Electrochemical Corrosion Behavior of Backward Extruded Mg-Zn-Ca Alloys in Different Media

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Mg-1.0Zn-xCa (x=0.2, 0.5, 0.8, 1.0; wt. %) alloys were prepared by zone purifying solidification followed by backward extrusion technology. The microstructures, electrochemical corrosion behaviors and the mechanisms in 0.9 wt. %, 3.5 wt. % NaCl solutions and simulated body fluid (SBF) were evaluated at ambient temperature. The corrosion properties of the specimens were remarkably influenced by the compositions of the media. According to electrochemical impedance spectroscopy (EIS), it revealed that the samples (lower 1.0 wt. % Ca) in the 0.9 wt. % and 3.5 wt. % NaCl solutions showed a single conductive loop. Conversely, Mg-1.0Zn-1.0Ca alloy was combined of a conductive loop and an inductive loop. In the case of SBF, EIS of all the samples turned to two conductive loops and an inductive loop. The BE-Mg-1.0Zn-0.5Ca alloy exhibited the most anti-corrosion properties in both 0.9 wt. % NaCl solution and SBF, while it changed to BE-Mg-1.0Zn-0.8Ca alloy in 3.5NaCl solution. The corrosion resistance. On the contrary, much Ca element can purify the melts to improve the corrosion resistance. On the contrary, much Ca element contributed to form the secondary phase, accelerating the pitting corrosion.

Keywords: Mg-Zn-Ca alloys; Microstructure; Electrochemical impedance spectroscopy; Corrosion mechanism

1. INTRODUCTION

Magnesium (Mg) is an essential element in the human body, and both its specific strength and Young's modulus are closer to human bone than the conventional used metallic implant materials. Moreover, Mg alloys can decrease the stress shield between the interfaces of bone/implant materials and stimulate the growth of bone [1]. Herein, Mg alloys have been tentatively designed as orthopedic implants [2]. At the early stage of the researches about Mg biomaterials (bio-Mg), some commercial

structural Mg alloys have been adopted as biomedical implants directly, such as AZ31, AM50 and WE54 alloys. However, the potential toxicity of products restricts the development of bio-Mg implants [3]. Therefore, it becomes a very urgent issue to develop some novel bio-Mg alloys.

Mg-Zn-Ca system is regarded as a most suitable one to develop Mg based biomaterials. Both zinc (Zn) and calcium (Ca) have been confirmed as beneficial metabolizing elements in human body and they can improve the mechanical properties simultaneously [4]. A recent study suggested that the adverse effects on chromatins and structure or function of heart, liver, kidney, or spleen have hardly observed in Mg-Zn alloys [5]. Lei et al. [6] have reported that Mg-based alloys reinforced by Mg-Zn intermetallic can enhance the mechanical properties and corrosion resistance. More recently, Li et al. [7] point out that Mg-1.0Ca (wt. %) exhibits good mechanical, high corrosion resistance and acceptable biocompatibility.

However, to data, there exists one key problem about Mg-Zn-Ca biomaterials. Namely, the fluctuation of degradation rate greatly affects the degradation process owing to strong local pitting corrosion [8]. It is well known that the degradation rate is closely related to the microstructure [9]. The homogenous microstructure becomes the prerequisite to obtain the uniform degradation rate. Wang et al. [10] have reported that the enrichment of metallic Zn can improve the corrosion properties of melt-spun glassy Mg₆₇Zn₂₈Ca₅ alloy. Recently, Gao et al. [11] pointed out that the Mg-2.0Zn-0.24Ca (wt. %) alloy treated by high pressure possesses the lowest biodegradation rate compared with the as cast and conventional extrusion samples. Nevertheless, the melt-spun glassy Mg-Zn-Ca is deficient in formability, whilst the high pressure sample possesses secondary phase, which is prone to pitting corrosion potential and reduce the degradation rate of the extruded Mg-Zn-Ca alloy in SBF. Unfortunately, the effects of Ca content and different media on the corrosion properties and their mechanisms in Mg-Zn-Ca system are unclear.

In the present work, backward extrusion technology (BE), confirmed as an effective approach to improve the degradation properties of Mg-xZn biomaterial in our previous work [13], has been employed to prepare Mg-1.0Zn-xCa (x=0.2, 0.5, 0.8, 1.0; wt. %) alloys. The influences of Ca content and different media on the corrosion properties of the alloys were investigated and the corrosion mechanisms were discussed.

2. EXPERIMENTAL PART

2.1 Preparation of materials

Mg-1.0Zn-*x*Ca (x=0.2, 0.5, 0.8, 1; wt. %, all the following is the same if no special comment) alloys have been prepared by zone solidification technology. Briefly, the alloys have been prepared in a tantalum (Ta) crucible under protection by a mixture of CO₂ and SF₆. After mixing at 730 °C for 1.5 h, the alloy was cast into a mold preheated at 500 °C. The filled mold was held at 670 °C for 1 h under the protective gas. Subsequently, the whole Ta crucible with the melt was immersed into the flowing water at 30 mm/s. As soon as touched the water, the bottom of the Ta crucible stopped for 2 s. The

solidification process was finished when the liquid level of the crucible inside was aligned with the height of water outside. The size of the ingot was φ 70 mm × 180 mm.

The ingot was held at 530 °C for 10 h, and then quenched into hot water (60 °C). Before BE process was taken, the ingot was preheated at 400 °C for 1 h. The extruded ratio and speed were 12.25 and 50 mm/min, respectively. After extrusion, the samples were heat treated at 150 °C for 30 minutes to eliminate the residual stress.

| Alloys | Element (| Element (wt. %) | | | | | | | | |
|--------|-----------|-----------------|---------|---------|------|--|--|--|--|--|
| | Zn | Ca | Cu | Fe | Mg | | | | | |
| MZ0.2C | 0.92 | 0.14 | < 0.003 | < 0.002 | Bal. | | | | | |
| MZ0.5C | 0.91 | 0.39 | < 0.002 | < 0.002 | Bal. | | | | | |
| MZ0.8C | 0.84 | 0.77 | < 0.001 | < 0.001 | Bal. | | | | | |
| MZ1.0C | 0.83 | 1.01 | < 0.001 | < 0.001 | Bal. | | | | | |

Table 1. The detailed chemical compositions of the BE state alloys

X-ray fluorescence spectroscopy was used to measure the chemical composition of the BE-Mg-1.0Zn-*x*Ca (MZ0.2C, MZ0.5C, MZ0.8C and MZ1.0C). The detailed compositions are listed in Table 1. All four alloys were high purity, and the concentrations of the impurities, such as iron (Fe), nickel (Ni) and copper (Cu), were lower than the impurity tolerance limits. Meantime, the Ni element is too little to be detected. It can be seen that the content of the alloying element was lower than that of nominal composition owing to the burning loss. Moreover, the mass loss of Ca content is more obvious than that of Zn owing to higher chemical activity.

2.2 Corrosion properties

Electrochemical tests were carried out using a Bio-logic VSP potentiostat/frequency response analysis system to evaluate the electrochemical behaviors. Experiments were carried out in a three-electrode electrochemical cell, with a saturated calomel electrode (SCE) as the reference electrode, a platinum mesh as counter electrode and the investigated specimen as the working electrode. The experiments were carried out in 0.9 wt. %, 3.5 wt. % NaCl aqueous solutions (0.9NaCl, 3.5NaCl), and SBF at ambient temperature, respectively. For all the solutions were prepared by double distilled water. Samples were polished with successively finer grade of emery papers (up to 2000 grit), washed with distilled water and dried in flowing warm air. The ion composition and preparation of SBF was reported in our previous ref. [13].

The open circuit potentials (OCP) were measured for duration of 12 h. The polarization curves of various alloys were obtained by exposing them into corrosion media. The polarization curves were used to estimate the corrosion and breakdown potentials (E_{corr} , E_{bp}), and corrosion current density (i_{corr}) at E_{corr} by the Tafel extrapolation. The EIS were carried out at open potential with the amplitude of 10 mV over the frequency range of 100 kHz - 0.1Hz. The specimens were exposed to the corrosion media

at different times, viz., 2, 4, 6, 8 and 12 h, to investigate the mechanism of corrosion. The EC-Lab software was employed to fit the EIS by the equivalent circuit.

2.3 Phase identification and microstructural characterization

The microstructure of BE-Mg-1.0Zn-*x*Ca (BE-MZ*x*C) before and after corroded was studied by optical microscopy. The samples were prepared by standard metallographic procedures and were etched in picral. After the samples were exposed into SBF for 12 h, corrosion morphology observation and ingredient identification of the corrosion products were carried out by energy dispersive spectrum (EDS).

3. RESULTS AND DISCUSSION

3.1 Microstructures



Figure 1. Microstructures of BE-MZxC, (a) *x*=0.2; (b) *x*=0.5; (c) *x*=0.8; (d) *x*=1.0

The microstructures of BE-MZxC alloys are shown in Fig. 1. The microstructures of the alloys are homogeneous and uniform. All the specimens are composed of regular equiaxed grains with some black precipitates in the grain interior or along the grain boundary. The average grain size is decreased with the increment of Ca content. The value of BE-MZ0.2C alloy is about $25 \pm 5 \mu m$, which is 1.7 times as high as that of BE-MZ1.0C alloy. Furthermore, a large number of fine grains in the triple junction are detected in BE-MZ1.0C alloy owing to the dynamic recrystallization. With increasing the concentration of Ca, the fraction of secondary precipitates is increased correspondingly. Thus, the

more precipitates can act as effective cores to form new grain during the dynamic recrystallization, leading to the reduction of grain size. In addition, some twins are clearly observed in BE-MZ0.2C alloy in contrast to other three samples. It reveals that the addition of Ca can impede the formation of twin during the mechanical polishing. The similar results are also found in other Mg alloys [14].

3.2 Electrochemical behavior



Figure 2. Evolution of open circuit potentials as a function of exposing time for BE-MZ*x*C in different solutions, (a) 0.9NaCl; (b) 3.5NaCl; (c) SBF

Fig. 2 shows the time dependence of the potential in BE-MZxC alloys immersed in different media, where OCPs of alloys in both 0.9NaCl and 3.5NaCl show the similar tends. Namely, the potential drifts rapidly toward the noble side at the initial stage of immersion, and then follows by a slight fluctuation. Furthermore, the addition of Ca element is attributed to enhance the potential of the alloys in both of the two solutions. Conversely, as the immersion time is increased, the continuous increment of potential is observed in SBF during the whole immersion process. It is demonstrated the corrosion mechanisms of the alloys in NaCl and SBF solutions are different. The amount of Ca hardly plays a role on OCP in SBF.

The OCP usually varies with the immersion time because of the changed composition of the surface during exposure to a corrosion medium. Basically, OCP is determined by both the anodic and cathodic reactions [15]. As soon as the alloy is immersed into NaCl and SBF media, electrochemical reactions generate on the surface of the alloy with the formation of a passivation layer. And then the anodic current decrease and the OCP shifts toward noble side. Finally, both OCP and anodic current maintain at a steady level accordingly providing a stable passivation layer is achieved [16]. In addition, the fluctuation is elucidated of the occurrence of pitting corrosion or the process of depassivation-repassivation caused by the loss and re-growth of the passivation layer [17]. The slightly increment of the potential in SBF is associated to the infections of buffer solution on passivation behavior.

| Table 2. Evaluated corrosion potential (E_{corr}) and breakdown potential (E_{bp}), passive potential r | egion |
|--|-------|
| (ΔE) [mV] and corrosion current density (i_{corr}) [×10 ⁻⁵ mA/mm ²] | - |

| Alloys | 0.9NaCl | | | 3.5NaCl | | | SBF | | |
|--------|-------------------|-------------------|----------|-------------------|-------------------|----------|-------|-------------------|-----------------|
| | E _{corr} | I _{corr} | E_{bp} | E _{corr} | I _{corr} | E_{bp} | Ecorr | I _{corr} | E _{bp} |
| MZ0.2C | -1524 | 1.482 | -815 | -1575 | 0.907 | -1448 | -1569 | 1.411 | -1500 |
| MZ0.5C | -1529 | 0.167 | -960 | -1569 | 1.658 | -1452 | -1538 | 0.079 | -1513 |
| MZ0.8C | -1537 | 0.816 | -1106 | -1527 | 0.112 | -1353 | -1505 | 0.048 | -1504 |
| MZ1.0C | -1411 | 0.432 | -729 | -1496 | 2.290 | -1368 | -1449 | 0.205 | -1178 |

The potentiodynamic polarization behaviors of BE-MZxC in different solutions are shown in Fig. 3. The E_{corr} , i_{corr} and E_{bp} were derived from the plots by Tafel extrapolation. The detailed values are shown in Table 2. As far as E_{corr} is concerned, four alloys exhibit the similar trends in three solutions. With the increased Ca content, the E_{corr} shifts towards the positive position. Namely, compared with other three samples, the increment of E_{corr} is related to the passivative behavior [18]. In this work, the ΔE is decreased with the increment of Ca content. It starts to slightly increase after reaching the inflexion value. Namely, the approximate "V-shaped" trend is observed in three solutions. The corrosion rate is generally determined by the i_{corr} [19]. The corrosion rate is reduced with the addition of micro-alloying Ca when the content of Ca is less than 1.0 wt. %. For example, the corrosion current density of BE-MZ0.2C is $1.482 \times 10^{-5} \text{ mA/mm}^2$, which is 1.8 time as high as that of BE-MZ0.8C in 0.9NaCl.



Figure 3. Potentiodynamic polarization curves of BE-MZxC alloys immersed in the (a) 0.9NaCl; (b) 3.5NaCl; (c) SBF



Figure 4. Nyquist diagrams of BE state (a) MZ0.2C; (b) MZ0.5C; (c) MZ0.8C; (d) MZ1.0C exposed to 0.9NaCl for different immersion times



Figure 5. Nyquist diagrams of BE state (a) MZ0.2C; (b) MZ0.5C; (c) MZ0.8C; (d) MZ1.0C exposed to 3.5NaCl for different immersion times



Figure 6. Nyquist diagrams of BE state (a) MZ0.2C; (b) MZ0.5C; (c) MZ0.8C; (d) MZ1.0C exposed to SBF for different immersion times



Figure 7. Equivalent electrical circuit models for BE state (a) MZxC (*x*=0.2, 0.5, 0.8); (b) MZ1.0C alloys in 0.9NaCl and 3.5NaCl; (c) MZxC (*x*=0.2, 0.5, 0.8, 1.0) alloys in SBF



Figure 8. Non-linear least square fitting obtained for the EIS data of BE-MZxC (*x*=0.2, 0.8) in (a) 0.9NaCl; (b) 3.5NaCl; (c) SBF

The EISs of BE-MZxC alloys were detected after immersion in different solutions for different time. Four alloys exhibit the similar trend in both 0.9NaCl and 3.5NaCl (Fig. 4 and Fig. 5). Namely, when the Ca content is lower than 1.0 wt. %, the EIS mostly contains a capacitive loop in high frequency (HF) and medium frequency (MF). However, an inductive loop in low frequency (LF) is also detected in BE-MZ1.0C alloy apart from a capacitive loop in HF and MF. In the case of SBF solution (Fig. 6), the same configuration of EIS of the four samples is identified. The EIS is mostly composed of two capacitive loops in HF and MF and an inductive loop in LF. It is well known that a HF capacitive loop is mostly associated with the charge transfer resistance and double layer capacitance at the metal/solution interface [20]. The capacitive loop at MF is related to the diffusion of ions through the corrosion product layer. The inductive behavior at LF is generally attributed to high concentration of Mg ions on relatively film-free areas or with an intermediate step in the corrosion process involving the presence of adsorbed surface species. The existence of inductive loop commonly displays the occurrence of pitting corrosion [21].



Figure 9. Resistances of BE-MZxC (x= 0.2, 0.5, 0.8, 1.0) estimated from the Nyquist diagram in (a) 0.9NaCl; (b) 3.5NaCl; (c) SBF

To analyze the EIS spectra of BE-MZxC alloys, the equivalent electrical circuit models are shown in Fig. 7. For 0.9NaCl and 3.5NaCl, the fitting plots can be represented by $R_s(CPE_1R_{ct})(CPE_2(W_1R_w))$. The BE-MZ1.0C can be represented by $R_s(CPE_1R_{ct})(CPE_2(L_1R_L))$. In the case of immersion in SBF solution, the model turned to be $R_s(CPE_1R_{ct})(CPE_2(R_f(R_LL_1)))$. In all of the

equivalent circuits, R_s was solution resistance. Since the Nyquist plots exhibited depressed semicircles, the constant phase elements (CPE_1 and CPE_2) were employed instead of C_{dl} in the proposed model. CPE₁ and R_{ct} in parallel were attributed to the charge transfer resistance and capacitance in the electric double layer, respectively. W₁ was Warburg diffusion element. R_w was the Warburg resistance. W₁ and CPE₂ were in parallel, which accounted for the corrosion process of film-free areas dominated by the diffuse procedure. R_f and CPE₂, were introduced for the capacitance and resistance of the mass transfer procedure in the matrix. To account for the inductive behavior, an inductor, L₁ and a resistance, R_L were introduced into the second and third models. The fitting obtained for the EIS data of the BE-MZxC (x=0.2, 0.8) are shown in the Fig. 8. The validity of the model was confirmed based on the better non-linear least square fitting of the experiment date within 5% error. The detailed data for the fitting are shown in Fig. 9. The corrosion resistance immersed into the solutions is increase with the increment of the immersion time. It indicates that the BE-MZxC alloys can be well resistant to the corrosion medium during a certain long time despite of the composition of the medium. The BE-MZ1.0C shows a lower resistance in all the corrosion media compared with the other samples. In the 0.9NaCl and SBF, the corrosion resistance is enhanced by the addition of Ca when the content is no more than 0.5 wt. %. However, BE-MZ0.8C shows the most resistance among all the samples in 3.5NaCl.

3.3 Corrosion mechanism



Figure 10. (a) SEM graph of the surface morphology; (b) optical microstructure of cross section of the BE-MZ1.0C alloys after immersed in SBF for 12 h

The microstructure of the corroded BE-MZ1.0C immersed in SBF for 12 h is shown in Fig. 10. After immersed in corrosion media for 12 h, the surface of the sample was covered by a film of corrosion products. Some circular-like oxides were segregated on the surface (Fig. 10a). Some small pits were found among the corrosion products. Furthermore, the corrosion expands along the grain boundaries (Fig. 10b). It reveals that the pitting corrosion emerges during the corrosion process.



Figure 11. EDX of the different sections on the surface, (a) the etch pit; (b) the film-free area; (c) the mass of corrosion products.

SEM morphology and the chemical composition of different areas on the surface of BE-MZ1.0C are shown in Fig. 11. The Ca concentration in etched pit (noted A) is lower than other area (noted B and C). On the contrary, the contents of Zn and Mg in "A" area are higher. It demonstrates that the addition of Ca was dissolved into the medium or segregated in corrosion products (noted C). The relative concentration of both Zn and Mg is enhanced since the dissolution of Ca. According to the result of cross section (Fig. 10b), it can be confirmed that the aggregated Ca near to the grain boundaries during the solidification acts as the cathode during the immersion process.

The maximum solid solubility of Ca in Mg matrix is 1.34 wt. % at 516 °C [22]. When the added content is lower than 0.8 wt. %, the Ca is well distributed in the matrix. At the same time, due to the high chemical activity, the impurities, such as Fe, Ni and Cu, can be effective separated from the melt by formation of compounds. Therefore, anti-corrosion properties are improved correspondingly. For example, Ca element is one of effective slag agents in the smelting industry of iron [23]. Conversely, when the content of Ca is 1.0 wt. %, it is prone to form the secondary phase (Mg₂Ca) in MZ1.0C alloy during the solidification. The increased fraction of particle accelerates the pitting

corrosion. Consequently, the anti-corrosion properties are decreased in BE-MZ1.0C alloy. The similar phenomena have also been confirmed in other Mg alloys [24].

4. CONCLUSIONS

•The addition of 1.0 wt. % Ca can significantly promote the dynamic recrystallization, leading to the grain refining.

•The potential shifts to positive direction as the content of Ca is increased based on the results of open circuit potential and polarization curves.

•As the concentration of Ca is increased, backward extruded Mg-1.0Zn-xCa exhibits concaveshaped trend in three solutions. Namely, the corrosion rate is decreased by getting rid of impurities at the initial stage, and then increased with the formation of secondary phase.

•The backward extruded Mg-1.0Zn-0.5Ca alloy exhibits the most anti-corrosion properties in both 0.9 wt. % NaCl and SBF solutions, while it turns to backward extruded Mg-1.0Zn-0.8Ca in 3.5 wt. % NaCl solution.

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