Improving the corrosion resistance of $MgZn_{1.2}Gd_xZr_{0.18}$ ($x = 0, 0.8, 1.4, 2.0$) alloys via Gd additions

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ABSTRACT

Effects of Gd addition on microstructure, corrosion behavior and mechanism of cast and extruded $MgZn_{1.2}Gd_xZr_{0.18}$ alloys are investigated through microstructure observation, weight loss and electrochemical tests. Increasing Gd from 0 to 2.0 at.%, grains are refined, $MgZn_2$ phase, W-phase and X-phase are formed successively, and basal texture intensity is decreased. The significantly decreased grain size by extrusion and Gd addition induces formation of protective Gd_2O_3 and MgO layer. The extruded $MgZn_{1.2}Gd_{2.0}Zr_{0.18}$ alloy shows decreased corrosion rate of 3.72 ± 0.36 mm/year, owing to fine and homogeneous microstructure, dual-role (micro-anode and barrier) of X-phase, compact oxidation layer and basal crystallographic texture.

Keywords: A. Magnesium; A. Rare earth elements; B. Polarization; B. XPS; C. Intergranular corrosion; C. Passive films

1. Introduction

Magnesium (Mg) alloys have received increasing potential for engineering applications, such as transportation industry, automobile, electronics and biomedical fields owing to their low density, excellent machinability, positive electromagnetic shield ability and excellent biocompatibility [1-5]. Moreover, as easily recycled and reusable green engineering material, magnesium alloys are clean to the environment without pollution and beneficial to the energy and environmental conservation [6-10]. Unfortunately, the inferior corrosion resistance severely limits the wide application of Mg alloys, which stems from their highly active nature and porous oxide layer [11-15].

In the past few decades, numerous researchers have attempted the alloying approach to enhance their mechanical properties, which is proved to be valid [16-18]. Zn is one of the candidates due to its relatively high solubility (6.2 wt.%) in Mg, and Mg alloys could achieve solid solution strengthening and second phase strengthening by adding Zn [19]. To date, Mg-Zn based alloys containing rare earth (RE) element Gd have exhibited superior comprehensive mechanical properties and creep resistance, related to the high solid solubility of Gd in Mg matrix and the formation of Mg-Zn-Gd ternary phases. For example, the tensile strength of 387 MPa and elongation of 23.2% were achieved in $Mg_{97.1}Zn_1Gd_{1.8}Zr_{0.1}$ (at.%) alloy after 16 passed equal channel angular pressing, mainly because of the generation of massive X-$Mg_{12}GdZn$ phase. [20]. Our previous research also obtained a superior plasticity of 863% at 250 °C and excellent room-temperature strength in Mg-7Zn-5Gd-0.6Zr (wt.%) alloy with quasicrystal I-phase [21]. The ultimate tensile strength, tensile yield strength and elongation of extruded ZK30 ($MgZn_{1.2}Zr_{0.18}$ (at.%)) alloy were about 300 MPa, 215 MPa and 9%, respectively [22]. However, the Gd containing $MgZn_{1.2}Gd_2Zr_{0.18}$ (at.%) alloy exhibited more outstanding mechanical properties (ultimate tensile strength, tensile yield strength and elongation were nearly 340 MPa, 230 MPa and 15%) than the extruded $MgZn_{1.2}Zr_{0.18}$ (at.%) alloy [23]. Furthermore, the porous oxide film is a vital factor for inferior corrosion resistance of Mg alloys and the second phases precipitation is also crucial for the micro-galvanic corrosion behavior [24-26]. Simultaneously, dependable information concerning the corrosion properties is limited and only a few scholars have focused on the relationship between the corrosion resistance and alloying element concentration of Mg-Zn-Gd alloys [27]. Generally, RE element Gd is famous as "refining element" because it owns + 3 valence and low electronegativity and primarily forms compounds with noble elements, such as Fe, Cu and so on [28]. Additionally, the Gd oxide film is also stable on corrosion interface and Gd compounds usually own lower potentials in order to reduce general potentials of the cathode phases [29-31]. Zhang *et al.* [32] elucidated that minor Gd addition in $MgZn_1Y_2$ (at.%) could refine the grain size and form complete network eutectic and large volume fraction of LPSO phase, resulting in better corrosion resistance, and the corrosion rate of cast $Mg_{96.5}Zn_2Y_1Gd_{0.5}$ (at.%) alloy was 11.55 mm/year in 3 wt.% NaCl solution through weight loss test. Wang *et al.* [33] also indicated that the corrosion resistance of Mg-4.75Zn-15.24Gd (wt.%) alloy was improved due to the dual-role of LPSO phase, i.e., anode during the micro-galvanic corrosion and corrosion barrier prevention. The corrosion rate of T6 treated

Mg-4.75Zn-15.24Gd (wt.%) alloy in 3.5 wt.% NaCl solution was decreased to 4.98 mm/y compared with the one under as-cast condition. Simultaneously, contradictory results also exist in other researches. Srinivasan expounded that dramatic micro-galvanic corrosion appeared in Mg-6Zn-10Gd alloy, and the alloy corrosion rate in 0.5 wt.% NaCl solution was over 40 mm/year, the reason was that lamellar LPSO phase acted as cathode and facilitated the filiform corrosion [34]. Liu *et al.* [35] observed that the deteriorated corrosion rate of cast Mg-2Zn-15Gd-0.39Zr alloy was mainly caused by the micro-cathode acceleration of β-(Mg, Zn)$_3$Gd eutectic phase and the LPSO structure X-phase. Miao *et al.* [36] proposed that the characteristic microstructures with numerous non-recrystallization grains and black band structure of extruded Mg-8Gd-2.4Zn (wt.%) alloy led to high ratio of anodic and cathodic regions and inferior corrosion rate of about 0.2 mm/year in Hank's solution through hydrogen evolution test. Based on the published reports, effects of various kinds and morphologies of second phases involving Gd element on the corrosion behaviors of Mg-Zn-Gd alloys are distinct from the alloy compositions and manufacturing technologies. Meanwhile, the corrosion mechanism variation may cause the misunderstanding on the corrosion rate. It's worth noting that the corrosion rates of above-mentioned alloys are much greater than intrinsic Mg (0.3 mm/year) in a concentrated chloride solution, because the alloying elements and second phases could always cause micro-galvanic corrosion to increase the corrosion rate. However, the comprehensive properties of these alloys should be considered for practical applications, and it is crucial to figure out how to improve the corrosion properties of Mg-Zn-Gd alloys by alloying elements and second phases adjustment. Consequently, it is necessary to carry out more systematic and practical researches about the corrosion behavior to investigate the corrosion mechanism and effect of second phases for significantly developed purpose of new structural and engineering Mg-Zn-Gd alloys.

Depending on Zn/Gd ratio, basically three ternary equilibrium phases emerge in the cast Mg-Zn-Gd alloys, namely W-$Mg_3Gd_2Zn_3$ phase, X-$Mg_{12}GdZn$ phase and I-Mg_3Zn_6Gd phase [37]. Although the strengthening and toughening mechanisms of several Mg-Zn-Gd alloys with X-phase or I-phase have been widely carried out, the available information concerning their corrosion properties and mechanism is incomplete. Subsequently, the cast and extruded $MgZn_{1.2}Zr_{0.18}$ alloys with different Gd concentrations of 0, 0.8, 1.4 and 2.0 at.% have been prepared in this work, where the relationship between corrosion mechanism and diverse kinds or contents of second phases was systematically evaluated. The aim of this work is to assess synergistic influence of alloy composition and processing method on the corrosion resistance, and to accelerate the development of Mg alloys that are especially suitable for the industrial application.

2. Experimental procedures

2.1. Materials

The cast $MgZn_{1.2}Zr_{0.18}$, $MgZn_{1.2}Gd_{0.8}Zr_{0.18}$, $MgZn_{1.2}Gd_{1.4}Zr_{0.18}$ and $MgZn_{1.2}Gd_{2.0}Zr_{0.18}$ alloys (in at.%, denoted as C0, C1, C2 and C3, respectively) were prepared by smelting Mg (99.98 wt.%), Zn (99.95 wt.%), and Mg-30 wt.% Zr intermediate alloys in a resistance furnace with a protected gas mixture of SF_6 and CO_2 at 710 °C. Then different contents of Mg-25 wt.% Gd intermediate alloys were added into molten Mg-Zn-Zr alloys to ensure the uniformity of other alloying elements [36]. The cast alloys (solidified in warm copper mold) were homogeneously treated at 430 °C for 12 h. Subsequently, the ingots were indirectly extruded at 400 °C into Φ 12 mm bars under the fixed extrusion ratio of 15, and the corresponding extruded alloys were expressed by E0, E1, E2 and E3, respectively. Chemical constituents of the alloys were detected through the inductively coupled plasma atomic emission spectrometry (ICP-AES; Varian 715-ES). The actual constituents are listed in Table 1. In all cases, the total concentration of Fe, Cu, and Ni impurities is lower than 3 ppm, demonstrating that they did not cause major corrosion response.

2.2. Immersion and electrochemical tests

The cast and extruded specimens for calculating weight loss and microstructure observation were performed through the immersion test. They were cut into cubes with the dimension of 10 mm × 10 mm × 5 mm, then grinded with several SiC papers and mechanical polishing. The immersion test was conducted at 25 ± 1 °C in 3.5 wt.% NaCl solution and the ratio of media volume to sample surface was 30 mL/cm^2 [23]. The tested NaCl solution was prepared through dissolving 72.5 g NaCl into 2000 mL distilled water, and then about 1 g $Mg(OH)_2$ was added into the solution and stewed for 2 h. Subsequently, the solution was stirred with a glass rod for 10 min to make it equilibrated, then it was filtered with a slow filter paper for three times to eliminate the impurities. The NaCl solution was saturated with $Mg(OH)_2$ before corrosion experiments to maintain a stable pH value. After 24 h immersion, specimens were cleaned with chromate acid containing 50 g CrO_3, 2.5 g $AgNO_3$ and 250 mL water, followed with ultrasonic cleaning, dried and weighted. The steady state corrosion rate obtained from the weight loss could be expressed as CR (mm/year) and calculated by the following formula on account of ASTM G31-72 [38]:

$$CR=\frac{8.76\times10^4\times\Delta g}{A\times t\times\rho} \tag{1}$$

Where Δg is the value of loss in weight (g), A refers to the sample surface area (cm^{-2}), ρ is the alloy density (g/cm^3), and t refers to the immersion time (h). The alloy density was evaluated on basis of Archimedes theory.

The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were acquired through a standard three-electrode cell electrochemical workstation (Princeton VersaSTAT 3F, AMETEK, lnc., USA) in 3.5 wt.% NaCl solution. A platinum plate electrode (CE) acted as the counter electrode and a saturated calomel electrode (SCE) was the reference electrode. Mg alloy specimen as the working electrode (WE) with surface area of 1 cm^2 was taken along the extruded longitudinal section. Potentiodynamic polarization curve was performed with a scan rate of 1 mV s^{-1} after stabilization at open-circuit potential (OCP) for 3600 s. Tafel extrapolation method on cathodic branches was applied to evaluate the corrosion current density (I_{corr}) at corrosion potential (E_{corr}). EIS was conducted from 100 kHz to 0.01 Hz frequency range under a 5 mV sinusoidal perturbing signal. The obtained Nyquist plots, Bode impedance and phase angle plots were fitted through ZView 3.10 software. The hydrogen evolution reflected Mg^{2+} dissolved to the solution, so the hydrogen evolution rates represented alloy corrosion rates to some extent. Consequently, the instantaneous corrosion rate (P_i) derived from the hydrogen volume measurement could be estimated through Tafel extrapolation of the cathodic branch curves by the following equation [39, 40]:

$$P_i = 22.85\, I_{corr} \tag{2}$$

Each measurement was carried out in triplicate to ensure reproducibility and reliability.

2.3. Microstructures characterization

The specimens for microstructures observation were mechanically ground and polished by diamond paste, then were etched by a picric acid and acetic acid solution. Microstructures and morphologies of corroded surfaces were observed by polarized microscopy (Olympus SX-53, Japan) and scanning electron microscope (SEM; Zeiss Ultra 55, Germany) equipped with an energy dispersive X-ray (EDX) analyzer. The phase identifications were carried out using an X-ray diffraction (XRD; D8 Advance, Germany). The diffraction peaks were normalized to quantitatively and qualitatively analyze the phases. The oxide layer on the alloy surface was probed with X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi, USA) with Al Kα radiation (1486.6 eV) and 150 W power after the alloy immersed for 2 h in 3.5 wt.% NaCl solution and 24 h quiescence in dried air. Data were obtained after 30 s ion etching. The profile of atomic percent of Mg, Gd, O and C elements was acquired by depth sputtering rate of 4.5 nm/min. All energy values were standardized on account of the adventitious C 1s signal (284.6 eV). The relevant result was processed by Xpspeak 4.1 software. The grain sizes and phases volume fractions were approximated by linear intercept method through more than ten fields of view with Image-Pro plus software. A scanning Kelvin probe force microscope (SKPFM; MFP-3D Asylum Research, Germany) was used to gauge the localized potential distribution, and the SKPFM results were manipulated using Asylum Research software. The electron back scattering diffraction (EBSD) tests were performed over longitudinal section of the specimens by Zeiss Ultra 55 microscopy with the step length of 0.5 μm. The acquired result was dealt with the orientation imaging microscopy software HKL-Channel 5 and the measured pole figures containing {0002} and {11-20}. The extruding direction (ED), transverse direction (TD) and normal direction (ND) represented different directions in extrusion.

3. Results

3.1. Microstructures analysis

Fig. 1 shows the XRD patterns of experimental alloys. It indicates that C1 and C2 alloys contain α-Mg matrix and W-$Mg_3Gd_2Zn_3$ phase, whereas the C3 alloy is composed of X-$Mg_{12}GdZn$ and minor Mg_5(Gd, Zn) phases. There is only a weak $MgZn_2$ phase diffraction peak detected in the C0 alloy, demonstrating it is composed of α-Mg matrix and minor $MgZn_2$ phase. During the hot extrusion deformation, $MgZn_2$ phase and W-phase show no obvious change but the Mg_5(Gd, Zn) phase is dissolved into the matrix. The intensity of X-phase diffraction peaks is stronger than those in cast condition due to the dynamic precipitation in the supersaturated solid solution [23].

Fig. 2 exhibits the microstructures and grain sizes distribution of the alloys. The cast alloys show typical equiaxed grains and the grain sizes decrease with increasing Gd concentration. The average grain sizes of the four cast alloys are 104 ± 10 μm, 74 ± 9 μm, 68 ± 11 μm and 57 ± 11 μm, respectively. Almost complete dynamic recrystallization happens during the hot extrusion deformation and the average grain sizes of the extruded alloys are obviously refined to 27 ± 3 μm, 7 ± 1 μm, 5 ± 1 μm and 3 ± 1 μm, respectively.

The representative SEM images are presented in Fig. 3. It is clearly seen in Fig. 3a$_1$ that some intermetallic phase particles distribute along the grain boundaries and its volume fraction is only 0.8%. According to the EDX analysis, the granular second phase is composed of Mg (35.26 at.%), Zn (64.55 at.%) and Zr (0.19 at.%). It could be confirmed that the intermetallic phase is $MgZn_2$ phase combined with the XRD results in Fig. 1. With the increase of Gd element, microstructures of C1 and C2 alloys are characterized by the white net-like eutectic structure at grain boundaries with the volume fraction of 14.8% and 18.7%, respectively, as shown in Fig. 3a$_2$ and a$_3$. EDX examination result taken at the net-like second phase regions is Mg (62.69 at.%), Zn (21.60 at.%) and Gd (15.69 at.%). The Zn to Gd ratio is 1.38, which is close to W-$Mg_3Gd_2Zn_3$ phase together with the XRD result (Fig. 1). Similarly, the volume fraction of white net-like W-phase is 18.1% in C3 alloy, and about 5.4% of the grey flaked structure is adjacent to the W-phase, which involves Mg-10.35 at.% Zn-9.46 at.% Gd as shown in Fig. 3a$_4$. The Zn/Gd ratio is 1.09, which is in accordance with X-$Mg_{12}GdZn$ phase showed in XRD result. The white particles in C3 alloy show very regular block shape. The EDS elemental analysis indicates that it consists of Mg (81 at.%) and minor Gd and Zn, and it is normally referred to as Mg_5(Gd, Zn) phase. The Mg_5(Gd, Zn) phase is almost dissolved and part of W-phase is changed into X-phase during the homogenization treatment of 430 °C for 12 h [23].

Through 400 °C extrusion, the second phases are crushed into very small particles and distributing parallel to ED. The volume fraction of $MgZn_2$ phase is also 0.8% after extrusion in E0 alloy (Fig. 3b$_1$). It is demonstrated in Fig. 3b$_2$ and b$_3$ that large volume fraction of block-like phase is the crushed W-phase and its chemical constitution is Zn (42.39 at.%) and Gd (27.13 at.%). The volume percent of W-phase is almost identical to the cast alloys. Meanwhile, X-phase is partly fractured into lamellar-like and several bulk-like W-phase could be observed inside the X-phase as displayed in Fig. 3b$_4$. Accordingly, the corresponding average grain sizes and second phase volume fractions are displayed in Fig. 4 and Table 2. It is clear that the grain sizes decrease sharply after the extrusion deformation and the volume fractions of second phases in C0 and E0, C1 and E1, C2 and E2 alloys are nearly identical in the cast and extruded conditions. The volume fraction of X-phase in E3 alloy is higher due to the phase transformation of W-phase during the homogenization and extrusion processes.

3.2. Corrosion behavior of cast and extruded alloys

3.2.1. Potentiodynamic polarization measurement

The OCP of the cast and extruded alloys is determined in 3.5 wt.% NaCl solution for a period of 3600 s to reveal the variation of electrode potential with soaking time, as displayed in Fig. 5a. The OCP *vs.* time curves could be divided into three stages. During the monitoring stage, the OCP values increase rapidly within 600 s and then gradually increase to approximately steady potentials. The values fluctuate within a narrow range with the increasing immersion time. The relatively steady OCP values are shown in Table 3, and the E3 alloy exhibits the most positive OCP value of -1.572 ± 0.015 V. It is noticeable for E3 alloy that a fluctuation occurs at about 3000 s and subsequently reaches another stable OCP value combined with discernible corrosion pits on the surface, which is due to the hydrogen bubbles formation on the surface and the following $Mg(OH)_2$ layer formation [41]. Additionally, the sudden decrease at the end of peak value for C1 and C3 alloys is probably attributed to the activation actions, such as Cl^- absorption on the native oxide film, a large amount of cathodic second phases in the matrix and "cathodic activation" ($2H_2O + 2e^- = 2OH^- + H_2$) reaction.

The potentiodynamic polarization experiment is performed to evaluate the instantaneous polarization response as described in Fig. 5b. Normally, the cathodic reaction is associated with hydrogen evolution ($H_2O + 2e^- \rightarrow OH^- + 1/2H_2$), and the anodic reaction refers to matrix dissolution process ($Mg \rightarrow Mg^{2+} + 2e^-$) [11]. It is clearly seen in Fig. 5b that the cathodic branches exhibit extensive linear Tafel region, and the fitted corrosion parameters of E_{corr}, I_{corr} and P_i are listed in Table 3. For the cathodic branches, extrusion deformation decreases the cathodic current, revealing a restrained corrosion rate owing to the cathodic corrosion reaction in terms of kinetics [42]. The relatively low I_{corr} and P_i values of E3 alloy are due to the inferior micro-galvanic corrosion accelerating result of X-phase through generating micro-galvanic couple with Mg matrix. By considering the anodic branches, an extended low-current region appears, revealing that protective $Mg(OH)_2$ corrosion product film is developed on each alloy surface during the immersion. The dense corrosion product film could hinder the anodic dissolution of the alloys [43, 44]. In addition, difference between the pitting potential and E_{corr} of E3 alloy is almost 100 mV, which is higher than the other alloys. The higher value indicates better corrosion resistance of the oxidation film to chloride corrosion and restrained corrosion tendency in thermodynamics [45, 46].

3.2.2. Weight loss experiment

The corrosion rates obtained according to the weight loss experiment and Tafel extrapolation method are displayed in Fig. 6. Expectedly, the corrosion rate of E3 alloy is 3.72 ± 0.36 mm/year, which is the lowest among these alloys. It is worth noting that the corrosion rates of the experimental alloys are quite higher than the intrinsic Mg (0.3 mm/year) in a concentrated chloride solution. It is attributed to the large amount of micro-galvanic corrosion caused by alloying elements, and the influence of impurity particles. With Gd content variation, the corrosion rates at cast condition could be ranked as: $C3 < C0 < C1 < C2$, and also ranked as: $E3 < E1 < E0 < E2$ at extruded condition. The variation trend of the extruded condition is similar to the cast condition. Meanwhile, the overall corrosion rates of extruded alloys are lower than the cast alloys. It is worth noting that the corrosion rates calculated from the weight loss test are relatively higher than that determined from Tafel extrapolation method. It is mainly because that P_i is the measurement of electrochemical part and *CR* is the total corrosion reaction measurement. Besides, the Tafel extrapolation measurement represents the momentary specimen immersion and the corrosion rate is not related to steady state corrosion [47, 48]. Generally, it exhibits a strange phenomenon that both the amount of Mg^{2+} ions and hydrogen evolution increase during anodic polarization of Mg alloys. The reason is that the part of the corrosion reaction is chemical rather than electrochemical. The value of CR (corrosion rate measured by weight loss test) is the total corrosion reaction rate, and the value of P_i (corrosion rate measured by Tafel extrapolation method) is the electrochemical part corrosion rate of the total corrosion reaction. The consequence is that the ratio of CR/ P_i would be greater than 1. Results demonstrate that the deviation of corrosion rates exists between electrochemical and weight loss tests, but they reveal similar regularity. The Tafel extrapolation method is a meaningful assistant for evaluation of the corrosion rate because it is quick and easy.

3.2.3 Electrochemical impedance spectrum

Fig. 7 exhibits the corresponding Nyquist and Bode curves of EIS measurement in 3.5 wt.% NaCl solution. The impedance spectra (Fig. 7a) of C0, C1, C2, E0 and E2 alloys are composed of two definite capacitance loops at high frequency and middle frequency ranges, indicating the charge transfer by corrosion product layer and charge transfer reaction (localized corrosion) at the alloy surface, respectively. Additionally, an inductance loop at low frequency range indicates the mass diffusion of ions by porous corrosion product layer [49, 50]. The radiuses of the loops are different, which indicates the identical corrosion mechanism with diverse corrosion rates. Conversely, only a well-defined high frequency capacitance loop and a low frequency inductance loop are existed in C3, E1 and E3 alloys, suggesting different corrosion mechanisms with different corrosion rates [51]. With continuous increase of Gd, the capacitive loop radiuses of both cast and extruded alloys show a fluctuant tendency, and also the radiuses of capacitive loops increase after extrusion, suggesting higher charge transfer resistance and more protective oxide film. It is noticed in phase angle *vs*. frequency diagram (Fig. 7b) that obvious wave crests appear in high frequency region, and the peak value and full width at half maximum of the phase angle are higher for extruded alloys. The phenomenon manifests smaller capacitance and bigger resistance, along with lower corrosion rates [52]. The impedance modulus *vs.* frequency curves (Fig. 7b) illustrate that the E3 alloy owns the highest impedance modulus, representing the largest polarization resistance and optimal corrosion resistance performance [53, 54].

A compatible equivalent circuit with the scheme of the layers is displayed in Fig. 8, and the fitting data is listed in Table 4, aiming to further illustrate the corrosion mechanism of the alloys. In Fig. 8, R_s refers to the solution resistance; the CPE_{dl} and R_{ct} refer to electric double layer capacitor and charge transfer resistance from alloy surface to the solution (capacitive loop at high frequency region); CPE_f and R_f are the corrosion product film capacitance and surface film resistance (capacitive loop at medium frequency region); the inductance L and resistance R_L in series describes the breakdown of fragmentary protective layer in the effect of absorbed Mg^+ reaction with H_2O (inductance loop at low frequency region) [55]. Two parameters Y_0 and n are used to define the CPE components, Y_0 is the non-ideal capacitance which causes by the second phases, cracks and impurities, and n represents the distribution index which ranges between 0 and 1. Combined with Table 4, R_s values are almost unchanged among the experimental alloys because R_s is irrelevant with electrode process. The fitting R_{ct} and R_f results of extruded alloys are higher than the cast alloys, implying the lower dissolution rate and higher protective impact on the surface film. Accordingly, the lower CPE_{dl} and CPE_f values of extruded alloys indicate the smaller corrosion area and denser oxide film on the alloy surface. In particular, the lowest CPE_{dl} and highest R_{ct} values of E3 alloy demonstrate the best corrosion resistance. Meanwhile, the Brug formula [56] is applied to evaluate the double layer capacitance CPE_{dl}, and the dielectric capacitance CPE_f is verified through the Orazem formula [57-59] and Hsu and Mansfeld expression [60]. The values and variation tendency derived from the above expressions are consistent with the fitted data by Zview software as shown in Table 4. The EIS results further agrees with the potentiodynamic polarization experiment, which reflects that the amount of micro-galvanic corrosion couples of $MgZn_{1.2}Gd_xZr_{0.18}$ alloys can be reduced by increasing Gd content and extrusion deformation.

3.3. Local potential distribution in experimental alloys

Fig. 9 illustrates the surface Volta potential maps and corresponding localized potential distribution results between second phase and matrix. The dark areas in Volta potential maps are equal to more negative potential while the bright regions are electrochemically nobler than the dark areas. It is distinct that the local potential of the second phase is higher than the matrix, and the average Volta potential difference of W-phase and the matrix, X-phase and the matrix is about 150 mV and 90 mV, respectively, implying W-phase and X-phase serve as micro-cathodes during corrosion. Moreover, partial X-phase is sacrificed in the form of micro-anode in the W-phase and X-phase coexisted C3 and E3 alloys to reduce the Mg matrix corrosion. The larger contact area between cathode and anode leads to a more reduced Mg matrix corrosion condition, which significantly affects the galvanic corrosion rate. Similarly, the Volta potential between the strip-like X-phase and matrix in E3 alloy is nearly equal to the cast condition, representing the lamellar eutectic structure at the grain boundaries is crushed into banded phase along the ED during extrusion process.

3.4. Corrosion morphology and surface film after immersion

Fig. 10 exhibits the secondary electron morphologies of the alloys after 2 h and 24 h soaking in 3.5 wt.% NaCl solution. The corrosion surface with corrosion product is shown at the upper right corner (under the same magnification). It is visible when the soaking time prolongs from 2 h to 24 h, fresh metallic surface disappears, and the corrosion areas extend to the whole surface in the cast and extruded conditions. In addition, the corrosion product layer of cast alloys is thicker than extruded alloys. With increasing Gd content, the most serious corrosion occurs in the C2 and E2 alloys, and part of initial matrix is presented on E3 alloy surface, demonstrating lower localized corrosion and diffusion rate.

Secondary electron microstructures of corrosion surface with removal of corrosion products are also provided in Fig. 10. With soaking time varies from 2 h to 24 h, the corrosion originates from second phase boundaries, subsequently continues to spread toward the center of cast alloy grains. In the extruded condition, corrosion begins around the elongated second phases, and a fraction of deep corrosion pits and grooves are formed after 24 h immersion. Part of fresh matrix exists in the alloys exposed for 2 h, while severe corrosion pits spread over the entire surface after 24 h immersion, which indicates inferior corrosion resistance. It is worth noting that the corrosion starts at the interface of MgZn$_2$ phase and α-Mg matrix of C0 alloy, and the MgZn$_2$ phase falls off rapidly after the corrosion of surrounding α-Mg matrix. The minor content of MgZn$_2$ particles is ineffective on corrosion inhibition. Analogously, deeper honeycomb corrosion pits could be observed in E2 alloy compared with the other two extruded alloys. The result is in consistent with the weight loss and electrochemical measurements.

Fig. 11 reveals the morphologies of corrosion surface at high magnifications (under different magnifications to intuitively observe the corrosion phenomenon) of the alloys immersed for different time intervals. It is visually observed in Fig. 11a$_1$ and a$_5$ that the corrosion initiates at the grain boundaries and near the MgZn$_2$ phase. Then the matrix is corroded and extended quickly along the grain boundaries and ED. For C1 alloy (containing W-phase), initially, the matrix adjacent to eutectic W-phase is eroded through micro-galvanic corrosion, and the W-phase serve for micro-cathode during the corrosion process. With increasing corrosion time, corrosion rapidly spreads toward central region of the grains (Fig. 11d$_2$) and some corrosion pits could be found (Fig. 11c$_2$) due to the detached W-phase. Obviously, the identical corrosion mechanism and process could be seen in more Gd containing C2 alloy. Besides, the more severe corrosion of C2 alloy compared with C1 alloy is owing to the larger quantity of strong cathode W-phase. The corrosion of X-phase and W-phase containing C3 alloy also starts at the second phase boundaries as displayed in Fig. 11a$_4$, particularly Mg matrix next to W-phase. After 24 h corrosion, some lamellar X-phase could be seen sunk from the surface (Fig. 11d$_4$), demonstrating superficial X-phase is depleted as micro-anode with W-phase (micro-cathode) to decrease the erosion area of substrate. For E1 alloy, the granular W-phase which cracked during the extrusion still acts as micro-cathode to expedite the Mg matrix collapse (Fig. 11a$_6$). Plenty of corrosion pits exist in E2 alloy after immersion for 6 h (Fig. 11b$_7$), suggesting the W-phase particles detachment and inferior corrosion resistance. With the prolonged immersion time, micro-galvanic corrosion happens and forms very small pits, and then the pits propagate transversely around the dissolved α-Mg matrix and distribute more intensively. Afterwards, the corrosive medium Cl$^-$ penetrates part of the porous film (formed with the micro-galvanic reactions) and reaches the fresh α-Mg surface. The ambient matrix is continually corroded toward depth direction, resulting in the formation of pitting corrosion and the corrosion cycles in the light of this model.

In order to better understand the corrosion behavior of the alloys with various second phases, Fig. 12 manifests the morphologies of C2 and C3 alloys at longitudinal section after 24 h immersion. It is perceptible from Fig. 12a that some corrosion pits occur in the Mg matrix, because the net-like W-phase could not serve as barrier to hinder the solution penetration. The continuously distributed X-phase with lamellar morphology forms an interface as the corrosion barrier to impede the Mg matrix corrosion. However, the corrosion rate of C3 alloy is still quite higher than the intrinsic Mg due to its higher alloying content.

Fig. 13 presents the XPS results of the formed corrosion product layer. The survey scanning spectrum of the corrosion products (Fig. 13a) reveals the existence of Mg, O, Gd, C, Zn and Zr elements in the two E3 alloys under different conditions, and no significant differences exist on XPS spectra. Fig. 13b shows the variation of atomic percent with the etch time. It is obvious that the percent of Mg increases and O decreases with the increasing etch time and film depth, which reaches a relatively stable state after 360 s etch (~27 nm thickness). The high resolution spectra for Mg 1s (Fig. 13c, d) are divided into two peaks which could be fitted by MgO and Mg, MgO and $Mg(OH)_2$ of the two alloys, respectively. The peaks located at 531.2 eV and 142.7 eV in O 1s and Gd 4d spectrum of the alloy in dried air indicate the presence of Gd_2O_3 on the oxide film, which demonstrates the participation of dissolved Gd in the matrix during the film formation. The Gd_2O_3 oxide is nonreactive to the NaCl solution, which is a protective oxide film on the Mg-Zn-Gd alloy. Besides, the $Mg(OH)_2$ peak exists in the Mg 1s and O 1s spectrum of the alloy immersion in NaCl solution, which is mainly attributed to the OH^- in the solution [61]. Consequently, the predominant corrosion products of the alloy quiescence in dried air are compact and dense MgO and Gd_2O_3. Due to the uneven and traces of inert Gd_2O_3 oxide film, the protective effect is still restricted, leading to a much greater corrosion rate than the intrinsic Mg. The porous $Mg(OH)_2$ layer appears in the alloy immersed in NaCl solution.

4. Discussion

Results of microstructures and corrosion rate tests demonstrate that with the Gd addition from 0 to 2.0 at.%, there are differences in grain size, second phase and crystallographic texture (Fig. 14) of the cast and extruded $MgZn_{1.2}Gd_xZr_{0.18}$ alloys as displayed in Fig. 4. These factors lead to significant difference in corrosion performance for the Mg-Zn-Gd alloys. It is worth noting that the corrosion rates of the experimental alloys are still quite higher than the intrinsic Mg in a concentrated chloride solution. The reason is that large amount of micro-galvanic corrosion caused by alloying elements and second phases could always deteriorate the corrosion behavior of the alloys. The influence of microstructures caused by alloying element Gd variations on the corrosion performance is discussed in detail.

It is known that different α-Mg grains with different crystal orientations and exposed crystal planes could produce different electrochemical properties due to their unique surface energy and atomic density [62]. In general, the corrosion rate on {0002} basal plane is the most stable because it owns higher atomic density of 1.13×10^{15} compared with the non-basal planes, higher binding energy and activation energy for dissolution [62]. Jiang *et al.* [63] proposed that the increased basal plane intensity in the crystallographic texture of the extruded AZ31 sheet resulted in higher atomic coordination with more-closely packed plane and the decreased corrosion rate. As indicated in the weight loss test (Fig. 6) and electrochemical test (Fig. 7), the extruded alloys show relatively preferable corrosion resistance than the cast alloys. The corresponding EBSD orientation maps and pole figures are displayed in Fig. 14. The orientation of {0002} basal plane is preferentially along the ED and a majority of grains orientate with {0002} <10-10>, implying representative basal texture of extruded alloys [64]. The maximum basal texture intensity of Gd-free E0 alloy is 8.58, and the increasing Gd addition leads to the decreasing of the maximum basal texture intensity to 1.76, indicating element Gd could slightly weaken the conventional texture intensity of the $MgZn_{1.2}Gd_xZr_{0.18}$ alloys. Stanford [65] revealed that addition of Ca weakened the extrusion texture of Mg-Mn alloys, and element Ca behaved in a regular manner to RE elements, and it was due to the large radius of Ca atom. Liu *et al.* [66] observed that the maximum texture intensity of coarse grains was stronger than the fine grains for extruded Ca added Mg alloys, and the relatively strong basal texture intensity was related to the increased fraction of coarse grains. It is shown in Fig. 2b that the grain sizes decrease with the increasing Gd content after extrusion, which could lead to the weak basal texture intensity. As shown in Fig. 14a, the largest fraction of basal plane orientation is observed through 3D exhibition in E0 alloy, and it could be expected that shallow corrosion depth exists in this alloy. As illustrated in Fig. 14d, the E3 alloy presents a relatively weak crystallographic texture and more random distribution of grain orientation, suggesting micro-galvanic corrosion could occur among the grains with different crystallographic orientations. Similar results of lower cathodic I_{corr} could also be seen in Fig. 5. Although crystallographic texture plays a critical part in the extruded $MgZn_{1.2}Gd_xZr_{0.18}$ alloys corrosion, the whole corrosion behavior is under the comprehensive influences.

The improvement of strength and plasticity through grain refinement has gained much attention of Mg alloys. Recently, several researches have stated the influence of grain sizes on Mg alloys corrosion behavior. The effects are complicated and conclusions are contradictory. Among some intricate propositions, the physical corrosion barrier effect and preferentially corroded grain boundaries with crystallographic defect are two major perspectives during Mg alloys corrosion [67, 68]. Birbilis *et al.* [69] concluded that the significantly decreased grain size led to lower I_{corr} and better corrosion resistance, which was due to thicker and denser passive film on the corroded surface in ECAPed pure Mg. In this work, the average grain size decreases sharply through extrusion deformation, and it also decreases with increasing Gd. The $MgZn_{1.2}Zr_{0.18}$ alloy exhibits far bigger average grain size compared with the alloys containing Gd as shown in Figs. 2 and 6. Almost completely dynamic recrystallized (DRXed) grains appear during extrusion process (Fig. 2), which results in grain refinement compared with the cast alloys. Moreover, according to the latest reports, the addition of Gd makes an impact on grain refining through restraining the grain boundaries migration [20]. It has been proved that grain boundaries are favorable nucleation sites for a more protective corrosion product film formation [70, 71], which is the physical corrosion barrier to retard the corrosion expansion as shown in Table 4 with the lower CPF_f value (passive surface film) and Fig. 13 (stable MgO protective layer). Meanwhile, Song et al. [72] reported that the formation of surface film on Mg alloys was related to the OCP *vs.* time curves. The surface film formation mechanism related to the OCP *vs.* time curves (Fig. 5a) could be explained as [73]: (1) The improved OCP values during the initial stage is related to the oxide film formation on the fresh surface of the alloys; (2) At the gradually increased OCP value stage, $Mg(OH)_2$ film is formed, and the Cl^- is also absorbed on the film to bring some negative charges, leading to lower increased OCP values; (3) The breakdown and formation of

$Mg(OH)_2$ film is alternatively occurred in the fluctuant stage to reach an equilibrium reaction. Furthermore, refined grains may also weaken the surface film cracking as a consequence of lower residual stress in surface film. The lowest corrosion rate obtained in E3 alloy with the finest grains, and the schematic illustration of the grain size and corrosion layer combined effects are demonstrated in Fig. 15. In Fig. 15a, discontinuous MgO surface layer forms in E1 alloy under the condition of relatively coarse grain size, and it could not hinder the penetration of Cl^- into α-Mg matrix. Bland *et al.* [74] has confirmed that primary MgO film nucleated on Mg alloy surface and the plate-like $Mg(OH)_2$ film formed subsequently due to the hydration of inner MgO film. In a way, α-Mg is the anodic sites to preferentially dissolve and form $Mg(OH)_2$ through the reaction with OH^- in the electrolyte. Unfortunately, the generated $Mg(OH)_2$ product layer is porous and could not effectively obstruct the Mg anodic corrosion. With the increasing corrosion process, accumulated H_2 bubbles generate at the cathodic sites on the alloy surface. The rupture and detachment of corrosion product from the substrate would happen once the local hydrogen pressure passes the critical value [11]. The surface layer composition of Gd-free $MgZn_{1.2}Gd_xZr_{0.18}$ alloy is similar with the low-Gd containing $MgZn_{1.2}Gd_{0.8}Zr_{0.18}$ alloy. Meanwhile, the higher content of Gd atoms could penetrate in the surface hydroxide layer, so as to generate a stable protective layer and enhance the protective effect. When the Gd content is 2.0 at.%, continuously distributed surface layer which contains dense and compact MgO and Gd_2O_3 is observed on the fine-grained E3 alloy as shown in Figs. 13e and 15b. This implies that abundant grain boundaries might offer the possibility for the formation of strong protective film, and the Gd_2O_3 layer can inhibit the penetration of harmful Cl^- [75]. In addition, the lamellar X-phase could act as anodic sites due to the lower Volta potential with W-phase to reduce the α-Mg matrix corrosion. The surface layer which contains intact MgO and Gd_2O_3 would essentially prevent the alloy from corrosion expansion.

Generally, the second phase types, volume contents, morphologies and distributions play different roles in the corrosion of high alloying containing Mg alloys due to the micro-galvanic accelerating and corrosion shielding effects [34, 76]. Due to the absence of Gd, the E0 alloy shows typical eutectic grain morphology and large grain size, revealing the limited grain refining effect of trace Zn and Zr. The element Zn is pushed into the grain boundaries during the solidification and forms a small amount of $MgZn_2$ phase (Fig. 3a_1). In the Gd containing $MgZn_{1.2}Gd_xZr_{0.18}$ alloys, as shown in Fig. 3, the solute Gd and Zn atoms are concentrated at the front of solid-fluid interface and near the grain boundaries together with the α-Mg grain nucleation during the non-equilibrium solidifying process. Due to the low content of Gd in E1 alloy, the single eutectic W-phase precipitates at the grain boundaries. Increasing the Gd content to 1.4 at.% (E2 alloy), the higher volume fraction of W-phase precipitates. With continuously increased Gd content to 2.0 at.% of E3 alloy, X-phase initially precipitates near the grain boundaries and grows into the grains. Due to the higher solution temperature of X-phase and the fluctuant alloying elements concentration, then the W-phase emerges around X-phase. After extrusion deformation, the second phase types are not changed but the original network eutectic phases are crushed into particles and distribute parallel to the ED as shown in Figs. 1 and 3. Fig. 11a_5 distinctly shows that the micro-galvanic corrosion occurs in the α-Mg matrix next to $MgZn_2$ particles, demonstrating the $MgZn_2$ phase servers as micro-galvanic cathode to accelerate the erosion process. The relatively inferior corrosion resistance of $MgZn_{1.2}Zr_{0.18}$ alloy is demonstrated through above microstructures characterization. Furthermore, the corrosion performance of relevant Mg-Zn (-Zr) alloys in literature are summarized in Table 5 to make a comparison with this work. It could be seen in Table 5 that the corrosion behavior of the Mg-Zn-Zr alloys is consistent with the result in this work. It is clear from Fig. 9 that W-phase and X-phase are electrochemically nobler than the matrix and they act as cathode to consume the matrix, resulting in preferential corrosion of Mg matrix. Nonetheless, the X-phase is less efficient cathodes compared with W-phase and acts as micro-galvanic anode (W-phase acts as the cathode) during corrosion to protect Mg matrix from corrosion (Fig. 11d$_4$). In this sense, the lamellar-like X-phase in E3 alloy is continuously distributed along the ED, which could effectively impede the corrosion extension from grain to grain. Oppositely, due to the higher Volta potential difference between the W-phase and Mg matrix in E1 and E2 alloys as shown in Fig. 10b$_4$ and c$_4$, plenty of micro-galvanic couples are formed to consume the Mg matrix. The more deteriorated corrosion surface of E2 alloy is owing to larger volume fraction of W-phase. In the E2 alloy, micro-galvanic corrosion accelerates the collapse process, which appears severe pitting corrosion (Fig. 10c$_1$). The relatively superior corrosion resistance of present high Gd containing E3 alloy is partially concerned with the decreased micro-galvanic result of the matrix and X-phase, finely and uniformly distributed grains and more protective surface film.

The effects of second phases, grain sizes and texture on corrosion behaviors of extruded alloys are schematically explained in Fig. 16 to interpret the comprehensive corrosion mechanism. Therefore, the reason for the correspondingly preferable corrosion resistance of high Gd content Mg-Zn-Gd-Zr alloys is attributed to the comprehensive effects of fine grains and high concentration of Gd to form the protective surface layer, lamellar-like X-phase and the basal crystallographic texture.

5. Conclusions

The effect of Gd content on corrosion behavior and mechanism of $MgZn_{1.2}Gd_xZr_{0.18}$ alloys exposed in 3.5 wt.% NaCl solution was investigated, the following conclusions can be obtained:

(1) Increasing Gd alloying addition in $MgZn_{1.2}Gd_xZr_{0.18}$ alloys resulted in the second phase transformation from $MgZn_2$ phase, W-phase to X-phase, increased second phases volume fraction, decreased grain sizes and basal plane texture intensity. The immersion test, electrochemical measurement and corrosion morphologies manifested that the extruded $MgZn_{1.2}Gd_{2.0}Zr_{0.18}$ alloy had the superior corrosion resistance.

(2) The X-phase and W-phase were nobler than the matrix to accelerate the matrix micro-galvanic corrosion, and the $MgZn_2$ phase also acted as micro-galvanic cathode during corrosion. However, the lower localized potential of X-phase acted as micro-galvanic anode compared with W-phase, and the lamellar-like X-phase played corrosion shielding effect to reduce the corrosion area of matrix.

(3) Through hot extrusion and Gd addition, XPS result of the E3 alloy and decreased

grain size induced the existence of protective Gd_2O_3 and MgO mixed oxidation product layer to alleviate the penetration of Cl^-.

(4) The improved corrosion resistance of high Gd containing extruded $MgZn_{1.2}Gd_{2.0}Zr_{0.18}$ alloy was mainly related to the fine and homogeneous microstructure, dual-role of X-phase, existence of Gd_2O_3 and MgO protective layer as well as the basal crystallographic texture.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Competing interests statement

The authors declare they have no competing interests.

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Alloy	Nominal constituent	Actual constituent (at.%)			Analyzed composition (wt.%)			
		Zn	Gd	Zr	Fe	Ni	Cu	Mg
C0	$MgZn_{1.2}Zr_{0.18}$	1.20	0	0.18	0.0021	0.0018	0.0019	Bal.
C1	$MgZn_{1.2}Gd_{0.8}Zr_{0.18}$	1.19	0.78	0.18	0.0020	0.0017	0.0018	Bal.
C2	$MgZn_{1.2}Gd_{1.4}Zr_{0.18}$	1.18	1.39	0.18	0.0018	0.0017	0.0016	Bal.
C3	$MgZn_{1.2}Gd_{2.0}Zr_{0.18}$	1.18	2.00	0.17	0.0019	0.0017	0.0019	Bal.

Table 1. Chemical constituents of the investigated alloys.

Alloys	Average grain size (μm)	Second phase volume fractions (%)				
		X-phase	W-phase	Mg_5(Gd, Zn)	$MgZn_2$	α-Mg
C0	104±10	0	0	0	0.8	99.2
C1	74±9	0	14.8	0	0	85.2
C2	68±11	0	18.7	0	0	81.3
C3	57±11	5.4	18.1	0.4	0	76.1
E0	27±3	0	0	0	0.8	99.2
E1	7±1	0	15.2	0	0	84.8
E2	5±1	0	18.5	0	0	81.5
E3	3±1	8.7	15.3	0	0	76.0

Table 2. The statistic average grain sizes and second phase volume fractions of the alloys.

Alloy	*OCP* (V)	*E*corr (V)	*I*corr (μA cm-2)	*P*i (mm/year)
C0	-1.604±0.010	-1.522±0.029	117.29±5.27	6.63±0.54
C1	-1.596±0.008	-1.473±0.024	123.87±3.44	9.84±0.82
C2	-1.611±0.012	-1.527±0.031	235.86±7.58	11.73±1.31
C3	-1.591±0.018	-1.567±0.019	103.91±3.21	4.95±0.55
E0	-1.593±0.013	-1.462±0.022	84.03±4.58	3.78±0.33
E1	-1.577±0.009	-1.538±0.027	82.24±2.04	3.62±0.43
E2	-1.588±0.011	-1.542±0.016	109.26±2.27	6.28±0.34
E3	-1.572±0.015	-1.546±0.027	48.96±0.74	2.02±0.22

Table 3. Fitting parameters derived from the OCP and polarization curves of the alloys.

Alloy	R_s	CPE_{dl}	R_{ct}	CPE_f	R_f	L	R_L	χ^2

	(Ω cm^2)	Y_1 (μΩ^{-1}cm^{-2}s^n)	n_1	(Ω cm^2)	Y_2 (μΩ^{-1}cm^{-2}s^n)	n_2	(Ω cm^2)	(H cm^2)	(Ω cm^2)	
C0	8.9	28.75	0.95	146.7	11.35	0.71	2129.2	3.39×10^3	407.1	8.98×10^{-4}
C1	7.1	17.59	0.94	195.1	8.46	0.87	2113.3	3.45×10^3	412.4	3.02×10^{-5}
C2	8.6	34.27	0.91	125.8	13.97	0.74	2132.1	3.48×10^3	310.6	1.28×10^{-4}
C3	9.2	15.61	0.93	460.9				9.56×10^3	926.4	2.23×10^{-5}
E0	9.7	16.88	0.91	207.6	8.17	0.76	2289.6	8.74×10^3	659.0	7.17×10^{-4}
E1	10.7	11.60	0.92	529.5				1.42×10^4	761.2	4.52×10^{-4}
E2	11.6	16.33	0.96	216.8	7.09	0.69	2349.7	7.17×10^3	829.3	4.94×10^{-3}
E3	9.9	8.84	0.94	625.6				2.38×10^4	1379.1	7.39×10^{-4}

Table 4. Fitting electrochemical parameters from the EIS measurement.

		Corrosion properties		Mechanical properties			
Alloy (wt.%), condition	Solution	Measurement	Corrosion rate (mm year^{-1})	Ultimate tensile strength (MPa)	Tensile yield strength (MPa)	Elongation (%)	Refs.
Mg-1Zn, cast	Hank	P_W	1.25		60	14.5	[77]
Mg-2.4Zn, cast	3.5 wt.% NaCl	P_W	4.67	85		7.5	[78, 79]
Mg-2.4Zn, cast	3.5 wt.% NaCl	P_i	1.56	85		7.5	[79, 80]
Mg-3Zn, extruded	3.5 wt.% NaCl	P_W	9.6	270	190	16.5	[81]
Mg-3Zn, extruded	Hank	P_W	0.82		118	12	[77]
Mg-5Zn, extruded	3.5 wt.% NaCl	P_W	15.6	275		15.7	[78, 79]
Mg-1.5Zn-0.6Zr, cast	5 wt.% NaCl	P_W	4.01	168	83	9.1	[82]
Mg-1.5Zn-0.6Zr, cast	5 wt.% NaCl	P_i	1.28	168	83	9.1	[82]
Mg-1.5Zn-0.6Zr, cast	Hank	P_W	0.3045	168	83	9.1	[82, 83]
Mg-2Zn-0.5Zr, cast	Hank	P_W	2.5				[84]
Mg-2Zn-0.6Zr, cast	SBF	P_W	0.64	196	51	18	[85, 22]
Mg-2Zn-0.6Zr, cast	Hank	P_H	1.6	192	51	18	[77]
Mg-2Zn-0.6Zr, extruded	Hank	P_H	0.42	260	194	17	[77]
Mg-3Zn-0.6Zr, cast	SBF	P_W	1.2	219	65	21	[22, 86]
Mg-3Zn-0.6Zr, cast	3.5 wt.% NaCl	P_W	6.56	219	65	21	[22]
Mg-3Zn-0.6Zr, extruded	Hank	P_H	1.02	300	215	9	[87]
Mg-3Zn-0.7Zr, cast	SBF	P_W	2.74				[88]
Mg-4Zn-0.5Zr, cast	Hank	P_W	0.74	176	96	4	[89]
Mg-4Zn-0.6Zr, cast	Hank	P_W	0.85		91	5.6	[77]
Mg-4Zn-0.6Zr, cast	0.5 wt.% NaCl	P_H	0.51	225	101	12.8	[89]
Mg-6Zn-0.6Zr cast	Hank	P_W	1.12	210	150	6	[89, 90]
Mg-6Zn-0.6Zr, cast	Hank	P_i	0.932	210	150	6	[89, 91]
Mg-6Zn-0.6Zr, cast	3.5 wt.% NaCl	P_W	8.2	230	160	6.5	[91, 92]
Mg-6Zn-0.6Zr extruded	Hank	P_W	0.81	335	290	16	[89, 90]
Mg-6Zn-0.6Zr, extruded	3.5 wt.% NaCl	P_H	4.3	315	235	12	[89, 93]

(weight loss is represented by P_W, hydrogen evolution is represented by P_H, Tafel extrapolation method is represented by P_i)

Table 5. Corrosion performance and corresponding mechanical properties of Mg-Zn (-Zr) alloys summarized from literatures.