A High-Strength and Biodegradable Zn–Mg Alloy with Refined Ternary Eutectic Structure Processed by ECAP

He Huang¹ · Huan Liu^{1,2} · Li-Sha Wang¹ · Yu-Hua Li^{1,4} · Solomon-Oshioke Agbedor¹ · Jing Bai³ · Feng Xue³ · Jing-Hua Jiang¹

Received: 14 November 2019 / Revised: 12 December 2019 / Published online: 12 March 2020
© The Chinese Society for Metals (CSM) and Springer-Verlag GmbH Germany, part of Springer Nature 2020

Abstract

In this study, the microstructure, mechanical properties and corrosion behaviors of a Zn–1.6Mg (wt%) alloy during multi-pass rotary die equal channel angle pressing (RD-ECAP) processing at 150 °C were systematically investigated. The results indicated that a Zn + Mg₂Zn₁₁ + MgZn₂ ternary eutectic structure was formed in as-cast Zn–Mg alloy. After ECAP, the primary Zn matrix turned to fine dynamic recrystallization (DRX) grains, and the network-shaped eutectic structure was crushed into fine particles and blended with DRX grains. Owing to the refined microstructure, dispersed eutectic structure and dynamically precipitated precipitates, the 8p-ECAP alloy possessed the optimal mechanical properties with ultimate tensile strength of 474 MPa and elongation of 7%. Moreover, the electrochemical results showed that the ECAP alloys exhibited similar corrosion rates with that of as-cast alloys in simulated body fluid, which suggests that a high-strength Zn–Mg alloy was successfully developed without sacrifice of the corrosion resistance.

Keywords Zn–Mg alloy · Equal channel angular pressing · Eutectic structure · Mechanical property · Corrosion behavior

1 Introduction

Nowadays, biodegradable metallic materials (BMMs), such as zinc (Zn) [1–4], iron (Fe) [5], magnesium (Mg) [6–8] and their related alloys, have received much attention in both vascular and orthopedic applications due to their superior mechanical properties and biocompatibility. In particular, zinc and its alloys are known as the novel generation of BMMs, owing to their moderate corrosion rates and

essential element in the human body [3, 9]. However, pure zinc metal could hardly meet the requirements of mechanical properties for metallic implants [10]. It is generally accepted that the metallic implants should possess a relatively high tensile yield strength (TYS > 200 MPa) and ultimate tensile strength (UTS > 300 MPa), as well as adequate ductility. Moreover, the biodegradable metallic materials need to keep their integrity of mechanical properties in 3–6 months and be completely degraded after 12 months, which means their corrosion rates in human body should be in a proper range [11, 12]. Therefore, it is necessary to improve the mechanical properties of Zn alloys and tailor their corrosion behaviors for wider applications.

Alloying and plastic processing are two efficient methods to enhance the mechanical properties of metallic materials [13–15]. At present, the additions of Mg [16–22], Li [23, 24], Ca [25, 26], Mn [27, 28], Cu [29, 30], Sr [26] and Ag [31] elements in Zn matrix have been investigated, which suggests that the strength of Zn alloys could be enhanced via grain refinement and strengthening of various second phases. Among these alloys series, Zn–Mg-based alloys have been widely researched. Nevertheless, the highest strength of as-cast Zn–Mg alloys was still lower than 200 MPa [23–25,

Available online at <http://link.springer.com/journal/40195>.

✉ Huan Liu
liuhuanseu@hhu.edu.cn

✉ Jing Bai
baijing@seu.edu.cn

¹ College of Mechanics and Materials, Hohai University, Nanjing 210000, China

² Ocean and Coastal Engineering Research Institute, Nantong 226300, China

³ College of Materials Science and Engineering, Southeast University, Nanjing 211189, China

⁴ Suqian Research Institute of Hohai University, Suqian 223800, China

27]. As a result, subsequent processing is still needed to further increase the strength of Zn–Mg alloys.

Plastic deformation with large strains usually leads to grain refinement, fragment of second phases, elimination of segregation, etc., which could effectively improve the strength of metallic materials [13, 25, 32, 33]. In particular, as one of the severe plastic deformation (SPD) methods, equal channel angular pressing (ECAP) could produce bulk ultra-fine-grained (UFG) metallic materials without changing the shape of samples [34], thus exhibiting great potentials in industrial fields. Recent studies have already proved the beneficial effect of ECAP on refinement and enhancement of Zn metals [21, 35]. Unfortunately, little work concerns the refinement of Zn alloys with large volume fractions of second phases during ECAP. Therefore, in the present study, we systematically investigated the effect of multi-pass ECAP on the microstructure evolutions and mechanical properties of a high-Mg-content Zn–Mg binary alloy. Moreover, as corrosion behavior is an issue of great concern for biodegradable metallic materials, we also explored the corrosion behaviors of Zn–Mg ECAP alloys in simulated body fluid (SBF) via the electrochemical analysis.

2 Experimental

2.1 Preparation of Zn–Mg Alloys

The as-cast Zn–Mg alloy ingot was prepared from pure Zn (99.90 wt%) and pure Mg (99.95 wt%) metals. After melting in a low-carbon steel crucible under the protection of a mixed atmosphere of CO₂ and SF₆ (99:1), the molten metal was poured into a water cooling copper mold with an inner diameter of 60 mm and a length of 250 mm. Before melting, the crucible and all iron tools were coated with a protective layer via the mixture consisting of zinc oxide, sodium silicate and deionized water (mass ratio of 3:1:6). The chemical composition of the alloy was analyzed to be Zn-1.66 wt% by a MAXx LMF15 electric spark optical emission spectrometer. Cuboid samples with dimension of 20 mm × 20 mm × 45 mm were then cut from the ingot for subsequent plastic processing. ECAP processing was carried out at 150 °C in a rotary die (RD). Figure 1 illustrates the schematic diagram of the rotary die. After each pass of ECAP, rotate the die 90° along the direction marked in Fig. 1 to prepare for the next pass. Therefore, it is apparent that multi-pass ECAP could be easily realized by this rotary die without taking the sample out and in after each pass of pressing. In current study, the ECAP numbers were set as 4 and 8, respectively. Before the first pass and after four passes of ECAP, the die and the sample together were reheated and kept at 150 °C for 10 min.

Fig. 1 Schematic diagram of RD-ECAP processing

2.2 Microstructure and Mechanical Characterization

The microstructure of as-cast and ECAP alloys was characterized by an Olympus BHM optical metallographic microscope (OM) and a Sirion field emission scanning electron microscope (SEM) equipped with a GENESIS 60S X-ray energy spectrometer (EDS). The metallographic and SEM samples were prepared by mechanical grinding, polishing and etching. (The etchant was 4 wt% nitric acid in alcoholic solution.) The phase constitution of as-cast alloy was analyzed using a D8 DISCOVER X-ray diffractometer (XRD) with a copper target at a scanning speed of 3 deg min⁻¹ in scanning angle of 10°–90°. To further investigate the morphology of second phases and DRX grains, TEM observations were conducted by a Tecnai G2 transmission electron microscope. The TEM samples were prepared by twin-jet electron polishing in a 4 wt% perchloric acid alcohol solution. Moreover, the ECAP samples were also characterized by the electron back scattered diffraction (EBSD) to evaluate the grain size distribution and texture evolution.

Tensile tests of as-cast and ECAP alloys were carried out by a CMT-5105 electronic universal testing machine at room temperature at a strain rate of 1.1 × 10⁻³ s⁻¹. Dog-bone tensile samples with the gauge dimension of 7.5 mm × 2 mm × 2 mm were machined from both as-cast and ECAP alloys with the loading direction parallel to the ECAP ram direction. Three parallel specimens were employed, and the mean values were calculated as tensile properties for each processing state.

2.3 Electrochemical Corrosion Measurements

Electrochemical experiments were performed by a CHI660C electrochemical workstation, which was equipped with the classical three electrodes in an electrochemical cell. The electrochemical samples were ground by SiC papers (400–2000 grit) first, followed by a polishing treatment with diamond suspension. The mounted samples were polished and then ultrasonically cleaned in ethanol, and the area of 10 mm × 10 mm was exposed in simulated body fluid (SBF) at 37 °C. The detailed chemical composition of SBF is listed as follows: NaCl (8 g L⁻¹), KCl (0.4 g L⁻¹), CaCl₂ (0.14 g L⁻¹), NaHCO₃ (0.35 g L⁻¹), glucose (1 g L⁻¹), MgCl₂·6H₂O (0.1 g L⁻¹), MgSO₄·7H₂O (0.06 g L⁻¹), Na₂HPO₄·12H₂O (0.06 g L⁻¹) and KH₂PO₄ (0.06 g L⁻¹), and the value of pH should be kept at 7.4 [5]. When the working electrode was immersed in the SBF solution, the polarization curves were measured by sweeping the potential ranging from −1.5 V (vs. SCE) to −0.6 V at a scan rate of 0.1 mV s⁻¹. The analytical method described by Wu et al. [36] was employed to obtain the corrosion current density. Then, the corrosion rate (CR) of all alloys could be calculated by using Eq. (1):

$$CR = 3.27 \times 10^{-3} \frac{i_{\text{corr}} EW}{\rho}, \quad (1)$$

where i_{corr} is the corrosion current density, EW is the equivalent weight and ρ is the density of the alloy. After electrochemical experiments, the samples were taken out from the SBF solution, cleaned in ethanol and then subjected to SEM observation to characterize the corrosion morphologies.

3 Results and Discussion

3.1 Microstructure of As-Cast and ECAP Alloys

Figure 2 shows the XRD pattern of as-cast Zn–1.6Mg alloy. Two phases were mainly indexed: the Zn matrix and Mg₂Zn₁₁ second phase. Moreover, as shown in the enlarged region of Fig. 2, the tiny peaks of MgZn₂ phase were also detected at the angles between 40° and 45° [37]. Therefore, a three-phase microstructure was identified in this Zn–1.6 Mg alloy.

Figure 3a shows the optical microstructure of as-cast Zn–Mg alloy. The primary phase displays light color, which is surrounded by the continuous network-shaped second phase (dark region). As shown in its enlargement of SEM image (Fig. 3b), the dark region exhibits the typical feature of eutectic structure. EDS results of the matrix (Marked by capital letter A) and eutectic structure (marked by B) are

Fig. 2 XRD spectrum of as-cast Zn–1.6Mg sample. Inset is the enlargement of the marked rectangle region with 2θ angle between 40° and 45°

shown in Fig. 3c and d, respectively. Most of Mg is present in the eutectic structure, while little left within Zn matrix, which is consistent with Zn–Mg binary phase diagram [24]. According to Prosek et al. [38], the eutectic structure was often regarded as Zn + Mg₂Zn₁₁ phases. In this study, since MgZn₂ phase was detected in XRD, further TEM analysis was necessary to confirm the existence of MgZn₂ phase.

Figure 3e shows the TEM micrograph of eutectic structure, and it is apparent that the eutectic contains cellular Zn phase and continuous Zn–Mg phase frameworks. The Zn grains within eutectic structure range from a few hundred nanometers to several micrometers, which are obviously finer than primary Zn grains. Moreover, Figure 3f shows that the Zn–Mg second phase region in the eutectic structure exhibits nanocrystalline morphology, which is rarely reported in other literature of eutectic microstructure. The corresponding selected area electron diffraction (SAED) pattern shown in Fig. 3f demonstrates the coexistence of Mg₂Zn₁₁ phase and MgZn₂ phase. The diffraction spots demonstrate the existence of Mg₂Zn₁₁ phase, while the diffraction rings suggest the MgZn₂ nanocrystalline particles. The EDS result of Fig. 3f indicates the nanocrystalline particles possess the composition of Zn–6.6 wt% Mg alloy, which further confirm that the nanocrystalline particles are MgZn₂ phase (as the analyzed composition has higher Mg content than the stoichiometric value of Mg₂Zn₁₁). Therefore, it is rational to believe that the MgZn₂ nanoparticles and the Mg₂Zn₁₁ phase are formed together during solidification; namely, a three-component eutectic structure with Zn + Mg₂Zn₁₁ + MgZn₂ phases was observed in this alloy. According to the report of Ref. [38], MgZn₂ phase was observed in Zn–4 wt% Mg and Zn–8 wt% Mg alloys with

Fig. 3 Microstructures of as-cast alloy: **a** optical image; **b** SEM image; EDS results of **c** A area, **d** B area marked in **b**; **e** low-magnification, **f** high-magnification TEM images of the eutectic structure and insets of **f** are the corresponding SAED patterns of second phase within eutectic structure and the EDS result of nanocrystalline particles

higher Mg contents. As for this work, although the content of Mg is lower than 2 wt%, MgZn₂ phase was still identified, which might be resulted from the non-equilibrium solidification caused by the fast cooling rate of water cooling copper mold casting.

Figure 4 shows the SEM microstructures of deformed alloys after four and eight passes of ECAP. Multi-pass

ECAP promotes the refinement of microstructure gradually. The lamellar eutectic structure existed in as-cast alloy is crushed into fine particles after ECAP. Although some large Zn matrix grains and uncrushed eutectic structure regions could be observed in 4p alloy, they are further refined and tend to disappear in 8p alloy.

Fig. 4 SEM microstructures of Zn–Mg alloys after **a** four passes, **b** eight passes of ECAP processing

Fig. 5 EBSD analysis results of ECAP alloys: inverse pole figure maps of **a** 4p, **b** 8p alloys; **c** recrystallization distribution; **d** Schmid factor distribution; inverse pole figure textures of **e** 4p, **f** 8p alloys

To identify the grain size distribution and texture evolution of Zn–1.6 Mg alloy during ECAP processing, Fig. 5 shows the EBSD analysis results. As shown in the inverse

pole figure (IPF) maps of ECAP alloys (Fig. 5a, b), coarse grains with sizes larger than 50 μm could be observed in 4p alloy, while they are hardly detected for 8p alloy. The grain

size statistics of Fig. 4a and b reveal that the average grain sizes for 4p- and 8p-ECAP alloys are 12.6 μm and 8.3 μm , respectively. Figure 5c illustrates the distribution of dynamic recrystallization (DRX) grains, sub-grains and deformed grains, and it shows that 8p alloy possesses higher volume fraction of DRX grains. As shown in Fig. 5d, the 8p alloy exhibits a Schmid factor value of 0.41, which is also larger than that of 4p alloy (0.36). It is widely accepted that DRX grains show relative random orientations when compared with deformed grains in as-deformed HCP alloys [39, 40]. Consequently, higher volume fraction of DRX grains results in larger Schmid factor value of deformed alloy, consistent with the results of ECAP alloys obtained in this study. Furthermore, as shown in the inverse pole figures of ECAP alloys shown in Fig. 5e, f, both the 4p- and 8p-ECAP alloys exhibit weak texture intensities. The 4p alloy shows a basal texture with ECAP direction (ED)// $\langle 0001 \rangle$, while the ED deviated some angles away from $\langle 0001 \rangle$ for 8p alloy.

Figure 6 illustrates the typical TEM morphologies of crushed eutectic region and Zn matrix region after ECAP processing. Figure 6a shows that some of the eutectic structures in 4p alloy still exhibit network shape, though they are distorted to some extent. By contrast, most of the eutectic structures were crushed into fine particles after 8p-ECAP, as shown in Fig. 6b, which is consistent with the SEM images mentioned above. Owing to the high temperature employed in ECAP, the Zn grains and MgZn_2 nanocrystalline particles within the eutectic regions grew slightly when compared with as-cast alloy. As for primary Zn matrix, dynamic recrystallization occurred in both 4p and 8p alloys, and their grain sizes are usually in the range of 2–5 μm , as shown in Fig. 6c. Moreover, Fig. 6d shows that abundant precipitates were formed in a Zn grain within eutectic regions, which could be dynamically precipitated during multi-pass ECAP due to the combined large strains and high processing temperature. According to our previous study, these

Fig. 6 TEM images of eutectic structure in **a** 4p-, **b** 8p-ECAP alloys, **c** the DRX grains in primary Zn matrix, **d** dynamic precipitates within Zn grains in eutectic regions

precipitates are MgZn metastable phase [41]. However, it should be noticed that these precipitates are barely observed in DRX grains of primary Zn regions (shown in Fig. 6c), which might be caused by the segregation of Mg atoms in primary Zn region and eutectic Zn region. For eutectic Zn grains, parts of Mg–Zn second phases distributed around could supply Mg atoms for the precipitation of Mg–Zn particles during processing at elevated temperature.

3.2 Mechanical Properties of As-Cast and ECAP Alloys

Figure 7a shows the typical tensile engineering stress–strain curves of as-cast and ECAP alloys. The as-cast Zn–1.6Mg alloy exhibits an ultimate tensile strength (UTS) of 125 MPa and an elongation to failure of only 1%. After ECAP, both the strength and ductility of the alloys were improved simultaneously. The 4p-ECAP alloy shows slight ductility, while the 8p-ECAP alloy exhibits obvious improved ductility. Overall, the 8p-ECAP alloy possesses the optimal mechanical properties, with the UTS and elongation to failure of 474 MPa and 7%, respectively.

In addition, Fig. 7b shows the comparison of tensile properties of Zn–Mg binary alloys obtained in this study with those that have been developed in recent years [17, 24, 35, 42]. Generally, the 8p-ECAP Zn–1.6Mg alloy exhibits the highest ultimate tensile strength (UTS), which suggests the great potential of multi-pass on improving the strength of Zn–Mg alloys. In case of the ductility, although the ECAP alloy shows poorer elongation to failure than most of the reported Zn–Mg alloys, an obvious increase has been obtained when compared with that of as-cast alloy.

As proved by former microstructure characterizations, multi-pass RD-ECAP mainly introduces two obvious

microstructural evolutions, i.e., crush of eutectic structures, and refinement of Zn matrix via DRX. Both these two processes contribute to finer microstructure, and the fine microstructure becomes even more uniform with increasing ECAP passes. Thus, fine-grained strengthening plays an important role via the Hall–Petch relationship. Furthermore, as shown in Fig. 5c and d, the grain (particles) sizes of the crushed eutectic region are much finer than the DRX Zn regions, forming a typical heterogeneous distribution. The strengthening and toughening effect induced by the heterogeneous microstructure has received much attention in recent years and was already confirmed in some Mg and Al alloys [43], which might also contribute to the improved mechanical properties of this ECAP alloy. In addition, the increase in elongation after ECAP could be ascribed to two factors. On the one hand, the microstructure is remarkably refined after ECAP, and higher volume fraction of DRX grains results in larger Schmid factor values of deformed alloys, which contributes to the increase in elongation [40]. On the other hand, the uniformity of the microstructure is enhanced gradually and the strain concentration during tensile could be released to some extent, especially at higher ECAP passes [44].

3.3 Corrosion Behaviors of As-Cast and ECAP Alloys

Figure 8 shows the potentiodynamic polarization curves of as-cast and ECAP Zn–1.6Mg alloys. There are two stages on each polarization curve: the cathodic reaction stage (left branch) and the anodic reaction stage (right branch). As for anodic stage, all three alloys show self-passivation characteristics because passivity plateaus exist on the right branch of the polarization curves. The breakdown potentials of as-cast and ECAP alloys are approximately equivalent, indicating that the multi-pass ECAP has no obvious effect on the

Fig. 7 **a** Typical tensile engineering stress–strain curves of Zn–1.6Mg alloys in this study, **b** comparison of mechanical properties with developed Zn–Mg alloys [17, 24, 35, 42]

Fig. 8 Potentiodynamic polarization (PDP) curves of Zn–1.6Mg alloys

The values calculated from polarization curves using Tafel fitting are listed in Table 1. According to the fitting data, the values of corrosion potential (E_{corr}) were increased a little after ECAP process, while they are very close for two ECAP alloys. Moreover, it is apparent that the calculated corrosion rate of 8p-ECAP alloy shows only tiny increase when compared with that of as-cast alloy. This result implies that multi-pass ECAP processing could significantly improve both the strength and ductility of Zn–1.6Mg alloy without sacrificing its corrosion resistance.

Figure 9 shows the SEM images of severely corroded surface morphologies of Zn–1.6Mg alloys after being subjected to the electrochemical test without removal of the corrosion products. It is apparent that a large number of pits with different sizes and depths were distributed on the sample surfaces, which indicates that the surfaces of Zn–1.6Mg alloys

Table 1 Electrochemical parameters of potentiodynamic polarization calculated by cathodic Tafel extrapolation

Sample conditions	Corrosion potential E_{corr} (V vs. SCE)	Current density i_{corr} (A/cm ²)	Corrosion rate (mm/year)
As-cast	-1.25 ± 0.01	$(6.42 \pm 0.31) \times 10^{-6}$	$8.71 \pm 4.25 \times 10^{-2}$
4p-ECAP	-1.20 ± 0.01	$(7.33 \pm 0.49) \times 10^{-6}$	$9.95 \pm 6.71 \times 10^{-2}$
8p-ECAP	-1.20 ± 0.02	$(6.91 \pm 0.31) \times 10^{-6}$	$9.37 \pm 4.25 \times 10^{-2}$

Fig. 9 SEM images of corrosion morphologies on the surface of Zn–1.6Mg alloys after electrochemical test: **a** as-cast, **b** 4p-ECAP, **c** 8p-ECAP

Table 2 EDS results of selected areas in Fig. 8

Area	Elements (wt%)					
	C	O	Mg	P	Ca	Zn
A	7.15	5.33	2.16	0.41	0.26	84.49
B	10.05	16.24	0.18	0.30	0.28	72.95
C	7.54	5.40	0.81	0.52	0.26	85.47
D	7.50	23.92	1.55	1.98	1.43	63.62
E	6.50	4.79	2.95	0.14	0.23	85.40
F	8.94	19.07	0.46	0.14	0.58	70.81

passivation behavior of the film surface. However, there is little difference in the left branch. The slopes of 8p-ECAP and 4p-ECAP alloys are lower than that of as-cast alloy, which suggests that the value of intersection used to calculate the corrosion current density is larger for ECAP alloys.

were corroded seriously. The related EDS results of different regions on the surfaces are also listed in Table 2. It can be seen that the main difference of compositions between the severely corroded region (marked by B, D and F in Fig. 9) and the flat

region (marked by A, C and E in Fig. 9) is the content of O element.

According to Ref. [4], the oxide film ($\text{Zn}(\text{OH})_2$ or ZnO) first generates during corrosion process, following the chemical reactions (2–4):

anodic reaction:

cathodic reaction:

overall reaction:

However, owing to the existence of chloride ions, carbonate ions, and phosphate ions in SBF solution, the equilibrium of oxide film on the surfaces of Zn–1.6Mg alloys could be rapidly destroyed. The destroyed oxide film of the surfaces would then cause sudden galvanic corrosion reaction (B, D and F regions in Fig. 9), which leads to the generation of abundant corrosion products containing carbonate and phosphate with higher O concentrations [45]. As for the flat surface, A, C and E regions in Fig. 9, the oxide films remained with relatively low O contents.

Moreover, comparing the corrosion morphologies of as-cast alloy with ECAP alloys, it can be concluded that the corrosion pits in the as-cast alloy are larger but shallower than ECAP alloys. The corrosion of the as-cast alloy was expanded along the surface of the sample, while that of the ECAP alloys seemed more inclined to develop from the surface to the internal. The morphology of corrosion pits might be influenced by the morphology and distribution of eutectic structure. Owing to the higher standard electrode potential of Mg element than Zn, $\text{Mg}_2\text{Zn}_{11}$ phase (eutectic structure) is more vulnerable to be eroded than Zn matrix [6]. Therefore, the propagation of corrosion pits might be extended along the boundaries of eutectic structures. In as-cast alloy, the eutectic structure exhibits network shape, making the corrosion pits easy spread covering the surface. As for ECAP alloy, corrosion pits tend to extend deeper, as the eutectic network was broken and dispersedly distributed. Nevertheless, despite the different surface corrosion morphologies, the corrosion rates remain in a relatively stable range for both as-cast and ECAP Zn–Mg alloys. Therefore, it is rational to conclude that a high-strength Zn–Mg alloy without sacrifice of corrosion resistance was developed via multi-pass ECAP processing in this work.

4 Conclusions

In the present study, the microstructure evolutions, mechanical properties and corrosion behaviors of a Zn–1.6Mg alloy during multi-pass ECAP were systematically investigated. The following conclusions can be drawn.

1. The microstructure of the as-cast alloy was composed of primary Zn matrix and $\text{Zn} + \text{Mg}_2\text{Zn}_{11} + \text{MgZn}_2$ ternary eutectic structure, where MgZn_2 nanocrystalline particles were located on the $\text{Mg}_2\text{Zn}_{11}$ phase. After multi-pass ECAP, dynamic recrystallization occurred in primary Zn regions, and the eutectic structures were crushed into fine particles and mixed with DRX grains.
2. The 8p-ECAP alloy exhibited the optimal mechanical properties with ultimate tensile strength of 474 MPa and elongation to failure of 7%. The enhanced strength of the ECAP alloys could be ascribed to the refined Zn grains, ultra-fine $\text{Mg}_2\text{Zn}_{11}$ particles, MgZn_2 nanocrystallines and a heterogeneous grain (particle) size distribution.
3. The electrochemical results indicated that the corrosion rates of as-cast and ECAP alloys were nearly in the same range. Corrosion pits were observed on the surfaces of all samples after electrochemical test. The formation of corrosion pits was mainly ascribed to the broken of oxide film by attacking of chloride ions, carbonate ions and phosphate ions in SBF solution.

Acknowledgements This work was financially supported by the National Natural Science Foundation of China (Nos. 51901068, 51774109), the Nantong Science and Technology Project (No. JC2018109) and the Key Research and Development Project of Jiangsu Province (No. BE2017148).

References

- [1] Y. Liu, Y.F. Zheng, B. Hayes, *Sci. China Mater.* **60**, 377 (2017)
- [2] H.S. Han, S. Loffredo, I. Jun, J. Edwards, Y.C. Kim, H.K. Seok, F. Witte, D. Mantovani, S.G. Jones, *Mater. Today* **23**, 57 (2019)
- [3] P.K. Bowen, J. Drelich, J. Goldman, *Adv. Mater.* **25**, 2577 (2013)
- [4] H.T. Yang, C. Wang, C.Q. Liu, H.W. Chen, Y.F. Wu, J.T. Han, Z.C. Jia, W.J. Lin, D.Y. Zhang, W.T. Li, W. Yuan, H. Guo, H.F. Li, G.X. Yang, D.L. Kong, D.H. Zhu, K. Takashima, L.Q. Ruan, J.F. Nie, X. Li, Y.F. Zheng, *Biomaterials* **145**, 92 (2017)
- [5] R.Y. Liu, R.G. He, Y.X. Chen, S.F. Guo, *Acta Metall. Sin. Engl. Lett.* **32**, 1337 (2019)
- [6] E. Mostaed, M. Sikora-Jasinska, J.W. Drelich, M. Vedani, *Acta Biomater.* **71**, 1 (2018)
- [7] H.F. Li, Y.F. Zheng, L. Qin, *Prog. Nat. Sci. Mater. Int.* **24**, 414 (2014)
- [8] H. Liu, H. Huang, J.P. Sun, C. Wang, J. Bai, A.B. Ma, X.H. Chen, *Acta Metall. Sin. Engl. Lett.* **32**, 269 (2019)
- [9] P.K. Bowen, E.R. Shearier, S. Zhao, R.J. Guillory, F. Zhao, J. Goldman, J.W. Drelich, *Adv. Healthc. Mater.* **5**, 1121 (2016)

- [10] K. Pięła, M. Wróbel, K. Sztwiertnia, M. Jaskowski, J. Kawałko, M. Bieda, M. Kiper, A. Jarzębska, *Mater. Des.* **117**, 111 (2017)
- [11] J. Venezuela, M.S. Dargusch, *Acta Biomater.* **87**, 1 (2019)
- [12] E.R. Shearier, P.K. Bowen, W. He, A. Drelich, J. Drelich, J. Goldman, F. Zhao, *ACS Biomater. Sci. Eng.* **2**, 634 (2016)
- [13] H.L. Jin, S. Zhao, R. Guillory, P.K. Bowen, Z.Y. Yin, A. Griebel, J. Schaffer, E.J. Earley, J. Goldman, J.W. Drelich, *Mater. Sci. Eng., C* **84**, 67 (2018)
- [14] X. Tong, D.C. Zhang, X.T. Zhang, Y.C. Su, Z.M. Shi, K. Wang, J.G. Lin, Y.C. Li, J.X. Lin, C. Wen, *Acta Biomater.* **82**, 197 (2018)
- [15] W.L.R. Santos, C.B. Cruz, J.E. Spinelli, N. Cheung, A. Garcia, *Mater. Sci. Eng., A* **712**, 127 (2018)
- [16] J. Kubásek, D. Vojtěch, E. Jablonská, I. Pospíšilová, J. Lipov, T. Ruml, *Mater. Sci. Eng., C* **58**, 24 (2016)
- [17] E. Mostaed, M. Sikora-Jasinska, A. Mostaed, S. Loffredo, A.G. Demir, B. Previtali, D. Mantovani, R. Beanland, M. Vedani, J. Mech. Behav. Biomed. **60**, 581 (2016)
- [18] D. Vojtěch, J. Kubásek, J. Šerák, P. Novák, *Acta Biomater.* **7**, 3515 (2011)
- [19] C. Shen, X.W. Liu, B. Fan, P.H. Lan, F.Y. Zhou, X.K. Li, H.L. Wang, X. Xiao, L. Li, S. Zhao, Z. Guo, Z.J. Pu, Y.F. Zheng, *RSC Adv.* **6**, 86410 (2016)
- [20] J. Kubásek, D. Vojtěch, I. Pospíšilová, A. Michalcová, J. Maixner, *Int. J. Miner. Metall. Mater.* **23**, 1167 (2016)
- [21] A. Jarzebska, M. Bieda, J. Kawałko, Ł. Rogal, P. Koprowski, K. Sztwiertnia, W. Pachla, M. Kulczyk, *Mater. Lett.* **211**, 58 (2018)
- [22] M.S. Dambatta, S. Izmana, D. Kurniawan, S. Farahany, B. Yahaya, H. Hermawan, *Mater. Des.* **85**, 431 (2015)
- [23] S. Zhao, J.M. Seitz, R. Eifler, H.J. Maier, R.J. Guillory, E.J. Earley, A. Drelich, J. Goldman, J.W. Drelich, *Mater. Sci. Eng., C* **76**, 301 (2017)
- [24] Y.L. Dai, Y. Zhang, H. Liu, H.J. Fang, D. Li, X.M. Xu, Y. Yan, L.J. Chen, Y.J. Lu, K. Yu, *Mater. Lett.* **235**, 220 (2019)
- [25] Y.L. Zou, X. Chen, B. Chen, *Mater. Lett.* **218**, 193 (2018)
- [26] H.F. Li, X.H. Xie, Y.F. Zheng, Y. Cong, F.Y. Zhou, K.J. Qiu, X. Wang, S.H. Chen, L. Huang, L. Tian, L. Qin, *Sci. Rep.* **5**, 10719 (2015)
- [27] P. Sotoudeh Bagha, S. Khaleghpanah, S. Sheibani, M. Khakbiz, A. Zakeri (2018) *J. Alloy. Compd.* **735**, 1319
- [28] W. Bednarczyk, M. Wątroba, J. Kawałko, P. Bała, *Mater. Sci. Eng., A* **748**, 357 (2019)
- [29] W. Bednarczyk, J. Kawałko, M. Wątroba, P. Bała, *Mater. Sci. Eng., A* **723**, 126 (2018)
- [30] J.L. Niu, Z.B. Tang, H. Huang, J. Pei, H. Zhang, G.Y. Yuan, W.J. Ding, *Mater. Sci. Eng., C* **69**, 407 (2016)
- [31] M. Sikora-Jasinska, E. Mostaed, A. Mostaed, R. Beanland, D. Mantovani, M. Vedani, *Mater. Sci. Eng., C* **77**, 1170 (2017)
- [32] L.Q. Wang, Y.F. He, H. Zhao, H.B. Xie, S. Li, Y.P. Ren, G.W. Qin, *J. Alloy. Compd.* **740**, 949 (2018)
- [33] H. Liu, H. Huang, C. Wang, J.P. Sun, J. Bai, F. Xue, A.B. Ma, X.B. Chen, *JOM* **71**, 9 (2019)
- [34] C. Wang, A.B. Ma, J.P. Sun, H. Liu, H. Huang, Z.Q. Yang, J.H. Jiang, *J. Alloy. Compd.* **793**, 259 (2019)
- [35] M.S. Dambatta, S. Izman, D. Kurniawan, H. Hermawan, *J. King Saud. Univ. Sci.* **29**, 455 (2017)
- [36] P.P. Wu, F.J. Xua, K.K. Deng, F.Y. Han, Z.Z. Zhang, R. Gao, *Corros. Sci.* **127**, 280 (2017)
- [37] X.W. Liu, J.K. Sun, F.Y. Zhou, Y.H. Yang, R.C. Chang, K.J. Qiu, Z.J. Pu, L. Li, Y.F. Zheng, *Mater. Des.* **94**, 95 (2016)
- [38] T. Prosek, A. Nazarov, U. Bexell, D. Thierry, J. Serak, *Corros. Sci.* **50**, 2216 (2008)
- [39] Z.T. Li, X.D. Zhang, M.Y. Zheng, X.G. Qiao, K. Wu, C. Xu, S. Kamado, *Mater. Sci. Eng., A* **628**, 423 (2017)
- [40] K. Huang, R.E. Logé, *Mater. Des.* **111**, 548 (2016)
- [41] H. Liu, H. Huang, Y. Zhang, Y. Xu, C. Wang, J.P. Sun, J.H. Jiang, A.B. Ma, F. Xue, J. Bai, *J. Alloy. Compd.* **811**, 151987 (2019)
- [42] S.Y. Liu, D. Kent, N. Doan, M. Dargusch, G. Wang, *Bioact. Mater.* **4**, 8 (2019)
- [43] J.P. Sun, Z.Q. Yang, J. Han, H. Liu, D. Song, J.H. Jiang, A.B. Ma, *Mater. Sci. Eng., A* **734**, 485 (2018)
- [44] J.P. Sun, Z.Q. Yang, J. Han, T. Yuan, D. Song, Y.N. Wu, Y.C. Yuan, X.R. Zhuo, H. Liu, A.B. Ma (2019) *J. Alloy. Compd.* **780**, 443
- [45] J.M. Byun, J.M. Yu, D.K. Kim, T.Y. Kim, W.S. Jung, Y.D. Kim, *Korean J. Met. Mater.* **51**, 413 (2013)