Effect of ageing treatment on microstructures, mechanical properties and corrosion behavior of Mg-Zn-RE-Zr alloy micro-alloyed with Ca and Sr

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Abstract: Effects of ageing treatment on the microstructures, mechanical properties and corrosion behavior of the Mg-4.2Zn-1.7RE-0.8Zr-xCa-ySr [x=0, 0.2 (wt.%), y=0, 0.1, 0.2, 0.4 (wt.%)] alloys were investigated. Results showed that Ca or/and Sr additions promoted the precipitation hardening behavior of Mg-4.2Zn-1.7RE-0.8Zr alloy and shortened the time to reaching peak hardness from 13 h to 12 h. The maximum hardness of 77.1±0.6 HV for the peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy was obtained. The microstructures of peak-aged alloys mainly consist of α-Mg phase, Mg₅₁Zn₂₀ phase and ternary T-phase. The Zn-Zr phase is formed within the α -Mg matrix, and the Mg₂Ca phase is formed near T-phase due to the enrichment of Ca in front of the solid-liquid interface. Furthermore, fine short rod-shaped β'_1 phase is precipitated within the α -Mg matrix in the peak-aged condition. The peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy exhibits optimal mechanical properties with an ultimate tensile strength of 208 MPa, yield strength of 150 MPa and elongation of 3.5%, which is mainly attributed to precipitation strengthening. In addition, corrosion properties of experimental alloys in the 3.5wt.% NaCl solution were studied by the electrochemical tests, weight loss, hydrogen evolution measurement and corrosion morphology observation. The results suggest that peak-aged alloys show reduced corrosion rates compared with the as-cast alloys, and minor additions of Ca and/or Sr improve the corrosion resistance of the Mg-4.2Zn-1.7RE-0.8Zr alloy. The peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy possesses the best corrosion resistance, which is mainly due to the continuous and compact barrier wall constructed by the homogeneous and continuous second phases.

Key words: magnesium alloys; age-hardening; microstructure; mechanical properties; corrosion resistance

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1 Introduction

Magnesium (Mg) alloys have been attracting considerable attention because of their low density, high strength to weight ratio, superb castability, impressive damping, and outstanding recyclability ^[1,2]. These properties have made Mg alloys irreplaceable in automotive and aerospace applications ^[3, 4]. Among the Mg alloys available, precipitation hardening magnesium-rare earth (Mg-RE) alloys are the widely used commercial alloys for large complex thin-wall castings, such as aero-engine casings and gearbox housings. Despite its great potential, Mg alloys are confronted with some challenges, especially

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the poor corrosion resistance because of the high chemical reactivity of the Mg matrix, which can be a show stopper for their applications when exposed to the corrosive environment [5, 6].

The poor corrosion resistance of Mg alloys results from (i) the high intrinsic dissolution tendency of Mg, which is only weakly inhibited by corrosion product films, and (ii) the presence of impurities and second phases acting as local cathodes and thus causing local galvanic acceleration of corrosion ^[7, 8]. However, the second phases also have a beneficial effect on the corrosion performance. Peng et al. ^[9] investigated the corrosion behavior of heat-treated Mg-10Gd-3Y-0.4Zr alloy and concluded that ageing for longer periods could decrease the corrosion rate owing to a barrier effect by the nearly continuous precipitates network. To date, sustained studies have been carried out to address corrosion issues and to improve the corrosion resistance of Mg alloys through various methods, such

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as alloying^[10], grain refinement ^[11] and heat treatment ^[12, 13]. Yang et al. ^[14] studied the corrosion resistance of Mg-5Al-0.4Mn alloy with 0.2wt.%-4wt.% Ca additions and found that the discontinuous (Mg,Al)₂Ca phase acted as a sacrificial anode to suppress the corrosion of Mg matrix. Argade et al.^[15] proposed a power law relationship between corrosion rate and grain size, revealing a dominance of alloying elements on the corrosion rate over grain size. In addition, Miao et al.^[12] reported that solution treatment before extrusion could improve the corrosion resistance of Mg alloys due to the homogeneous microstructure.

Alkaline earth metals, Ca and Sr, are low cost elements with reduction potentials similar to $Mg^{[16, 17]}$. With the additions of Ca and Sr to the Mg-4Al-2Sn alloys, the corrosion resistance is improved by ennobling the corrosion potential of the Mg matrix^[16]. Moreover, Sr was reported to improve the corrosion resistance of AZ91 by the retardation of anodic activity ^[18]. Besides, provided that Ca content is kept below the solubility limit to avoid the Mg₂Ca formation, the corrosion is not accelerated, and the solid solution of Mg-Ca can exhibit appreciable ductility ^[18]. However, investigation in detail about the effects of minor Ca and Sr on the ageing behavior and the corrosion resistance of the Mg-Zn-RE-Zr alloy is still limited.

Mg-4.2Zn-1.7RE-0.8Zr alloy is one of the most popular magnesium alloys in the Mg-Zn-RE-Zr based alloys and has been widely used for aircraft gearboxes and generator housings on military helicopters. Based on the previous research, minor Ca and Sr can refine the grain size and improve mechanical

properties of the as-cast Mg-4.2Zn-1.7RE-0.8Zr alloy ^[19, 20]. In this study, the effect of ageing treatment on the microstructure, mechanical properties and corrosion behavior of Mg-4.2Zn-1.7RE-0.8Zr-xCa-ySr (x=0, 0.2 wt.%, y=0, 0.1, 0.2, 0.4 wt.%) alloys was investigated. This work will strive to better understand how these variables, mainly the grain size, alloying element and ageing treatment, affect the corrosion behavior of the Mg-4.2Zn-1.7RE-0.8Zr alloy.

2 Experimental procedures

2.1 Materials preparation and heat treatment

Mg-4.2Zn-1.7RE-0.8Zr-*x*Ca-*y*Sr (x=0, 0.2 wt.%, y=0, 0.1, 0.2, 0.4 wt.%) alloys were prepared using high-purity Mg, Zn, Ce-rich mischmetal (50wt.% Ce, 28wt.% La, 16wt.% Nd, 4%wt.% Pr and 2wt.% impurity), Mg-30Zr, Mg-20Ca and Mg-20Sr in an electronic resistance furnace under the protection of Ar gas. The molten alloy was poured into a preheated steel mould at approximately 730 °C. Table 1 lists the chemical compositions of the experimental alloys determined by X-ray fluorescent spectrometry (XRF). Furthermore, ageing treatment was conducted in an electric resistance furnace at 325 ± 5 °C for various times (0.125, 0.5, 1, 2, 4, 6, 8, 10, 12, 14, 16, 20, 24, 28 and 32 h). The Vickers hardness tests were performed with a 1 kg load. Ten indentations per sample were analyzed, and the average value was recorded.

Table 1: Chemical compositions of	f as-cast experimental alloys (wt.%)
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	Alloy	Mg	Zn	RE	Zr	Са	Sr
Alloy 1	Mg-4.2Zn-1.7RE-0.8Zr	Bal.	4.11	1.62	0.71	-	-
Alloy 2	Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca	Bal.	4.17	1.61	0.74	0.16	-
Alloy 3	Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.1Sr	Bal.	4.03	1.67	0.67	0.19	0.11
Alloy 4	Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr	Bal.	4.13	1.62	0.69	0.22	0.21
Alloy 5	Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.4Sr	Bal.	4.11	1.64	0.75	0.17	0.38

2.2 Microstructure characterization and mechanical properties testing

Microstructural examinations were conducted by optical microscopy (OM), scanning electron microscopy (SEM) coupled with energy dispersed spectroscopy (EDS). The samples for microstructure observation were ground, polished and then etched in the solution of 4% nitric acid and 96% ethanol. The average grain size (*d*) was measured based on the linear intercept method, where d=1.74 L, and *L* is the linear intercept length. Phase analysis was performed using X-ray diffraction (XRD) with the Cu K α radiation. Precipitates morphology and element distribution were characterized by transmission electron microscopy (TEM). The TEM specimens were prepared by focused ion beam (FIB). Tensile tests were conducted at room temperature at a strain rate of 2 mm·min⁻¹. Samples for tensile testing were machined to bars with a gauge dimension of 30 mm

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and 6 mm in diameter. Ultimate tensile strength (UTS), yield strength (YS) and elongation to failure (El) were obtained based on the average value of three tests.

2.3 Immersion testing

Specimens for immersion testing, with a dimension of 20 mm× 10 mm×10 mm, were ground to 2,000 grit SiC papers and cleaned ultrasonically in ethanol. A 3.5wt.% sodium chloride (NaCl) solution was used as a corrosive medium. Immersion tests were conducted at 25 ± 2 °C for 36 h, and the immersion solution was renewed every 12 h in order to keep a relatively stable pH value. Figure 1 shows the schematic illustration of the process to measure the volume of hydrogen evolution ^[21]. Evolved hydrogen gas was collected using this experimental device. After the immersion testing, the corrosion products were removed by specimen immersion for 8 min in a chromic acid solution

containing 15wt.% CrO₃, 1wt.% AgNO₃ and 400 mL H₂O at room temperature. After that, the samples were rinsed with distilled water and dried in hot flowing air, then weighed. Weight loss was obtained by weighing specimens to a precision of 0.01 mg before and after testing, and the corrosion rate was calculated based on three measurements. Moreover, the corrosion products were identified by means of XRD with Cu Ka radiation at the scan rate of 2 °·min⁻¹. The surface of corroded specimens was analyzed using SEM.



Fig. 1: Schematic illustration of device to measure volume of hydrogen evolved ^[21]

2.4 Potentiodynamic polarization measurement

Polarization measurements were carried out in a corrosion cell containing 3.5wt.% NaCl solution at 25 ± 2 °C. A threeelectrode cell containing a platinum wire was used as the counter electrode, a KCl-saturated Ag/AgCl electrode as the reference electrode, and the sample with an exposed area of 1 cm² as the working electrode. The measurements started from the stabilization of the open circuit potential (OCP) for 2,000 s. Potentiodynamic polarization curves of the samples were recorded between -1.80 V vs. Ag/AgCl and 0 V vs. Ag/AgCl under the scan rate of 0.5 mV·s⁻¹. Corrosion current density (i_{corr}) and corrosion potential (E_{corr}) were calculated by Tafel extrapolation of the cathodic branch. The fitting was applied at the potential range from E_{corr} to $E_{corr} - 0.1$ V, as presented in Ref. [6]. Measurements were repeated three times for better reproducibility.

3 Results

3.1 Age hardening responses

Hardness curves of the experimental alloys during ageing at 325 °C for various times are presented in Fig. 2. It can be observed that the hardness of Ca- and/or Sr-modified Mg-4.2Zn-1.7RE-0.8Zr alloys is a little higher than that of Mg-4.2Zn-1.7RE-0.8Zr alloy. From 0.125 h to 6 h, the hardness slightly



Fig. 2: Hardness evolution of experimental alloys during ageing at 325 °C

increases. Then, the hardness increases rapidly after ~6 h. The Ca- and/or Sr-modified Mg-4.2Zn-1.7RE-0.8Zr alloys take 12 h to reach the peak hardness. The peak hardness values are 73.5 ± 1.0 HV for Alloy 2, 75.5 ± 0.7 HV for Alloy 3, 77.1 ± 0.6 HV for Alloy 4, and 74.2 ± 0.9 HV for Alloy 5, while Alloy 1 takes 13 h to reach the peak hardness of 71.0 ± 0.8 HV. Finally, with further increasing of ageing time, the hardness of the alloys decreases rapidly. Therefore, the minor addition of Ca or/and Sr to Mg-4.2Zn-1.7RE-0.8Zr alloy accelerates the kinetics of precipitation during the initial ageing, and retards the kinetics of over-ageing.

3.2 Microstructure

Figure 3 shows the XRD patterns of the peak-aged alloys, suggesting that the peak-aged alloys mainly consist of α -Mg phase, Mg₅₁Zn₂₀ phase and ternary T-phase. Figure 4 presents the optical micrographs of the peak-aged alloys, wherein the microstructures consist of primary α -Mg grains and interdendritic phases dispersing along the grain boundaries, as well as the intermetallic particles existing inside grains. The average grain sizes for the as-cast and peak-aged experimental alloys are listed in Table 2, revealing a slight growth of α -Mg grains after peak-ageing at 325 °C compared with the as-cast alloys ^[19].

SEM images of the peak-aged alloys are presented in Fig. 5, and the corresponding EDS results are listed in Table 3. It can be



Fig. 3: XRD patterns of peak-aged alloys



Fig. 4: Optical micrographs of peak-aged alloys: (a) Alloy 1, (b) Alloy 2, (c) Alloy 3, (d) Alloy 4, (e) Alloy 5, and (f) partial enlarged drawing of Zone A in (d)

Table 2: Average grain sizes of experimental alloys in different conditions

		Average grain size (µm)			
	Alloy		325 °C peak-aged condition		
Alloy 1	Mg-4.2Zn-1.7RE-0.8Zr	48.4±2.2	49.6±2.7		
Alloy 2	Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca	36.7±2.9	37.5±2.4		
Alloy 3	Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.1Sr	33.8±2.1	34.8±2.1		
Alloy 4	Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr	31.3±2.0	32.5±2.5		
Alloy 5	Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.4Sr	34.9±2.4	35.2±2.1		

seen that interdendritic phases are quasi-continuously distributed along grain boundaries, and the volume fraction of the interdendritic phases increases with Ca and Sr additions. The particle in the grain centre (Point C) is the Zn-Zr phase from EDS analysis. The Zn-Zr particles act as heterogeneous nucleation sites for α -Mg grains and precipitate from the melt during the solidification process. The intermetallic compounds (Points B, E and G) located at the triple junctions of grain boundaries are identified as the ternary T-phase. Combining the XRD and EDS results, the interdendritic phases (Points D and F) are the Mg₅₁Zn₂₀ phase, while some RE, Ca and Sr elements are dissolved in it. The XRD and EDS results reveal that neither T-phase nor Mg₅₁Zn₂₀ phase dissolves into the α -Mg matrix after ageing treatment, indicating that these phases have a relatively good thermal stability. It's worth noting that the Ca content of Point E is a little high. To find out the reason, a TEM experiment was performed on the peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy (Alloy 4).

Figure 6 shows the bright-field TEM image of the peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy along with the corresponding EDS mappings for the intermetallic phases near the grain boundaries. The results indicate that the T-phase mainly contains Zn and Ce, although with a very slight Sr, Ca and Zr enrichment. In addition, a small number of Ca-enriched intermetallics [indicated by dotted circles in Fig. 6(c)] form in the interface between T-phase and matrix, which might be attributed to the enrichment of Ca in front of the solid-liquid interface during solidification. According to the Mg-Ca phase diagram, this enrichment would result in a high local concentration of Ca, leading to the formation of Mg₂Ca intermetallic phase. Mg₂Ca has a melting point of 715 °C, and is thus stable at ageing temperature ^[22]. It could be deduced that the formation of Mg₂Ca limits the amount of Ca dissolved in T-phase. Thus, the contribution of constitutional supercooling of Ca to grain refinement should be weakened.

Figures 7 (a) and (b) show the representative bright-field TEM images of the precipitates within the grain of the peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy (Alloy 4). It can be found that dense short rod-shaped precipitate is observed within the α -Mg matrix. The SAED pattern with the electron beam is parallel to the <2110> direction, as shown in Fig. 7(c), suggesting that the SAED pattern corresponds to Mg crystal structure. The β'_1 phase with hexagonal structure in Mg-Zn and Mg-Zn-RE alloys usually exists in rods with its long axis parallel to the $[0001]_{\alpha}$ direction $^{[23, 24]}$, thus, the short rod-shaped precipitate is thought to be β'_1 phase.

3.3 Mechanical properties

Figure 8 shows tensile properties of the ascast and peak-aged alloys. The peak-aged



Fig. 5: SEM micrographs of peak-aged alloys: (a and b) Alloy 1, (c and d) Alloy 2, and (e and f) Alloy 4; (b), (d) and (f) are enlarged drawings of Zones A, B and C, respectively

Positions	Mg	Zn	RE	Zr	Са	Sr
А	99.23	0.67	-	0.10	-	-
В	69.01	27.10	3.88	0.01	-	-
С	80.07	8.21	-	11.72	-	-
D	83.86	13.96	2.03	0.10	0.05	-
E	65.16	30.84	2.53	0.02	0.93	0.52
F	84.08	13.67	1.67	-	0.26	0.32
G	73.92	23.79	1.38	0.20	0.32	0.39

Table 3: EDS results in Fig. 5 (at.%)

Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy exhibits optimal mechanical properties with a UTS of 208 MPa, YS of 150 MPa and elongation of 3.5%. The strength enhancement is mainly ascribed to grain refinement and precipitation strengthening,

on the basis of microstructure observation. Grain size and yield strength are known to be inversely related and the relationship is derived by the Hall-Petch equation ^[25]. Grain refinement is achieved by minor Ca and Sr additions, leading to an increase in yield strength as a result of increased grain boundaries which can impede dislocation motion.

In addition, after peak-ageing at 325 °C, the experimental alloys obtain a significant increase in strength while a slight decrease in elongation compared with the corresponding mechanical properties of as-cast alloys ^[19]. The UTS/YS increment of Alloys 1 to 5 is 58.8 MPa/31.4 MPa, 62.8 MPa/28.6 MPa, 58.4 MPa/35.2 MPa, 63.9 MPa/35.6 MPa and 57.4 MPa/36.9 MPa, respectively. The improvement in strength can be explained by precipitation strengthening. According to the Orowan strengthening effect, fine rod-like β'_1 precipitate dispersed in the matrix plays a critical role in impeding the bypassing of dislocation lines ^[26]. Thus, the dense β'_1 precipitate contributes to increasing the



Fig. 6: TEM bright field image of peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy (a), and EDS mappings (marked with the box) of Mg, Ca, Zn, Ce, Sr and Zr for intermetallic particles on grain boundaries (b-g)



Fig. 7: (a), (b) Bright-field TEM images of peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy and (c) SAED pattern taken from the location indicated by arrow in (b) (electron beam is parallel to <2110> direction)



Fig. 8: Tensile properties of as-cast ^[19] (a) and peak-aged (b) experimental alloys

obstruction stress of dislocation, improving the strength of experimental alloys.

3.4 Corrosion resistance

3.4.1 Polarization curves

Figure 9 shows the potentiodynamic polarization curves of the as-cast and peak-aged alloys in 3.5wt.% NaCl solution. The results show that all the experimental alloys exhibit a similar polarization curve shape. The anodic and cathodic branches are not symmetrical. The cathodic polarization branches of the curves represent cathodic hydrogen evolution, while the anodic ones represent the dissolution of Mg. In addition, no passivity phenomenon happens in the alloys. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were calculated by

Tafel extrapolation of the cathodic branch. The fitting data of $E_{\rm corr}$ and $I_{\rm corr}$ extracted from the polarization curves are listed in Table 4. $E_{\rm corr}$ value represents the tendency towards corrosion and $I_{\rm corr}$ value indicates the corrosion rate. From Table 4, it can be seen that the $I_{\rm corr}$ value decreases significantly with 0.2wt.% Ca addition, and then the $I_{\rm corr}$ value further decreases with Sr addition increases from 0 to 0.2wt.%. The $E_{\rm corr}$ value shifts towards more positive direction after adding minor Ca and ySr (y = 0, 0.1, 0.2 wt.%) into Mg-4.2Zn-1.7RE-0.8Zr alloy. These results indicate that minor additions of Ca or/and Sr contribute to improvement of the corrosion rate of Mg-4.2Zn-1.7RE-0.8Zr alloy. TRE-0.8Zr-0.2Ca-ySr alloys decreases with the increase of Sr content from 0wt.% to 0.2wt.%, and then increases when



Fig. 9: Potentiodynamic polarization curves of as-cast (a) and peak-aged (b) alloys tested in 3.5wt.% NaCl solution

Table 4: Fitting results of potentiodynamic polarization curves

Alloys	E _{corr} (V)	I _{corr} (A·cm ⁻²)
As-cast Mg-4.2Zn-1.7RE-0.8Zr (Alloy 1)	-1.568	17.32×10⁻⁵
As-cast Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca (Alloy 2)	-1.546	2.64×10 ⁻⁵
As-cast Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.1Sr (Alloy 3)	-1.540	2.21×10 ⁻⁵
As-cast Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr (Alloy 4)	-1.531	2.09×10 ⁻⁵
As-cast Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.4Sr (Alloy 5)	-1.534	2.55×10⁻⁵
Peak-aged Mg-4.2Zn-1.7RE-0.8Zr (Alloy 1)	-1.548	8.75×10⁻⁵
Peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca (Alloy 2)	-1.543	5.89×10⁻⁵
Peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.1Sr (Alloy 3)	-1.534	5.08×10⁻⁵
Peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr (Alloy 4)	-1.476	2.06×10 ⁻⁵
Peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.4Sr (Alloy 5)	-1.509	2.16×10⁻⁵

Sr further increases to 0.4wt.%. The $E_{\rm corr}$ and $I_{\rm corr}$ variations of peak-aged alloys are similar to those of as-cast alloys. The peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy possesses the highest corrosion resistance among the experimental alloys.

3.4.2 Hydrogen evolution and weight loss measurements

Figure 10 shows the hydrogen evolution in 3.5wt.% NaCl solution for the as-cast and peak-aged alloys. It can be seen that the hydrogen evolution volume continuously increases with increase of immersion time. The rate of hydrogen evolution is high at the initial stage, then, decreased after approximately 8 h for as-cast and peak-aged alloys. In addition, the Mg-4.2Zn-1.7RE-0.8Zr alloy exhibits a considerably higher hydrogen evolution volume compared with the Ca- or/and Sr-modified Mg-4.2Zn-1.7RE-0.8Zr alloys. The hydrogen evolution volume of peak-aged alloys is lower than that of as-cast alloys. Moreover, the peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy (Alloy 4) exhibits the lowest hydrogen evolution volume among the experimental alloys, which are in a good agreement with those of electrochemical tests.

Corrosion rates obtained from weight loss measurements in 3.5wt.% NaCl solution under constant immersion time of 36 h are shown in Fig. 11. In comparison to the as-cast alloys, the peak-aged alloys show reduced corrosion rates. In addition, minor additions of Ca and/or Sr improve the corrosion resistance of Mg-4.2Zn-1.7RE-0.8Zr alloy. The corrosion rate of

as-cast and peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-ySr alloys decreases with the increase of Sr content from 0 to 0.2wt.%, and then increases with the further increase of Sr content from 0.2wt.% to 0.4wt.%. The peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy possesses the lowest corrosion rate (P_w) of 2.19 cm·year⁻¹. The corrosion rate obtained from weight loss measurement represents the uniform corrosion rate of the alloys. In the late stage of corrosion, some uncorroded second phases distributing in grain boundaries will fall off as the adjacent Mg is corroded seriously. Thus, the corrosion rate calculated from weight loss tests is always higher than the actual one.

3.4.3 Corrosion morphology

Figure 12 shows the corrosion morphologies of the Alloys 1 and 4 after different immersion times with removal of corrosion products. As shown in Figs. 12 (a), (d), (g) and (j), the samples with corrosion time of 10 h show that corrosion pits preferentially form nearby the second phases inside the Mg grains and along grain boundaries. Combined with galvanic corrosion theory, initial pitting occurs around Zn-Zr particles within the Mg grains and T-phase along grain boundaries. The electrode potentials of the Zn-Zr particles and T-phase are more positive than the Mg matrix ^[27]. Thus, the Zn-Zr and T-phase act as cathodes of the adjacent Mg matrix, leading to galvanic couples between the second phases and Mg matrix. After 20 h immersion, it is obvious that Mg matrix is corroded severely due to galvanic corrosion, leaving channels along grain boundaries and craters inside the grains [Figs. 12 (b), (e), (h) and (k)]. Finally, the corroded Mg grains fall out of the alloy surface, leaving the semi-continuous and continuous skeleton of T-phase, as shown in Figs. 12 (c), (f), (i) and (l). The distribution of cathodic T-phase becomes an important factor affecting



Fig. 10: Hydrogen evolution in 3.5 wt.% NaCl solution for as-cast (a) and peak-aged (b) alloys





the corrosion resistance. With the decrease of grain size and increase of volume fraction of second phases in peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy (Alloy 4), the continuous netlike distribution of T-phase contributes to forming a compact barrier layer. The barrier layer effectively prevents Cl⁻ ions from penetrating into the Mg matrix, which can improve the corrosion resistance of the alloys.

4 Discussion

The corrosion mechanism is elaborated in the two aspects of the matrix and second phases. The corrosion resistance of the matrix mainly depends on the protectiveness of the surface oxide film. Figure 13 shows the SEM image and XRD patterns of the corrosion layer on the as-cast alloy after 20 h immersion. The XRD results indicate that the main corrosion product is



Fig. 12: SEM images of corroded surface for as-cast and peak-aged alloys immersed in NaCl solution for different times. The insets in Figs. 12 (a), (h) and (i) are microstructures with high magnification





Mg(OH)₂. The surface morphology suggests the thick and loose Mg(OH)₂ film is stacked on the corroded surface, and covers corrosion pits. The Mg(OH)₂ film will be broken by the large amount of hydrogen produced by the corrosion reaction. Due to the breakdown of Mg(OH)₂ film, the Cl⁻ ion penetrates the Mg(OH)₂ film along the cracks and attack the fresh Mg matrix. Mg(OH)₂ film cannot drastically prevent the penetration of damaging Cl⁻ ion into the Mg matrix ^[28]. As a result, the Mg(OH)₂ film provides little protection against Mg matrix corrosion. In addition, the grain refined Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy is shown to have a reduced corrosion rate, which might be ascribed to the higher density of grain boundaries brought by grain refinement. The increased grain boundaries and triple junctions may contribute to make the oxide layer cling to the alloy surface, forming a more compact and protective Mg(OH)₂ film with enhanced resistance to cracking ^[29]. Since the grain sizes studied are in the narrow range of 30-50 µm, the influence of grain size on the corrosion rate of the experimental alloys is minor in comparison with the second phases.

As shown in Fig. 12, corrosion occurs near the Zn-Zr particles and T-phase. Thus, in order to better illustrate the effect of second phases on the corrosion behavior of the alloys, a schematic diagram of corrosion process is given, as shown in Fig. 14. It is well known that the second phases play dual roles in corrosion process. The discontinuous second phases accelerate the corrosion rate due to the galvanic corrosion, while the finely and continuously distributed second phases improve the corrosion resistance due to the barrier effect of the second phases. As shown in Fig. 14(a), the corrosion pits initiate in the Mg matrix adjacent to the Zn-Zr particles and T-phase in the initial period of corrosion. Due to the presence of micro-galvanic corrosion between the Zn-Zr particles/T-phase and the neighboring Mg matrix, the shallow channels around T-phase and crater around Zn-Zr particles are formed. Then, micro-galvanic acceleration corrosion further aggravates the corrosion process. The second phases and adjacent matrix areas are continually corroded along the depth direction, resulting in deep and wide corrosion pits, as



Fig. 14: Schematic diagram of corrosion process for experimental alloys

shown in Fig. 14(b). In the late stage of corrosion [Fig. 14(c)], the persistent dissolution of matrix areas favors the detachment of the adjacent intermetallic phases. Finally, in Fig. 14(d), when intermetallics fall out of the alloy surface, the barrier wall is left behind without potential differences. The micro-galvanic corrosion of Mg alloys is affected by the volume fraction and the distribution of the second phase. The large volume fraction of grain boundaries combined with the fine grain size in the alloys facilitate to construct a compact and continuous barrier wall, contributing to improve the corrosion resistance. In addition, the peak-aged alloys present the lower corrosion rate with the nano-sized precipitate of β'_1 phase. This might be because fine precipitate causes a uniform attack, and it has a less adverse influence on oxide film formation. Therefore, the peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy possesses the better corrosion resistance than other alloys.

5 Conclusions

Influence of ageing treatment on the microstructures, mechanical properties and corrosion behavior of Mg-4.2Zn-1.7RE-0.8Zr alloy micro-alloyed with Ca and Sr was investigated. The main conclusions can be drawn as follows:

(1) The addition of Ca or its combined addition with Sr promotes the precipitation hardening of the Mg-4.2Zn-1.7RE-0.8Zr alloy and shortens the time reaching peak hardness from 13 h to 12 h. The maximum hardness of 77.1 ± 0.6 HV for peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr is obtained (ageing at 325 °C for 12 h).

(2) The microstructures of peak-aged alloys mainly consist of α -Mg phase, Mg₅₁Zn₂₀ phase and ternary T-phase. Zn-Zr phase is formed within α -Mg matrix and Mg₂Ca phase is formed near T-phase due to the enrichment of Ca in front of the solid-liquid interface. Fine short rod-shaped β'_1 phase is precipitated within the α -Mg matrix under peak-aged condition.

(3) The peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy exhibits optimal tensile properties with an ultimate tensile strength of 208 MPa, yield strength of 150 MPa and elongation of 3.5%. The improvement in strength of peak-aged alloys is mainly attributed to precipitation strengthening.

(4) The peak-aged alloys show reduced corrosion rates compared with the as-cast alloys. In addition, minor additions of Ca and/or Sr improves the corrosion resistance of the Mg-4.2Zn-1.7RE-0.8Zr alloy. The peak-aged Mg-4.2Zn-1.7RE-0.8Zr-0.2Ca-0.2Sr alloy possesses the best corrosion resistance. This phenomenon is mainly attributed to the continuous and compact barrier wall constructed by the homogeneous and continuous second phases.

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