Effect of Zn Addition on the Microstructure and Mechanical Properties of Cast Mg–10Gd–3.5Er–xZn–0.5Zr Alloys

Qiu Zhang¹ · Wencai Liu¹ · Guohua Wu¹ · Liang Zhang¹ · Wenjiang Ding¹

Received: 28 February 2020 / Revised: 8 May 2020 / Accepted: 8 May 2020 / Published online: 23 July 2020
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Abstract

In this work, the effects of Zn content (0–2 wt%) on microstructural evolution and mechanical properties of cast Mg–10Gd–3.5Er–0.5Zr alloys are studied. The results show that the as-cast Mg–10Gd–3.5Er–xZn–0.5Zr alloys are mainly composed of Mg matrix and secondary (Mg, Zn)₃(Gd, Er) phases distributed along grain boundaries. With the increase in Zn content, the volume fraction of secondary (Mg, Zn)₃(Gd, Er) phases increases and the grains get refined. In the process of solid solution treatment, Zn addition can lead to the formation of long-period stacking ordered (LPSO) structures and the volume fraction of LPSO structures increases with Zn content. In addition, the Zn addition can reduce the vacancy formation energy and accelerate the diffusion rate of RE elements in Mg matrix. Because of the comprehensive effect of secondary phases and the accelerated diffusion rate, the base alloy and 2Zn alloy have less grain growth after solid solution treatment than that of the 0.5Zn alloy and 1Zn alloy. The precipitation process is also accelerated by enhanced diffusion rate. At room temperature (RT), the strengthening effect of $\beta' + \beta_1$ precipitates is more effective than that of LPSO structures, so the peak-aged 0.5Zn alloy exhibits the most excellent mechanical performance at RT, with yield strength of 219 MPa, ultimate tensile strength 296 MPa and elongation of 6.4%. While LPSO structures have stronger strengthening effect at elevated temperature than that of $\beta' + \beta_1$ precipitates, so the 1Zn alloy and 2Zn alloy have more stable mechanical performance than that of the base alloy and 0.5Zn alloy with the increase in tensile temperature.

Keywords Mg alloy · Mg–Gd–Er–Zn · Microstructure · Mechanical properties · Strengthening mechanism

1 Introduction

Magnesium alloy is an ideal material for lightweight structures because of its low density, high specific strength and good recyclability [1–6]. However, the inherent low strength and poor deformation formability of magnesium alloy limit the further applications [7, 8]. Therefore, it is essential to develop novel magnesium alloys with excellent mechanical performances. Alloying with rare earth (RE) elements

can lead to grain refinement strengthening, solid solution strengthening and precipitation strengthening, which is an effective way to enhance the mechanical performance of magnesium alloys. In particular, Gadolinium (Gd) is one of the most efficient RE elements for precipitation strengthening [6] and a lot of studies have been carried out on Mg–Gd based alloys with other RE elements (Y, Dy, Nd and Sc [9–12]). Erbium (Er) and Gd have similar atomic radius and high solid-solubility in Mg matrix at elevated temperature. Therefore, Mg–Gd–Er alloy system exhibits high mechanical performance by precipitation strengthening. For example, for peak-aged Mg–8Gd–3Er–0.5Zr alloy (all compositions are in wt% hereafter unless otherwise noted), the yield strength (YS) and ultimate tensile strength (UTS) can reach 173 and 261 MPa at room temperature (RT), 122 and 203 MPa at 250 °C, respectively. However, the elongation (EL) of peak-aged Mg–8Gd–3Er–0.5Zr alloy at RT is less than 5.5% [13]. It is reported that long-period stacking ordered (LPSO) structures can enhance the ductility of Mg alloys without reducing the strength [14, 15]. Since Zn is

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

✉ Wencai Liu
liuwc@sjtu.edu.cn

✉ Guohua Wu
ghwu@sjtu.edu.cn

¹ National Engineering Research Center of Light Alloy Net Forming and Key State Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

much cheaper than RE elements and can promote the formation of LPSO structures, the effects of Zn addition into Mg–Gd–RE alloys have received much industrial interest.

Due to their unique crystallographic features and promising mechanical properties, LPSO structures have received considerable attention in recent years. Some researchers attribute the mechanical improvement of cast Mg–Gd–RE alloy containing Zn to the strengthening effect of LPSO structures [16–19]. However, other researchers propose that the strengthening effect of LPSO structures is less effective than precipitation strengthening in cast magnesium alloys, suggest that the RE elements are more effective for strengthening in the form of precipitates than in LPSO structures [20–23].

In order to study the effects of Zn addition on the microstructure and mechanical properties of cast Mg–Gd–Er alloys, different contents of Zn are added into Mg–10Gd–3.5Er–0.5Zr alloy, and the nominal compositions of the studied alloys are Mg–10Gd–3.5Er– x Zn–0.5Zr ($x=0, 0.5, 1$ and 2). For brevity, the Mg–10Gd–3.5Er– x Zn–0.5Zr ($x=0, 0.5, 1$ and 2) alloys are denoted as base alloy, 0.5Zn alloy, 1Zn alloy and 2Zn alloy, respectively. The effects of Zn content on microstructure, age-hardening behaviour and mechanical properties of 10Gd–3.5Er– x Zn–0.5Zr alloys are studied.

2 Experimental

The studied alloys were prepared by conventional gravity casting. The ingots were prepared from high purity ($\geq 99.9\%$) Mg, Zn, Mg–30 wt%Gd, Mg–20 wt%Er and Mg–wt%Zr master alloys. All these component metals were preheated to 200 °C in a baking oven to evaporate the moisture, and then melted in an electric resistance furnace under protecting atmosphere consisting of CO₂ and SF₆. The melt was refined and purified by anti-oxidizing flux at 720 °C for 5–10 min. Then, the melt was held at 780 °C for 10 min to let Gd, Er, Zn and Zr atoms fully diffuse and inclusions subside to the bottom of the crucible. Finally, the melt was poured into a steel mould preheated to 200 °C and cooled in the air naturally.

The actual chemical compositions of the four as-cast alloys were determined by an inductively coupled plasma atomic emission spectroscopy analyser (ICP-AES,

Perkin-Elmer, Plasma 400). Subsequent thermal analysis was performed using a differential scanning calorimetry (DSC; STA 449 F3 Jupiter) at a heating rate of 10 °C/min from RT to 550 °C. Based on the results of DSC, the volume fraction of secondary phases and previous study [24], the base alloy and 0.5Zn alloy were solution treated at 500 °C for 6 h, the 1Zn alloy and 2Zn alloy are at 520 °C for 10 h in an electric furnace under the protection of SO₂ atmosphere, then the alloys were quenched in warm water of about 70 °C. The actual compositions accompanied with corresponding solution regimes are listed in Table 1. The following ageing treatment was performed at 225 °C in an oil bath for various time. As for the ageing hardness response, the hardness tests of alloys were taken by Vickers hardness tester with 5 kg load and 15 s dwelling time. Each Vickers hardness (HV) value was averaged from at least five individual measurements to ensure data reliability.

The mechanical properties of the alloys under various thermal conditions were tested by tensile tests at RT, 150 °C, and 300 °C. The gauge size of flat tensile samples was 10 mm long, 3.5 mm wide and 2 mm thick. The high-temperature tensile samples were heated and held at the specific temperature for 10 min to ensure the uniformity of the temperature. Due to the short holding time, the microstructure of the samples was unlikely to change. The tensile test was carried out at a strain rate of 1×10^{-3} /s on a Zwick/Roell-Z020 test machine equipped with an extensometer, and the data of tensile properties such as the YS, UTS and EL after fracture were averaged from at least three samples to ensure the data reliability.

After polishing and etching in an acetic-picric solution, the microstructures of the alloys were observed by optical metallograph (OM). The average grain size was measured by average linear intercept method. The phase constitution of the alloys was characterized by X-ray diffraction (XRD; Rigaku) with the scanning speed of 5°/min and the scanning range from 20° to 80°. The phase morphology and chemical composition were characterized by scanning electron microscopy (SEM) in Backscattered electron mode (SEM-BSE, Phenom XL) equipped with an energy dispersive spectroscopy (EDS). The fracture surfaces of tensile samples were observed by SEM in secondary electron mode (SEM-SE).

The precipitates in the peak-aged samples were characterized by transmission electron microscopy (TEM, JEM2100).

Table 1 Actual chemical compositions and solution regimes of the studied alloys

Alloy	Gd	Er	Zn	Zr	Mg	Solution regimes
Base	9.80	3.38	–	0.57	Bal.	500 °C × 6 h
0.5Zn	10.20	3.66	0.60	0.54	Bal.	500 °C × 6 h
1Zn	9.82	3.76	1.12	0.58	Bal.	520 °C × 10 h
2Zn	9.89	3.67	2.10	0.64	Bal.	520 °C × 10 h

Thin foil specimens were punched into discs with a diameter of 3 mm, mechanically ground to about 80 μm , then ground to 10 μm by dimple grinder (Fischione model 2000). Finally, the thin area was expanded and modified by ion milling thinner (Fischione model 691) with ion-accelerating voltage of 5 V and inclination angle of $\pm 10^\circ$.

3 Results

3.1 Microstructures of the as-Cast Mg–10Gd–3.5Er–xZn–0.5Zr Alloys

The OM and SEM-BSE images of the as-cast Mg–10Gd–3.5Er–xZn–0.5Zr alloys are shown in Fig. 1. It can be observed that the microstructures of the as-cast alloys are mainly composed of rosette-like grains and semi-continuous eutectic phases distributed along grain boundaries. With the increase in Zn content, the volume fraction of eutectic secondary phases increases continuously and the morphology of eutectic phases transforms from the discrete island into the continuous network. The grains of the as-cast alloys are also refined with the increase in Zn content. The

average grain size of the base alloy, 0.5Zn, 1Zn and 2Zn alloys is 76.2, 74.2, 72.8 and 61.1 μm , respectively.

Line scanning was carried out on the as-cast 0.5Zn alloy to characterize the element distribution. According to the scanning results of the 0.5Zn alloy shown in Fig. 2, Gd, Er and Zn elements are mainly enriched in secondary phases and grain boundaries. The atomic concentration peak of Gd and Er are sharper than that of Zn, indicating that Gd and Er are more concentrated in the secondary phases than Zn.

Figure 3 shows the XRD patterns of the as-cast Mg–10Gd–3.5Er–xZn–0.5Zr alloys, which indicates that the microstructures of the as-cast alloys are mainly composed of α -Mg matrix and $(\text{Mg}, \text{Zn})_3(\text{Gd}, \text{Er})$ secondary phases. The intensity of diffraction peaks corresponding to $(\text{Mg}, \text{Zn})_3(\text{Gd}, \text{Er})$ phases is increasing with Zn content, which further confirms that the volume fraction of eutectic $(\text{Mg}, \text{Zn})_3(\text{Gd}, \text{Er})$ phase increases with the increase in Zn content.

The DSC curves of the as-cast Mg–10Gd–3.5Er–xZn–0.5Zr alloys are shown in Fig. 4. The results show that the base alloy has no apparent endothermic peak, while the 0.5Zn, 1Zn alloy and 2Zn alloy have clear endothermic peaks sited at about 520 $^\circ\text{C}$, indicating that $(\text{Mg}, \text{Zn})_3(\text{Gd}, \text{Er})$ secondary phases can be dissolved into

Fig. 1 Optical and SEM-BSE images of the as-cast Mg–10Gd–3.5Er–xZn–0.5Zr alloys: **a** base alloy; **b** 0.5Zn alloy; **c** 1Zn alloy; **d** 2Zn alloy

Fig. 2 Line scanning results of the as-cast Mg–10Gd–3.5Er–0.5Zn–0.5Zr alloy

the Mg matrix at about 520 °C. Moreover, the intensity of endothermic peaks rises with the Zn content. Since the area of endothermic peak is related to the amount of secondary phase, it can be induced that the volume fraction of $(\text{Mg}, \text{Zn})_3(\text{Gd}, \text{Er})$ secondary phases increases with Zn content, which is consistent with the results of OM and XRD.

3.2 Microstructures of the as-Quenched Mg–10Gd–3.5Er– x Zn–0.5Zr Alloys

The XRD patterns of the as-quenched Mg–10Gd–3.5Er– x Zn–0.5Zr alloys are presented in Fig. 5. Compared with the XRD results of the as-cast alloys, the diffraction peaks of $(\text{Mg}, \text{Zn})_3(\text{Gd}, \text{Er})$ after solid solution

treatment almost disappear, indicating that most of the secondary phases are dissolved into Mg matrix.

The microstructures of the as-quenched Mg–10Gd–3.5Er– x Zn–0.5Zr alloys are shown in Fig. 6. Compared with the microstructures of the as-cast Mg–10Gd–3.5Er– x Zn–0.5Zr alloys, most of $(\text{Mg}, \text{Zn})_3(\text{Gd}, \text{Er})$ secondary phases are dissolved into Mg matrix and the grains are coarsened after solution treatment. The average grain sizes of the as-quenched base alloy, 0.5Zn alloy, 1Zn alloy and 2Zn alloy are 78.2, 88.4, 95.2 and 68.5 μm , the corresponding coarsening rate are 2.7%, 19.1%, 30.7% and 8.8%, respectively. It can be observed that the grains of the 0.5Zn alloy and 1Zn alloy grow obviously after solution treatment, while there is no obvious growth for grains in the base alloy and 2Zn alloy. In addition, the as-quenched

Fig. 3 XRD patterns of the as-cast Mg–10Gd–3.5Er–xZn–0.5Zr alloys

Fig. 5 XRD patterns of the as-quenched Mg–10Gd–3.5Er–xZn–0.5Zr alloys

Fig. 4 DSC curves of the as-cast Mg–10Gd–3.5Er–xZn–0.5Zr alloys

microstructural constitutions of the Zn-containing alloys (0.5Zn alloy, 1Zn alloy and 2Zn alloy) and Zn-free alloy (base alloy) are quite different. In as-quenched state, the base alloy is only composed of super-saturated Mg matrix, while in the Zn-containing alloys, there are lamella-shaped structures distributed along grain boundaries, which are reported to be 14H-LPSO structures [18].

The SEM and point scanning results of the as-quenched 0.5Zn alloy are shown in Fig. 7. After solid solution treatment, there are residual cubic phases and lamella-shaped LPSO structures in the as-quenched 0.5Zn alloys. According to the results of point scanning, residual secondary phases are enriched with Gd and Er, LPSO structures are enriched with Gd, Er and Zn. The residual cuboid phases are also

found into other Mg–Gd–RE alloys [25, 26], but the structure and formation mechanism are still unclear.

3.3 Microstructures and Mechanical Properties of Peak-Aged Mg–10Gd–3.5Er–xZn–0.5Zr Alloy

The ageing hardness curves of Mg–10Gd–3.5Er–xZn–0.5Zr alloys aged at 225 °C are shown in Fig. 8, and it can be observed that all the studied alloys have age-hardening response. The Vickers hardness values of the as-quenched alloys are 62.0, 71.8, 76.6 and 72.0 HV, respectively. The as-quenched hardness values of the Zn-containing alloys (0.5Zn, 1Zn and 2Zn alloys) are relatively higher than those of the Zn-free alloy due to solid solution strengthening. At 225 °C, the hardness values of the Mg–10Gd–3.5Er–xZn–0.5Zr alloys increase gradually with ageing time until peak-aged. After aged for 128 h, the hardness of all the studied alloys reach the peak value. The peak-aged hardness values of the base alloy, 0.5Zn alloy, 1Zn alloy and 2Zn alloy are 79.5, 99.7, 91.7 and 75.6, respectively, and the corresponding hardness increments of each peak-aged alloy are 17.5, 27.9, 15.1 and 4.5. Thus, it can be seen that the 0.5Zn alloy shows the most potent age-hardening response, while that of the 2Zn alloy is relatively inferior.

The bright-field (BF) images of the peak-aged studied alloys and the corresponding selected area electron diffraction (SAED) patterns are exhibited in Fig. 9. According to the BF images and corresponding SAED patterns in Fig. 9a, c, e, the precipitates in the base alloy and 0.5Zn alloy are densely distributed on prismatic planes with a triangular arrangement, while the precipitates in the 1Zn alloy are quite scarce and coarse. The morphology of precipitates in the peak-aged Zn-free alloy and Zn-containing

Fig. 6 OM images and corresponding BSE images (insets) of the as-quenched Mg–10Gd–3.5Er–xZn–0.5Zr alloys: **a** base alloy; **b** 0.5Zn alloy; **c** 1Zn alloy; **d** 2Zn alloy

alloy is different too. The precipitates in the base alloy are lath-shaped with an average length of 250 nm. While the precipitates in the 0.5Zn alloy and 1Zn alloy are both rosary-shaped, which are connected by several bead-like units, and each unit has a rhombus dark core. The dark cores are β_1 precipitates, and the surrounding parts are β' precipitates. The average length of precipitates in the 0.5Zn alloy is about 145 nm, while the average size of precipitates in the 1Zn alloy is difficult to get since the precipitates in the 1Zn are too scanty. Figure 9f is an enlarged view of Fig. 9e, which shows more details about precipitates in the peak-aged 1Zn alloy. Compared with the 0.5Zn alloy, The rosary-shaped precipitates in the 1Zn alloy are not perfectly continuous. A broken point, β' phase and β_1 phase are pointed out by the arrows in Fig. 9f. In summary, the precipitates of the base alloy are mainly lath-shaped early-stage β' phases, while those of the 0.5Zn alloy and 1Zn alloy are mainly β' phases and β_1 phases. In particular, the average length of precipitates in the 0.5Zn alloy is relatively shorter than that in the base alloy. The precipitates in the 1Zn alloy are more discontinuous, coarser and scarcer than that in the base alloy

and 0.5Zn alloy. Figure 9b and d shows the bright images and corresponding SAED with electrical beam parallel to $[2\bar{1}\bar{1}0]$ of the base alloy and 0.5Zn alloy. For the 0.5Zn alloy, there are several linear structures perpendicular to $[0001]$ lattice direction in Fig. 9d, indicating the existence of LPSO structures, similar results were reported in many previous works [27, 28].

The mechanical properties of the as-quenched and peak-aged Mg–10Gd–3.5Er–xZn–0.5Zr alloys are presented in Fig. 10. As shown in Fig. 10a, due to the solid solution strengthening effect, the YS and UTS of the as-quenched Zn-containing alloys are relatively higher than those of the as-quenched base alloy. The as-quenched base alloy and 2Zn alloy have higher ductility than that of the 0.5Zn alloy and 1Zn alloy. The mechanical properties of the peak-aged alloys at RT are shown in Fig. 10b, for the base alloy and 0.5Zn alloy, the YS and UTS are enhanced a lot along with ductility decreased after ageing treatment. While the precipitation strengthening effect of the 1Zn alloy and 2Zn alloy is negligible, and the strength at RT is not obviously improved after ageing treatment. The peaked-aged 0.5Zn alloy shows the best comprehensive mechanical property at RT, and its

Fig. 7 SEM, and point scanning results of as-quenched Mg–10Gd–3.5Er–0.5Zn–0.5Zr alloy: **a** SEM with point scanning location labelled; **b–d** point scanning results of cubic phases; **e** point scanning results of LPSO structures

Fig. 8 Vickers hardness curve of Mg-10Gd-3.5Er- x Zn-0.5Zr alloys aged at 225 °C

UTS, YS and EL are 216 MPa, 296 MPa and 6.4%, respectively. The base alloy and 2Zn alloy exhibit excellent ductility whose EL is about 11%, but the EL of the 0.5Zn and 1Zn alloy is relatively low with the value of about 6.5%.

The results of tensile test at 150 °C are shown in Fig. 10c, the EL of all the tested alloys is significantly higher than that at RT. With the increase in tensile temperature from RT to 150 °C, the strength of the base alloy and 0.5Zn alloy decreases obviously, while the strength of the 1Zn alloy and 2Zn alloy is relatively stable. For the tensile test at 300 °C (Fig. 10d), the strength of all the tested alloys decreases further, and the strength of the 1Zn alloy and 2Zn alloy is higher than that of the 0.5Zn alloy.

Figure 11 shows the SEM-SE images of fracture surfaces of the Mg-10Gd-3.5Er- x Zn-0.5Zr alloys at RT, 150 °C, and 300 °C. The fracture surfaces of the alloys tested at RT are mainly composed of cleavage planes and tear ridges, which indicates the fracture mode is quasi-cleavage fracture. At 150 °C, shallow dimples are observed on the fracture surfaces of the 1Zn alloy and 2Zn alloy, and dimples appear on fracture surfaces of all alloys at 300 °C. It can be induced that the 1Zn alloy and 2Zn alloy can transit to ductile fracture at a relatively lower temperature compared with the base alloy and 0.5Zn alloy, indicating that Zn addition is beneficial to the ductility of the alloys.

4 Discussion

Based on the results of microstructural analysis and mechanical properties of the Mg-10Gd-3.5Er- x Zn-0.5Zr ($x = 0, 0.5, 1, 2$) in as-cast, as-quenched and peak-aged conditions, the effect of Zn content on microstructures and mechanical properties will be discussed as follows.

4.1 Effect of Zn Content on As-Cast Microstructures

Mg, Gd, Er and Zn have the same hexagonal close-packed (hcp) crystal structure. However, compared with Gd and Er, Zn has the same valence state with Mg, and the atomic radius of Zn is closer to Mg. Therefore, according to the Hume-Rothery Rules [29], Zn can dissolve into Mg matrix more easily than Gd and Er. During the solidification stage, Zn atoms can reduce the equilibrium solubility of RE atoms and decrease the solute partition coefficient of Gd and Er. At the solid-liquid frontier, more solute RE atoms will be expelled into the melt, leading to the formation of constitutional supercooling. As a result, with the increase in Zn content, the volume fraction of (Mg, Zn)₃(Gd, Er) eutectic phases of as-cast alloys increases and the grains get refined. It is also reported that the Zn addition into Mg-Gd-Y-Zr alloys can lead to larger volume fraction of eutectic phases and grain refinement [24, 30].

4.2 Effect of Zn Content on As-Quenched Microstructures and Mechanical Properties

Generally, the thermal-stable secondary phases can inhibit the grain coarsening during solid solution. Considering that the volume fraction of eutectic secondary phases increases with Zn content, the grain coarsening rate after solid solution treatment should have decreased with the increase in Zn content. However, the OM results indicate that the grain coarsening rate after solution treatment of the base alloy and 2Zn alloy is less than that of the 0.5Zn alloy and 1Zn alloy, which is different from the general situation.

Grain coarsening during solution treatment is a process related to grain boundary diffusion [31]. The atomic radii of Mg, Gd, Er, Zn are relatively close, which are 173, 238, 232 and 139 pm, respectively, which are relatively close. Therefore, the diffusion mechanism is substitutional diffusion, and the corresponding diffusion coefficient can be calculated by the following equation:

$$D = D_0 \exp \left(\frac{-\Delta U_v - \Delta U_m}{kT} \right) \quad (1)$$

where D_0 is diffusion constant, ΔU_v is the vacancy formation energy, ΔU_m is atom migration energy, k is Boltzmann constant, T is the temperature in degree Kelvin. Since the substitutional diffusion process needs adequate vacancies to activate [32], the diffusion coefficient D is not only related to the atom migration energy ΔU_m , but also the vacancy formation energy ΔU_v . According to the result of simulation [33], the addition of Zn can reduce the vacancy formation energy, which means that Zn addition can promote the formation of vacancies. Therefore, for the RE elements in Mg matrix, the diffusion rate during solution treatment and ageing treatment

Fig. 9 TEM bright-field images and corresponding SAED patterns of peak-aged Mg–10Gd–3.5Er–xZn–0.5Zr alloys: **a, b** peak-aged base alloy with electron beam parallel to [0001] and $[2\bar{1}\bar{1}0]$; **c, d** peak-aged 0.5Zn alloy with electron beam parallel to [0001] and $[2\bar{1}\bar{1}0]$; **e, f** peak-aged 1Zn alloys with electron beam parallel to [0001] and the precipitates in higher magnification

Fig. 10 Mechanical properties of Mg-10Gd-3.5Er-xZn-0.5Zr alloys in various conditions: **a** as-quenched at RT; **b** peak-aged at RT; **c** peak-aged at 150 °C; **d** peak-aged at 300 °C

will be accelerated because of the low vacancy formation energy.

In the process of solution treatment, the addition of Zn has two opposite effects on grain coarsening. On the one hand, the $(\text{Mg}, \text{Zn})_3(\text{Gd}, \text{Er})$ secondary phases can restrain the grain coarsening during solution treatment, and Zn addition can increase the volume fraction of $(\text{Mg}, \text{Zn})_3(\text{Gd}, \text{Er})$ secondary phases. On the other hand, the addition of Zn can reduce the vacancy formation energy and increase the diffusion rate, thus promoting grain coarsening. In a word, the grain coarsening after solid solution is determined by the inhibition of the secondary phases and the promotion of the diffusion rate from lower vacancy formation energy. For the 0.5Zn alloy, the grain coarsening rate after solution treatment is higher than that of the base alloy because the amount of secondary phase is not enough to counter the promoted diffusion. For the 2Zn alloy, with the increase in Zn content, the amount of secondary phase gets enough to counter the effect of promoted diffusion, so the grains of the 2Zn alloy coarsened less than that of the 1Zn alloy after solution treatment.

According to the study of LPSO structures [34, 35], the mechanical properties of the as-quenched Mg-10Gd-3.5Er-xZn-0.5Zr alloys mainly depend on solid solution strengthening, the amount of LPSO structures and grain size. For the Zn-containing alloys, the LPSO structures are formed during solid solution treatment and the volume fraction of LPSO structures increases with Zn content. The strengthening effect of LPSO structures is sensitively dependent on size and morphology [36–38], while the size of LPSO phases in cast Mg-RE-Zn alloys is generally too large to effectively strengthen the alloys [6]. However, LPSO structures can improve the ductility by increasing the critical resolved shear stress (CRSS) of basal plane and promote the activation of non-basal plane slip [39, 40]. The activation of non-basal slip promotes more homogeneous plastic deformation of grains and reduces the stress concentration. For the as-quenched alloys, due to the solid solution strengthening effect, the Zn-containing alloys have higher YS and UTS, but lower EL than base alloy. For the alloys containing Zn, the 0.5Zn and 1Zn alloys have coarser grains and less LPSO

Fig. 11 SEM-SE images of fracture surfaces of the peak-aged alloys in different thermal conditions

structures, so the EL of the 0.5Zn and 1Zn alloys is lower than that of the 2Zn alloy.

4.3 Effect of Zn Content on Peak-Aged Microstructures and Mechanical Properties

As mentioned above, the Zn addition can promote the diffusion of RE in Mg matrix by reducing the vacancy formation energy. Because precipitation is a process related to

diffusion, the addition of Zn can also accelerate the precipitation. The precipitation sequence of the Mg–Gd–Er alloys is SSSS (super-saturated solid solution) $\rightarrow \beta''$ (hcp, D0_{19}) $\rightarrow \beta'$ (cbco) $\rightarrow \beta_1$ (fcc) $\rightarrow \beta$ (fcc) [41–43]. A part of the ageing sequence is illustrated in Fig. 12. According to the results of TEM, for the peak-aged alloys, the precipitates are mainly β' phases for base alloy, but β' and β_1 phases for the 0.5Zn and 1Zn alloys. Moreover, the precipitates in the 1Zn alloy are riper than that in the base alloy and 0.5Zn

Fig. 12 A part of the ageing sequence for Mg–Gd–Er alloy: **a** lath-shaped early-stage β' phase distributed on $\{11\bar{2}0\}$ planes; **b** β' phase with necks; **c** β_1 phase forming on $\{10\bar{1}0\}$ planes in the necking area of β' phase; **d** β' phase between two β_1 phases will break after a long time ageing treatment

alloy. It is also reported that the addition of a small amount of Zn can promote the nucleation and growth of β_1 phase in Mg–Gd–Zn alloy [44]. In addition, due to the formation of precipitates and LPSO structures will consume RE elements, high Zn content will lead to the formation of a large amount of LPSO structures and the scarcity of precipitates, which is harmful to mechanical performance at ambient temperature.

14H-LPSO structures are formed in the process of solution treatment and are stable in the stage of ageing treatment [45]. It has been reported that nano-hardness of different phases in Mg–6.0Gd–1.2Zn–1.2Zr alloy obeys the following order: α -Mg matrix < LPSO structure < eutectic phase. Nie et al. [22, 41] also reported that the strengthening effect of plate-shaped precipitates forming on prismatic plane is more effective than those forming on basal plane. Since the LPSO structure is essentially periodic stacking faults which is formed on the basal plane, the introduction of LPSO is unlikely to achieve substantial strength improvement. In other words, no matter the morphology is lamella-shaped or block-shaped, the strengthening effect of LPSO structures at ambient temperature is not as effective as β' and β_1 precipitates.

The results of high-temperature tensile tests show that the strength of the base alloy and 0.5Zn alloy decreases obviously with the increase in temperature, while the strength of the 1Zn alloy and 2Zn alloy is relatively thermal-stable. The strengthening effect of LPSO structures at ambient temperature is not as effective as β' precipitates, because the deformation of Mg alloys is mainly carried by basal slip and β' precipitates can become effective obstacles to basal slip. But dislocation climbing may be activated at elevated temperatures and LPSO structures can obstruct dislocation climbing

more effectively. In summary, for magnesium alloys with precipitates and LPSO structures, the main strengthening phases depend on thermal conditions. The precipitates are more strengthening-effective at ambient temperature, while LPSO structures contribute more to strengthening at elevated temperature.

5 Conclusions

The microstructures, mechanical properties and ageing hardening behaviour of the Mg–10Gd–3.5Er– x Zn–0.5Zr ($x = 0, 0.5, 1$) alloys are studied, the following conclusions can be drawn:

1. Zn addition can increase the volume fraction of secondary (Mg, Zn)₃(Gd, Er) phase in the as-cast alloys and LPSO structures in the as-quenched alloys.
2. Zn addition can accelerate the diffusion rate of RE elements in Mg matrix by reducing vacancy formation energy. Due to comprehensive effect of accelerated diffusion rate and inhibition effect of secondary phases, the base alloy and 2Zn alloy have smaller grain coarsening rate compared with the 0.5Zn alloy and 1Zn alloy. The precipitates in the Zn-containing alloys are ripier than those in the Zn-free alloys because of the accelerated diffusion rate.
3. The mechanical performance of the peak-aged alloys is mainly determined by $\beta' + \beta_1$ precipitates and LPSO structures. At ambient temperature, the strengthening effect of $\beta' + \beta_1$ precipitates is more effective than that of LPSO structures, while LPSO structures are more effective at elevated temperature.

tive strengthening at elevated temperature since they can efficiently hinder dislocation climbing.

Acknowledgments This work is financially supported by the National Natural Science Foundation of China (Nos. 51771115, 51775334 and 51821001), the National Science and Technology Major Project (No. 2017ZX04006001), the National Key R&D Program of China (Grant No. 2016YFB0701205) and the Joint Fund for Space Science and Technology (No. 6141B06300401).

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