In vitro degradation behavior of as-cast Mg-3Zn-1Ca-0.5 Sr alloy

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Abstract

Recent advancements in bone implant materials have led to the development of various alloys. In this study, the degradation behavior of the as-cast Mg-3 wt% Zn-1 wt% Ca-0.5 wt% Sr alloy in vitro was investigated using x-ray diffraction (XRD), scanning Kelvin probe force microscopy (SKPFM), and scanning electron microscopy (SEM). Our results demonstrated that the alloy microstructure was composed of α-Mg, a Ca\textsubscript{2}Mg\textsubscript{6}Zn\textsubscript{3} phase, and a Mg\textsubscript{17}Sr\textsubscript{2} phase. The Ca\textsubscript{2}Mg\textsubscript{6}Zn\textsubscript{3} phase, which had the smallest absolute potential, was shown to have cathodic protection, while the α-Mg, which had the largest absolute potential, was shown to prefer corrosion. The in vitro corrosion products of the as-cast alloy were Mg(OH)\textsubscript{2}, a Ca-P compound, and HA. At the beginning of the corrosion, the hydrogen evolution rate of the alloy was fast due to the thin corrosion product layer. With the extension of the corrosion time, the corrosion layer thickened and the hydrogen evolution rate slowed down and stabilized to 1.25 \times 10^{-5} \text{ mol cm}^{-2} \cdot \text{h}. Due to the high concentration of Ca and Mg ions near the second phase, HA was quickly deposited and an ion exchange channel between the solution and the alloy was formed, making it easier for the Mg, Ca, and Sr ions to enter the solution and promote the formation of HA. The hysteresis effect of Sr element was found, that is, Sr ions were released into the solution after etching for a period of time, which promoted the formation of HA and HA-containing Sr (Sr/HA).

1. Introduction

In recent years, bone implant metal materials have rapidly advanced and Fe, Ti, Co, and other alloys have been widely studied [1]. However, a number of problems remain to be solved in the implantation of metal materials into bone, including (1) the Young’s modulus of these materials is very different from that of human bone, which has a stress shielding effect; (2) after the human bone has healed, the surgical removal of these materials is necessary, increasing the patient’s pain and cost; and (3) these metal materials often contain some harmful elements that are released through corrosion and wear, resulting in adverse effects on the human body [2, 3]. Recent advances have indicated that the characteristics of magnesium alloys may make it possible to solve these problems. First, the Young’s modulus of magnesium alloys is similar to that of human bone, which effectively avoids the stress shielding effect. Second, magnesium alloys can be completely degraded in the human body, which avoids surgical removal. Finally, the Mg ions released by the magnesium alloy during degradation can be discharged with body fluid and are harmless to the human body. Collectively, these advantages make magnesium alloys a bone implant material with good biocompatibility [4–7]. While magnesium alloys do have some disadvantages, including a fast corrosion rate and poor mechanical properties, these can typically be improved by alloying, deformation, and surface modification [8–10]. Indeed, Zn, Ca, and Sr have been studied as alloying elements of magnesium alloys implanted in bone and have demonstrated good biocompatibility [11–13].
The degradation behavior of magnesium alloys in vitro has been widely studied, with the main form of corrosion being galvanic in nature. In general, micro-galvanic corrosion is formed by the potential difference between the second phase and the $\alpha$-Mg [14]. Due to the complex environment of the human body, in vitro degradation experiments are often used to simulate the corrosion of alloys under these conditions [15]. Li et al studied the degradation behavior of the bone degradable material Mg-x wt% Ca (x = 1, 2, 3) in vitro [16]. The authors found that mixed products of Mg(OH)$_2$ and HA were formed on the surface of the alloy with the extension of corrosion time. The Mg-1Ca alloy is considered the most favorable alloy for orthopedic biodegradable materials. Gu et al studied the microstructure and properties of the Mg-x wt% Sr (x = 1, 2, 3, 4) alloy and found that the addition of the Sr element could improve the strength and corrosion resistance of the alloy, but too much Sr was harmful [17]. In addition, Bornapour et al studied the degradation of the Mg-x wt% Sr (x = 0.3–2.5) alloy in vitro and found that Mg-0.5 Sr had the slowest corrosion rate and the Mg-0.5 Sr alloy would form HA-containing Sr during corrosion [18]. This had a good effect on promoting the formation and growth of new bone. Furthermore, Harpreet et al studied the degradation behavior of the Mg-x wt% Zn-0.5 Sr (x = 2, 4, 6) alloy and found that the alloy had good strength and corrosion resistance when the content of the Zn element was 2 wt% and 4 wt%. At the same time, the regulation of the microstructure of the alloy is known to be involved in its degradation behavior. He et al studied the corrosion morphology of the Mg-1Ca-0.5Sr-x wt% Zn (x = 0, 2, 4, 6) alloy after degradation in vitro for 10 days and found that the hydrogen evolution rate of the alloy decreased with increasing Zn content, with the 6 wt% Zn alloy demonstrating good antibacterial effects [19]. Although a number of studies have observed and described the degradation behavior of alloys in vitro, the degradation behavior of alloys under these conditions is a complex process varying with time. Currently, the description of this process is primarily limited to a discussion of the changes in the corrosion products on the alloy surface. While useful, this description is not considered detailed enough. Indeed, changes in the alloy microstructure at the bottom of the corrosion layer during the corrosion process have a significant effect on the service behavior of the alloy. In addition, when the alloy contains a variety of second phases, the potential difference between these phases would be expected to affect the corrosion process of the alloy. Therefore, further study of the role of different second phases in the corrosion process of alloys is warranted.

In this study, the Mg-3 wt% Zn-1 wt% Ca-0.5 wt% Sr alloy was selected to prepare the as-cast Mg-3 wt% Zn-1 wt% Ca-0.5 wt% Sr alloy, and the degradation behavior of the alloy in vitro was studied. The corrosion surface morphology of the alloy and changes to its microstructure after removing the corrosion products were observed. In addition, a degradation model of the as-cast alloy in vitro was established and the role of different second phases in the degradation process was described. The results of the current study should help lay the foundation for continued research and application of the alloy.

2. Materials and methods

2.1. Material preparation

Based on our previous research results and those presented in the literature, the alloy composition used in this study was 3 wt% Zn, 1 wt% Ca, 0.5 wt% Sr, with the remainder composed of Mg. Magnesium ingots, pure Zn, 80 wt% Mg/20 wt% Ca master alloys, and 70 wt% Mg /30 wt% Sr master alloys were used to smelt the designed alloy. C$_2$H$_2$F$_4$ and Ar were used to protect the melt from contact with the air. After melting the magnesium ingot in a steel crucible at 973 K, the temperature was increased to 1023 K. Pure Zn, Mg-Ca, and the Mg-Sr master alloys were then added in that order before reducing the temperature to 993 K. After melting was completed, the melt remained for 20–30 min and then was stirred and filtered. Finally, the temperature was reduced to 303 K with water.

2.2. Instrumentation

The microstructure of the homogenized alloys were investigated by an Optical Microscope (OM), and the grain size was measured by Image Pro Plus. An X-pert PRO MPD polycrystalline x-ray diffractometer (XRD) was used for the phase analysis of the samples. The microstructure, phase composition, and element distribution of the alloys were observed by scanning electron microscopy (SEM) using a Carl Zeiss EVO18. Scanning Kelvin probe force microscopy (SKPFM) system and a Bruker Dimension ICON to assess local differences in the Volta potential of the corrosion.

2.3. Immersion test

Before erosion testing, the sample was wrapped with self-setting dentifrice powder to expose a 10 mm × 10 mm surface. The amount of hydrogen evolution (mL) was then measured in simulated body fluid (SBF). After the corrosion products were removed with chromic acid (200 g l$^{-1}$ CrO$_3$ + 10 g l$^{-1}$ AgNO$_3$), the weight loss of each sample was measured and the corrosion morphology of each sample was observed by SEM.
3. Results

3.1. Microstructure

As shown in figure 1, the grain size of the alloy was coarse (96 μm), the second phase, distributed in a continuous network at the grain boundary, had a large volume fraction.

As shown in figure 2(a), the contrast between the bone-like A phase and the spherical C phase was similar, and the block B phase distributed at the grain boundary. Table 1 indicated that the MgZnCa ternary phase was at positions A and C and a segregation of Sr elements was at B position, a second phase containing Sr Combined with the results of the XRD analysis, as shown in figure 2(b), the microstructure of the as-cast alloy was determined to be composed of α-Mg, a Ca₂Mg₆Zn₃ phase with continuous distribution, and a Mg₁₇Sr₂ phase with block distribution. Due to the high eutectic temperature of Mg₁₇Sr₂ phase, it was wrapped by Ca₂Mg₆Zn₃ phase. When analyzing the composition of Mg₁₇Sr₂ phase, because Ca₂Mg₆Zn₃ phase was also distributed under Mg₁₇Sr₂ phase, a small amount of Zn and Ca elements appeared in EDS results.

![Figure 1. OM Morphology of the alloy.](image1)

![Figure 2. Microstructure of the alloy. (a) SEM morphology; (b) XRD results.](image2)

| Position | A     | B     | C     |
|----------|-------|-------|-------|
| Mg/at%   | 66.5  | 82.3  | 72.2  |
| Zn/at%   | 20.7  | 7.64  | 14.6  |
| Ca/at%   | 11.5  | 2.80  | 11.6  |
| Sr/at%   | /     | 7.29  | /     |

Table 1. EDS analysis of positions A, B, and C.
The main corrosion mode of magnesium alloys is galvanic corrosion [20]. In this process, two adjacent phases with different potentials form micro-galvanic corrosion [21]. The structure with the largest absolute value of the potential (absolute potential) is then corroded as the anode and the structure that acts as a cathode has cathodic protection [22]. As shown in figure 3, the potentials of the α-Mg, the Ca2Mg6Zn3 phase, and the Mg17Sr2 phase were all negative, with the absolute potential of the α-Mg determined to be the largest. Due to the fact that the Zn element was easily segregated near the grain boundary, there was a difference in the potential between the middle part of the grain and the edge of the grain, resulting in a decrease in the absolute potential at this position. The absolute potential of the Ca2Mg6Zn3 phase was the smallest and thus protected as the cathode. The absolute potential of the Mg17Sr2 phase was less than that of the α-Mg, but greater than that of the Ca2Mg6Zn3 phase. Therefore, according to the difference in potential, three pairs of micro-galvanic corrosion were constructed, namely, α-Mg/Ca2Mg6Zn3, α-Mg/Mg17Sr2, and Mg17Sr2/Ca2Mg6Zn3.

3.2. Hydrogen evolution rate and pH changes during in vitro degradation
As shown in figure 4, the pH value of the alloy was stable when it reached 9.3, with increased corrosion time. When the α-Mg became corroded, OH− was released. Therefore, the faster the corrosion rate of the alloy, the faster the pH value increased. However, some studies have shown that Mg(OH)2 is stable in an alkaline environment, thus the rising rate of the pH slows down gradually [23]. The hydrogen evolution rate of the as-cast alloy was determined to be $1.25 \times 10^{-5} \text{ mol cm}^{-2} \cdot \text{h}$. According to the slope change of the hydrogen evolution curve of the as-cast alloy, it was divided into three stages. Accordingly, during the early stage of corrosion, the alloy corroded rapidly and the amount of hydrogen evolution increased accordingly. During the middle stage of corrosion, the corrosion rate of the alloy was unstable and was sometimes fast and sometimes slow. During the later stage of corrosion, the corrosion rate tended to be stable.
3.3. Degradation behavior in vitro

3.3.1. Corrosion products

As shown in figure 5, the primary corrosion product of the alloy at 310 K in SBF was Mg(OH)$_2$. A small amount of Zn, Ca, and Sr elements was also released with the corrosion of α-Mg and the Mg$_{17}$Sr$_2$ phase, forming a thin hydroxide $(\text{Zn, Ca, Sr})(\text{OH})_x$ corrosion layer, which has been found to promote the formation of HA and the Ca-P compound on the alloy surface [24]. Under the combined action of the Mg, Ca, and Sr ions, along with the formation of the $(\text{Zn, Ca, Sr})(\text{OH})_x$ layer, a strong diffraction peak representing the Ca-P compound and HA appeared on the surface of the alloy. These results indicated that the Ca-P compound and HA were deposited on the alloy surface, making the as-cast alloy an implant material with good biocompatibility.

3.3.2. Surface corrosion morphology

As shown in figure 6(a) and table 2, after etching for 1 h, the α-Mg became corroded and H$_2$ and Mg(OH)$_2$, along with a small amount of the Ca-P compound, were formed and covered the grains (position A). It was also observed that the continuous distribution of the second phase was exposed to the surface (position B and the blue dotted line), with Sr segregation in the second phase position. The white chimney-like structure was found at position C, which was determined to be HA from the EDS results.

As shown in figure 6(b) and table 2, after 24 h of etching, the second phase was covered by a flaky corrosion product (position D), which appears as the blue dashed line on the surface of the alloy. In addition, our EDS results demonstrated that the corrosion product was the Ca-P compound. At the same time, the appearance of corrosion pits (at the yellow dotted line) was observed, with the thick corrosion products having been redeposited on the corrosion pits.

As shown in figure 6(c) and table 2, after etching for 96 h, Mg(OH)$_2$ and the Ca-P compound, grow from flaky to bulk, completely covered the surface of the alloy with (position E), and deposited a lot of small bulk HA (position F) on the surface. The thickening of the alloy corrosion layer not only enhanced its protective effect, but also transformed the chimney-like HA structure into pore-like structure.

As shown in figure 6(d) and table 2, after etching for 96 h, the alloy was completely covered by surface corrosion products. At this stage, the exposed second phase could not be seen and the appearance of large pores was observed. In addition, our EDS results demonstrated that chunks of HA-containing Sr (Sr/HA) were deposited on the surface of the alloy (position G). The corrosion product layer on the surface of the alloy was complete and had a good protective effect.

3.3.3. Morphology of the de-corrosion products

As shown in figure 7(a), after 1 h of etching, the α-Mg near the grain boundary had serious corrosion and more pitting pits appeared (shown by the red arrow). On the contrary, the α-Mg in the middle of the grain was relatively complete. There was obvious segregation of Sr elements at the grain boundary, enlarged one of them (the red dotted line) as shown in figure 7(b). The shape of Mg$_{17}$Sr$_2$ was intact and the phase boundary was straight, indicating that the α-Mg/Mg$_{17}$Sr$_2$ micro-galvanic has not been activated and the Mg$_{17}$Sr$_2$ phase had not been corroded.
As shown in figure 8(a), after 24 h of etching, a small number of pits appeared in the middle of the grain and the α-Mg corrosion near the grain boundary was intensified, which served to expose the Ca$_2$Mg$_6$Zn$_3$ phase. In addition, the Sr element had obvious segregation in the second phase. The dashed line position in figure 6(a) was enlarged, as shown in figure 6(b), and the Sr element segregation position was enlarged, as shown in figure 8(c). Table 3 shows the EDS results indicating that position A was the Ca$_2$Mg$_6$Zn$_3$ phase and position B was the Sr element.

Table 2. EDS results of the alloy etched at 310 K in SBF for different time periods.

|       | A    | B    | C    | D    | E    | F    | G    |
|-------|------|------|------|------|------|------|------|
| Mg/at%| 38.40| 54.63| 20.43| 7.44 | 20.67| 11.72| 12.89|
| Ca/at%| 3.32 | 7.47 | 3.48 | 15.89| 5.65 | 10.62| 9.41 |
| Sr/at%| /    | 0.77 | /    | /    | /    | /    | 0.15 |
| P/at% | 6.21 | /    | 2.72 | 19.05| 5.57 | 8.02 | 7.47 |

As shown in figure 8(a), after 24 h of etching, a small number of pits appeared in the middle of the grain and the α-Mg corrosion near the grain boundary was intensified, which served to expose the Ca$_2$Mg$_6$Zn$_3$ phase. In addition, the Sr element had obvious segregation in the second phase. The dashed line position in figure 6(a) was enlarged, as shown in figure 6(b), and the Sr element segregation position was enlarged, as shown in figure 8(c). Table 3 shows the EDS results indicating that position A was the Ca$_2$Mg$_6$Zn$_3$ phase and position B was the Sr element.
Mg$_{17}$Sr$_2$ phase. There are many pits on the Mg$_{17}$Sr$_2$ phase and the boundary of the Mg$_{17}$Sr$_2$ phase became uneven, indicating that the micro-galvanic corrosion of Mg$_{17}$Sr$_2$/Ca$_2$Mg$_6$Zn$_3$ had begun due to the serious corrosion of $\alpha$-Mg near the grain boundary. As an anode, the Mg$_{17}$Sr$_2$ phase participated in corrosion and released Sr ions; however, the corrosion time was short, not considered serious, and the amount of Sr ions released was small.

As shown in figure 9(a), the corrosion of the $\alpha$-Mg at the surface layer was serious and the number of corrosion pits increased. A small amount of the Sr segregation region was still observed on the second phase, but it was clearly less than that at 24 h. The segregation position of the Sr element was enlarged, as shown in
figure 9(b). The Mg$_17$Sr$_2$ phase at the blue dashed line position was seriously corroded and corrosion pits were formed on the Ca$_2$Mg$_6$Zn$_3$ phase. As shown in figure 9(c), it was demonstrated that when the $\alpha$-Mg was completely corroded, the supporting effect of the crack position was weak, making it difficult to support the residual structure and cracking ensued.

As shown in figure 10, after 96 h of etching, due to the disappearance of the $\alpha$-Mg at the surface layer, surface cracking at the remaining second phase was serious. In addition, some of the cracks expanded and fell off, exposing the deep $\alpha$-Mg (at the blue dotted line), which continuing to participate in the corrosion and form

| Table 3. EDS results of the de-corrosion products of the alloy etched at 310 K in SBF for 24 h. |
|---------------------------------|--------|--------|
| Mg/at%                         | 68.58  | 78.60  |
| Zn/at%                         | 20.51  | 5.38   |
| Ca/at%                         | 10.01  | 3.62   |
| Sr/at%                         |        | 1.17   |
corrosion pits. The increase in the Sr element segregation zone indicated that when the $\alpha$-Mg previously covered by the Mg$_{17}$Sr$_2$ phase was corroded, more of the Mg$_{17}$Sr$_2$ phase was exposed and involved in the corrosion, which resulted in the release of a large number of Sr ions. When the concentration of the Sr ions was high, Sr/HA was deposited on the surface of the alloy. These results are consistent with those of the before de-corrosion products.

As shown in figure 11(a), the depth of the corrosion layer was 76.5 $\mu$m and unpeeled $\alpha$-Mg at the red dotted line was observed. With the increased corrosion time, the depth of the corrosion layer increased to 171.5 $\mu$m. As shown in figure 11(b), the $\alpha$-Mg at the bottom of the corrosion layer was almost completely corroded during the later stage of corrosion. The residual structure protected the deep $\alpha$-Mg from participating in the corrosion and slowed down the corrosion rate.

4. Discussion

In order to analyze the cause of the hole formation in the alloy, a magnified morphology of the hole is shown in figure 12(a). The bottom of the hole consisted of a rod-like structure, the middle was cylindrical, the edge was smooth, and the top was a semicircular depression. As shown in figure 12(b), the needle corrosion product layer at the bottom of the hole was loose, representing the structural characteristics of Mg(OH)$_2$ [18]. As shown in figure 12(c), the structure in the middle of the hole was considered dense and was composed of the Ca-P compound and HA.

A schematic diagram of the hole generation principle is shown in figure 13. In figure 13(a), because the $\alpha$-Mg near the second phase is preferentially involved in corrosion and the release of ions, produce fine bubbles near the grain boundary. As shown in figure 13(b), the fine H$_2$ bubbles produced by $\alpha$-Mg corrosion spill to the
surface of the Mg(OH)$_2$ layer and adhere to its surface. The concentration of Mg and Ca ions near the second phase was high, facilitating the deposit of Ca-P and the formation of HA, thus this structure appears easily near the second phase. As shown in figure 13(c), HA was observed to form around the bubble composed of many fine bubbles and the H$_2$ bubble wrap around the bubble formed a chimney-like structure. As shown in figure 13(d), with the bubble overflow, the format of the smooth stomata wall resulted in pores. These pores comprised the ion exchange channel between the solution environment and structure, which provided a means for the solution to cross the corrosion product layer in order to contact the matrix and accelerate the corrosion. However, the appearance of the pores also made it easier for the Mg, Ca, and Sr ions produced by corrosion to enter the solution, promoting the deposition of HA and Sr/HA on the surface of the alloy, which served to turn the dense and complete corrosion layer into a porous structure. This structure is similar to that of human bone and has good biocompatibility [25]. The effects of the stomata on bone tissue will be analyzed and discussed in future studies.

Figure 12 shows a dynamic model of the degradation of the as-cast Mg-3Zn-1Ca-0.5 Sr alloy in vitro. The corrosion is divided into three stages.

As shown in figures 14(a) (b), during the early stage of corrosion, due to the coarse grain size of the as-cast state, the α-Mg near the Ca$_2$Mg$_6$Zn$_3$ phase was corroded as the anode. In addition, H$_2$ was formed on the second phase as the cathodic reaction product and the Mg(OH)$_2$ corrosion product was formed on the surface. A small amount of the Ca-P compound, which has a weak protective effect, was deposited on the Mg(OH)$_2$, increasing the corrosion rate. Although the potential difference of corrosion micro-galvanic α-Mg/Mg$_{17}$Sr$_2$ is less than that of α-Mg/α-Mg/Zn$_3$, α-Mg is etched as an anode in two pairs of micro-galvanic, so the role of α-Mg/Mg$_{17}$Sr$_2$ and α-Mg/Ca$_2$Mg$_6$Zn$_3$ in the corrosion process is similar. The α-Mg corrosion near the second phase was faster, resulting in an increase in the concentration of Mg and Ca ions nearby and the formation of bulk HA with a smaller volume [26]. Part of the HA is formed by wrapping H$_2$ and becomes a chimney-like structure.

As shown in figures 14(c) (d), in the middle stage of corrosion, the Ca-P layer on the surface became thicker, the protective effect was enhanced, and the corrosion rate slowed down. Due to the potential difference between the Ca$_2$Mg$_6$Zn$_3$ phase and the Mg$_{17}$Sr$_2$ phase, the Mg$_{17}$Sr$_2$ phase was corroded as the anode and released Sr ions into the solution, promoting the formation of HA and Sr/HA [27]. After the surface α-Mg was corroded, the second phase appeared to crack and fracture, which resulted in the deep α-Mg being exposed to the solution to participate in the corrosion. This participation of α-Mg in the corrosion was shown to lead to the formation of layered corrosion pits, accelerating the corrosion rate. Because the concentration of Ca ions and pH value in the solution were higher than the initial state, the deposition rate of the corrosion products in the corrosion pit was...
faster. When the thicker corrosion product layer was re-formed on the surface of the corrosion pit, the corrosion rate of the alloy slowed down again. In this process, the phenomenon of fluctuating corrosion rates was observed.

As shown in figure 14(e), in the later stage of corrosion, a thick and dense Ca-P layer was observed on the surface of the alloy and the more massive HA corrosion layers became thicker. In this process, the protective effect of the corrosion product layer on the alloy surface was stronger and the corrosion rate of the alloy slowed down and tended to be stable [28]. This represented the slow corrosion stage. However, the pores produced by the H₂ spillover constructed ion exchange channels between the α-Mg and the solution environment, which play a serious role in destroying the corrosion product layer on the surface. When both the upper and deep α-Mg exposed to the solution were almost completely corroded, the continuous reticulated Ca₃Mg₆Zn₃ phase easily cracked and fell off, resulting in the increased release of Sr ions. This was shown to promote the formation of HA and Sr/HA. The corrosion rate of the alloy was slow and stable, but the layered corrosion pit was deeper. Sr/HA has been shown to promote the differentiation and proliferation of bone tissue and has good biocompatibility [29].

In our previous studies, we found that, although Sr elements have an obvious promoting effect on the production of HA, there was a certain lag in this effect. This promoting effect was weak at 24 h and strong after 48 h. Combined with the results of the current study, because the solid solubility of the Sr element in the α-Mg is very small, when the α-Mg became corroded, few Sr ions were released into the solution. Only when the Mg₈₁Sr₂ phase was corroded as an anode were more Sr ions released into the solution, resulting in a hysteresis effect. In
other words, at the beginning of the corrosion, there were fewer \( \text{Mg}_17\text{Sr}_2 \) phases involved in the corrosion and the concentration of Sr ions released into the solution was low, thus the effect of promoting the formation of HA was not obvious. With the extension of time, a large number of \( \text{Mg}_17\text{Sr}_2 \) phases became corroded and more Sr ions were released. In this process, the concentration of Sr ions in the solution increased and the effect on promoting the formation of HA was significant.

5. Conclusion

The potentials of the as-cast alloy microstructure were the \( \text{Ca}_2\text{Mg}_6\text{Zn}_3 \) phase, the \( \text{Mg}_17\text{Sr}_2 \) phase, and the \( \alpha \text{ Mg} \) from high to low. Three phases formed three micro-galvanic corrosions, with the \( \text{Ca}_2\text{Mg}_6\text{Zn}_3 \) phase protected as the cathode, the \( \alpha \text{ Mg} \) near the grain boundary preferring corrosion, and the activation of \( \alpha \text{ Mg}/\text{Mg}_17\text{Sr}_2 \) micro-galvanic make the \( \text{Mg}_17\text{Sr}_2 \) phase releasing Sr ions, which served to promote the formation of HA, resulting in a hysteresis effect.

The degradation products of the alloy were primarily composed of \( \text{Mg(OH)}_2 \), the Ca-P compound, and HA. The corrosion products of the as-cast alloy had a weak protective effect and a fast hydrogen evolution rate at 0–10 h. With the extension of the degradation time, the degradation product became thicker and a stronger protective effect was observed. In addition, the hydrogen evolution rate slowed down and stabilized at \( 1.25 \times 10^{-5} \text{ mol cm}^{-2} \cdot \text{h} \).

HA is preferentially formed near the second phase, and part of the HA wraps \( \text{H}_2 \) to form a chimney-like structure. With the thickening of the corrosion layer, pores appeared on the surface of the alloy and served to construct ion exchange channels between the matrix and the degradation environment. In addition, the corrosion products on the surface of the alloy become porous in nature, which is similar to the structure of human bone. The \( \alpha \text{ Mg} \) of the as-cast alloy was observed to easily fall off and the corrosion was uneven during the corrosion process. In addition, a sharp pit extending along the second phase appeared at the bottom of the corrosion pit, which may cause stress on the material, making the service behavior of the material unreliable and prone to early failure [30, 31]. The second phase plays an important role as the cathode of the micro-galvanic corrosion. The degradation mode of the alloy in vitro was changed by adjusting the size and distribution of the second phase of the alloy. The controllable degradation behavior of the alloy in vitro is particularly important for the clinical application of the alloy, which will be discussed in a follow-up study.

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