 10^{-6} A cm^{-2}, is equivalent to the passive current density of titanium and 316L stainless steel in Hanks’ solution.\textsuperscript{30} It was then revealed that the increase of treatment time is effective to improve the protectiveness of the HAp coating.

When the treatment time was 8 h (A-1, A-2 and A-3), the ocp curves showed a lot of fluctuations which can be attributed to occurrence and moderation of unstable localized corrosion under the defects of the HAp coatings. When the treatment time was 24 h (B-2), the fluctuation of the ocp did not take place. The smooth quasi-passive region of the B-2 indicates the decrease of defects of the HAp coating.

Figures 3(a) and 3(b) show the SEM images of the A-2 after the anodic polarization observed with the backscattering electron image detector. The shape and size of HAp crystals in the area without corrosion (Fig. 3(a)) are not noticeably different from those of the as-prepared crystals (Fig. 1(b)), respectively. On the other hand, a few numbers of pit with a diameter of 10~20\,\mu m were formed on the surface of the A-2. A pit with the typical size and shape is shown in Fig. 3(b). The pits were filled with corrosion products, indicating that the pitting corrosion was moderated immediately after the initiation.

3.2 Impedance behavior

Bode plots of the A-2 at 0.5 h and 6 h of immersion are shown in Fig. 4. The spectra shape of the A-1 and A-3 was...
similar to that of the A-2. The shape of impedance spectra did not change during 6 h of the immersion. The interface electrochemical property apparently remained for 6 h. The phase shift spectra showed two peaks at around \( \frac{3}{2} \times 10^4 \) Hz and \( \frac{5}{2} \times 10^{-1} \) Hz, and the slope of the impedance curve changed at around \( 10^2 \) Hz and \( 10^0 \) Hz. These results suggest that two time constants exist.

Below 1 Hz, the impedance and phase shift spectra of the A-1, A-2 and A-3 showed a lot of fluctuations which are attributed to the unstable localized corrosion under the defects of the HAp coatings. Magnitude and number of the fluctuations decreased with an increase in immersion time. It was reported that calcium phosphate spontaneously precipitated on as-polished and anodically oxidized pure magnesium in the m-Hanks.\(^{22}\) The decrease of the fluctuations with the immersion time then indicates that the defects of HAp coating were gradually filled with precipitated calcium phosphate in the simulated body fluid.

The ocp values of the A-1, A-2 and A-3 at which the impedance spectrum was measured are plotted in Fig. 5(a). The impedance value at \( 10^{-2} \) Hz (\( Z_{\text{low}} \)) is plotted in Fig. 5(b) to evaluate the protectiveness of the HAp coatings. The optical microscope images of the A-2 and as-polished specimen after the impedance measurement are shown in Fig. 6. Before the microscopic observation, the HAp coating and corrosion products were removed with a chromate solution.

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Fig. 3 SEM images of (a) surface area of A-2 without corrosion and (b) surface area of A-2 with a typical corrosion pit after anodic polarization in the m-Hanks.

Fig. 4 Bode plots of A-2 at 0.5 h and 6 h of immersion in m-Hanks: (a) impedance; (b) phase shift.

Fig. 5 Time dependence of (a) ocp and (b) impedance at \( 10^{-2} \) Hz of A-1~A-3 in m-Hanks.
In the case of the as-polished specimen, the ocp increased in the initial 0.5 h and became constant. The $Z_{\text{low}}$ increased in the initial 0.5 h and subsequently decreased continuously. The initial increase of ocp and $Z_{\text{low}}$ of the as-polished specimen is owing to the precipitation of calcium phosphate on the specimen surface from the m-Hanks. This is because the calcium phosphate spontaneously precipitated on the as-polished pure magnesium immediately after the immersion in the m-Hanks. The continuous decrease of $Z_{\text{low}}$ of the as-polished specimen is explained by the occurrence and growth of filiform and pitting corrosion observed in Fig. 6(b). It is indicated that the spontaneously precipitated calcium phosphate layer is not so protective to prevent the stable localized corrosion.

In the case of A-1, A-2 and A-3, the transient of ocp and $Z_{\text{low}}$ depended on the pH of the treatment solution. The A-1 showed the highest $Z_{\text{low}}$ in the beginning; however the $Z_{\text{low}}$ decreased in the initial 1 h and became almost constant around $10^5 \, \Omega \cdot \text{cm}^2$. The A-2 showed almost constant $Z_{\text{low}}$ around $10^5 \, \Omega \cdot \text{cm}^2$ from the beginning. The stable $Z_{\text{low}}$ value of the A-2 demonstrated the stable and high protectiveness of the HAp coating. The $Z_{\text{low}}$ of the A-3 gradually increased in the initial 2 h followed by the gradual decrease below $10^3 \, \Omega \cdot \text{cm}^2$. These results indicate that the protectiveness of the HAp coating depends on the pH of the treatment solution and the HAp coating formed at pH 7.3 is synthetically the most protective between the A-1, A-2 and A-3. This result agrees with the lowest anodic current density near corrosion potential of the A-2 between the A-1, A-2 and A-3 (Fig. 2(b)). It is again suggested that the pH of the treatment solution should be near the pH of the body fluid to increase the protectiveness of the HAp coating in the body.

It should be noted that the $Z_{\text{low}}$ values of the A-1, A-2 and A-3 were always 10 times higher than that of the as-polished specimen. Moreover, the substrate of the A-1, A-2 and A-3 showed no noticeable corrosion as shown in Fig. 6(a). On the contrary, the most part of the surface of the as-polished specimen showed filiform and pitting corrosion (Fig. 6(b)). It was demonstrated that the corrosion resistance of magnesium is able to be noticeably improved with the HAp coatings in the simulated body fluid.

### 3.3 Corrosion behavior under static immersion

The gross amount of Mg$^{2+}$ ions in the m-Hanks in which the A-1, A-2 and B-1 were statically immersed for 4 days is summarized in Fig. 7. No noticeable release of Mg$^{2+}$ ions was observed on all the HAp-coated specimens because the gross amount of Mg$^{2+}$ ions of the m-Hanks in which the respective specimens were immersed was equivalent to that of the blank solution (Fig. 7). No precipitate was observed inside the container used for the immersion test. Moreover, the surface of the immersed specimens did not show apparent corrosion. Thus, it was revealed that the dissolution of Mg$^{2+}$ ions from the HAp-coated magnesium was negligible in the simulated body fluid for 4 days.

The SEM images of the A-1, A-2 and B-1 after the immersion are shown in Fig. 8. The surface of all the specimens was uniformly covered with dome-shaped precipitates. On the surface of the B-1 after the immersion, hexagonal precipitates of 15~20 µm in length and 5~10 µm in width were additionally formed on the dome-shaped precipitates.

XRD pattern of the A-2 before and after the immersion is shown in Fig. 9. The XRD pattern of the A-2 immersed in the
m-Hanks was almost identical to that of the A-2 as-prepared. The XRD pattern of the A-1 and B-1 also did not significantly change after the immersion. These results indicate that the precipitates were HAp.

Figure 10 shows cross sectional images of the A-1 and A-2 after the immersion observed with the backscattering electron image detector. Blight and dark layers were formed on the substrate. To analyze the composition of each layer, qualitative analysis was carried out at spots #1–#4 marked on the images. The spots #1 and #2 are at outer and inner part of the blight layer, respectively. The spots #3 and #4 are at the dark layer and the substrate, respectively. The composition at each spot is summarized in Table 3.

In both the cases of A-1 and A-2, the spots #1 and #2 consist of calcium phosphate. Because Ca/P ratio of the spots are different each other, the bright layer can be divided into the original HAp layer and the HAp layer precipitated in the m-Hanks. The lower Ca/P ratio of the original HAp layer than that of the precipitates suggests the substitution of Mg atom for the Ca atom in the HAp structure and the existence of the other phosphate compounds. The spot #3 consists of mainly Mg and O. The Mg/O ratio of the A-1 and A-2 is around 0.5, indicating that the main component of the dark layer is Mg(OH)$_2$. The HAp and Mg(OH)$_2$ layers continuously covered the surface.

It was reported that the thickness of the HAp layer of the as-prepared A-1 and A-2 were 1.5–2µm and 3–5µm, respectively. After 4 days immersion, the HAp layer thickened to 4–8µm in both the cases of A-1 and A-2 (Fig. 10). The original HAp coating remained and the precipitated HAp layer was formed over it. Both the layers were dense by the microscopic observation. It was thus demonstrated that the defects of the original HAp coating was filled with the precipitated HAp.

It was reported that the Mg(OH)$_2$ intermediate layer was originally formed during the hydrothermal treatment and the thickness of the Mg(OH)$_2$ layer of the as-prepared A-1 and A-2 was 1.5–2µm. After 4 days immersion, the Mg(OH)$_2$ layer slightly thickened to 1.5–3µm in both the cases of A-1 and A-2 (Fig. 10). The thickening of the Mg(OH)$_2$ layer indicates the permeation of solution through the HAp layer. However, no traces of localized corrosion on the substrate suggest that the Mg(OH)$_2$ layer played like a
buffer preventing the localization of the penetrated solution. The magnesium substrate may be uniformly corroded at the boundary between Mg(OH)$_2$ layer and the substrate.

Almost no crack runs parallel to the surface at the boundary between the different layers and the substrate, indicating the good adhesion between the layers and the substrate. However, the Mg(OH)$_2$ layer appears to be brittle because the cracks parallel to the surface are sometimes formed inside the Mg(OH)$_2$ layer. On the other hand, several cracks are formed from the top surface toward the substrate and they stop inside the HAp layer or inside the Mg(OH)$_2$ layer. These perpendicular cracks might be formed during the drying of samples or the sample preparation for the observation because no pit was formed at the bottom of the cracks.

### 3.4 Change of the protectiveness with time

The change of the corrosion behavior of the HAp-coated specimens formed with 8-h treatment was examined. In the beginning of immersion in the simulated body fluid, the HAp coating formed at pH 7.3 showed the highest protectiveness as indicated by the lowest anodic current density near the corrosion potential (Fig. 2(b)) and the stable $Z_{\text{low}}$ transient during 6 h of the immersion (Fig. 5(b)). Since the generation of hydrogen gas in the beginning of the implantation is one of the problems of the existing magnesium alloys, the initial corrosion rate of magnesium is important. The current density near corrosion potential of the HAp-coated specimens were in the range of $10^{-5}$ to $10^{-6}$ A cm$^{-2}$. Assuming the cathodic reaction is $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$, the current density of $10^{-5}$ to $10^{-6}$ A cm$^{-2}$ corresponds to the hydrogen-gas generation rate of $10^{-11}$ to $10^{-10}$ mol s$^{-1}$ cm$^{-2}$ in a molar rate or $2 \times 10^{-10}$ to $2 \times 10^{-9}$ L s$^{-1}$ cm$^{-2}$ in volumetric rate. In the static immersion test in the simulated body fluid, no noticeable evolution of hydrogen gas was observed in the beginning of the immersion. These results reveal the HAp coatings can prevent the initial hydrogen-gas evolution in the body. Y. W. Song et al. reported that the HAp-coated AZ91 alloy showed about $10^{-7}$ A cm$^{-2}$ of corrosion current density in a SBF. Y. Song et al. reported that the hydrogen evolution volume in the initial 1 h from the brushite-coated Mg-Mn alloy in a SBF was about 0.25 mL cm$^{-2}$. H. X. Wang et al. reported that the Mg-Zn-Ca alloy with electrodeposited Ca-deficient HAp coating showed $25 \times 10^{-6}$ A cm$^{-2}$ of corrosion current density in a SBF.$^{10}$ These facts indicate that the protectiveness of our HAp coatings is equivalent to that of the other calcium phosphate coatings.

With a long term immersion, the protectiveness of HAp coatings was improved with the precipitation of HAp which filled the defects of the original HAp coatings. With the further precipitation of HAp, the original HAp coating was almost completely covered against the solution (Fig. 10). As the result, the Mg$^{2+}$ ions release was prevented regardless of the treatment condition. Consequently, the corrosion resistance of magnesium is able to be noticeably improved with the HAp coatings formed by the developed hydrothermal treatment.

### 4. Conclusion

The HAp coatings were formed on pure magnesium by the single-step hydrothermal treatment using the Ca-EDTA-KH$_2$PO$_4$ solution with pH 6.3, 7.3 and 11.3. The treatment time was 8 h or 24 h. The corrosion behavior of the HAp-coated specimens was investigated by the anodic polarization test, the impedance measurement for 6 h and the immersion test for 4 days in the simulated body fluid. The HAp coatings improved the corrosion resistance of pure magnesium by 10 times more than that of the as-polished specimen. Especially, stable localized corrosion was prevented with the HAp coatings. The protectiveness of HAp coating was improved with an increase in treatment time.
The initial protectiveness of the HAp coatings formed with 8-h treatment depended on the pH of the treatment solution. The pH is better to be equivalent to that of body fluids to show high protectiveness. With an increase in immersion time in the simulated body fluid, the defects of the HAp coatings were filled and subsequently the original HAp coatings were almost completely covered with the precipitated HAp. As the result, the Mg$^{2+}$ ion release from the HAp-coated specimens becomes negligible after 4 days immersion regardless of the treatment condition.

Hence, the HAp coatings formed by our developed hydrothermal treatment are effective to improve the corrosion resistance of magnesium inside the body.

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