

Influence of Gd, Nd and Ce Additions on Microstructures and Mechanical Properties of Ultra-light Dual Phase Mg-9Li-0.4Zr Alloys

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Effects of various rare-earth elements (RE: Gd, Nd and Ce) additions on microstructures and mechanical properties of ultra-light dual phase Mg-9Li-0.4Zr alloy were investigated. The results indicated that Mg-9Li-5RE-0.4Zr alloys exhibited α -Mg, β -Li and RE-containing intermetallic compound structures. 5 wt.% Gd, Nd and Ce additions enhanced the strength properties of as-extruded Mg-9Li-0.4Zr alloy, but greatly deteriorated the ductility. The final mechanical properties of Mg-9Li-5RE-0.4Zr alloys were 161MPa~167MPa in ultimate strength, 141MPa~156MPa in yield strength and 20.8%~32.5% in elongation. Heat treatment was hardly able to improve the mechanical properties for Mg-9Li-5RE-0.4Zr alloys.

Keywords: Rare-earth elements, Mg-Li alloys, Strengthening, Mechanical properties, Heat treatment

1. Introduction

Mg-Li based alloys, with extremely low density, are characterized by high specific strength and ductility, good magnetic screening and shock resistance ability¹⁻³. Li can decrease the *c/a* ratio of α -Mg so that none-basal slips become easier to be activated. Meanwhile, when Li content is between 5.5 and 10.3% (mass fraction, below the same), the crystal structure of a part of Mg-Li alloy transforms from HCP to BCC, which results in a α + β dual phase structure⁴. β phase is able to enhance the ductility and formability of dual phase Mg-Li alloys, some of these alloys even can be cold worked⁵. Therefore, Mg-Li alloys are still drawing industrial and academic interests nowadays⁶⁻⁸.

However, the strength properties and work hardening capacity of Mg-Li binary alloys are very low, which restrict the application of Mg-Li alloys. In order to strengthen them, some research works have been carried out recently. Alloying Mg-Li alloys by rare-earth elements (RE) is an effective approach due to the significant improvement of RE on strength properties and room stability of magnesium alloys⁹⁻¹¹. Many papers reported the strengthening effects of RE on Mg-Zn, Mg-Al or Mg-RE alloys¹²⁻¹⁴, but few on Mg-Li alloys, especially on high Li-containing alloy. The optimum amount of RE in high Li-containing Mg-Li alloy is still unclear. Therefore, three Mg-9Li-0.4Zr alloys strengthened by 5% Gd, 5% Nd and 5% Ce respectively were prepared in this work to investigate the influences of these RE elements on microstructures and mechanical properties in an attempt to provide some detailed and comprehensive experimental results to researchers in the field.

2. Experimental

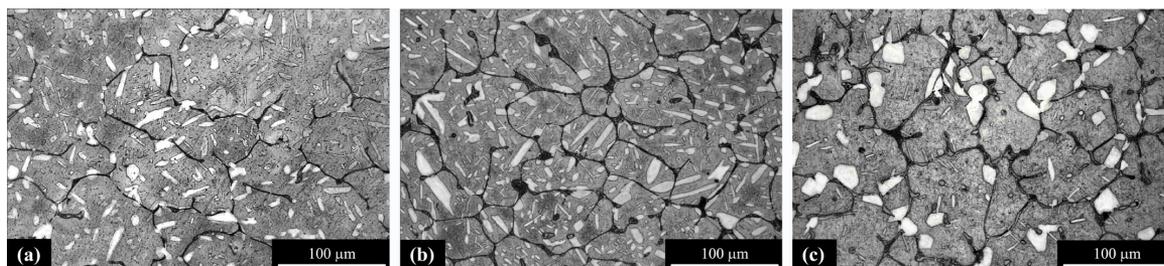
Commercial pure Mg (99.95%) and pure Li (99.9%), Mg-50%Gd, Mg-20%Nd, Mg-10%Ce, and Mg-30%Zr master alloys were used in this work. Pure Mg was firstly melted in a resistance furnace with an iron crucible under the protective atmosphere of CO₂ and SF₆ in the proportion of 20:1, then Mg-RE master alloys were put in the Mg melt at 780°C. Pure Li was added into the melt when the melt temperature dropped to 660°C. After 10 min's standing, the melt was poured into a 200°C pre-heated iron cylindrical mold with a diameter of 50mm. Chemical compositions of three Mg-9Li-5RE-0.4Zr alloys were analyzed by inductive coupled plasma atomic emission spectroscopy (ICP-AES) and the results were listed in Table 1. Densities of alloys were measured in the method of hydrostatics at 20°C and the results were given in Table 1. All ingots were homogenization treated at 320°C for 12h, then indirect extruded into Φ 12mm bars with 17:1 extrusion ratio at 100°C.

The specimens for optical microstructure observation were mechanical polished and further etched in a solution of 4% nitric acid in ethanol for 15~20s, and then examined by optical microscope (OM, Olympus-GX71). The constituent phases were observed and identified by scanning electron microscope (SEM, JEM-7001F), X-ray diffraction (XRD, MAX-A) and energy dispersive spectroscopy (EDS). Mechanical properties were obtained through tensile test conducted by electronic material testing machine (AG-X100kN) three times for each condition with a constant speed of 2mm/min at room temperature. The tensile test specimens were taken parallel to the extrusion direction. Heat treatment was carried out in an air circulative resistance furnace. Fractographies were observed by SEM. The heat treatment method for Gd-containing alloy was 373°C×1h solution-treated,

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Table 1. Chemical compositions and densities of as-cast Mg-9Li-5RE-0.4Zr alloys

Nominal constitution	Chemical analysis constitution (wt.%)					Densities (kg/m ³)
	Li	Gd	Nd	Ce	Zr	
Mg-9Li-5Gd-0.4Zr	9.05	4.36			0.45	1548
Mg-9Li-5Nd-0.4Zr	9.06		4.12		0.35	1535
Mg-9Li-5Ce-0.4Zr	9.09			5.55	0.36	1531


Figure 1. Microstructures of as-cast (a) Gd-containing, (b) Nd-containing and (c) Ce-containing alloys.

subsequently water quenching and 110°C×4h aging-treated; the heat treatment methods for Nd and Ce-containing alloys was 373°C×1h solution-treated, subsequently water quenching and 110°C×52h aging-treated. HV hardnesses of heat-treated alloys were examined by durometer (Qness, Q250) three times for each condition.

3. Results and Discussion

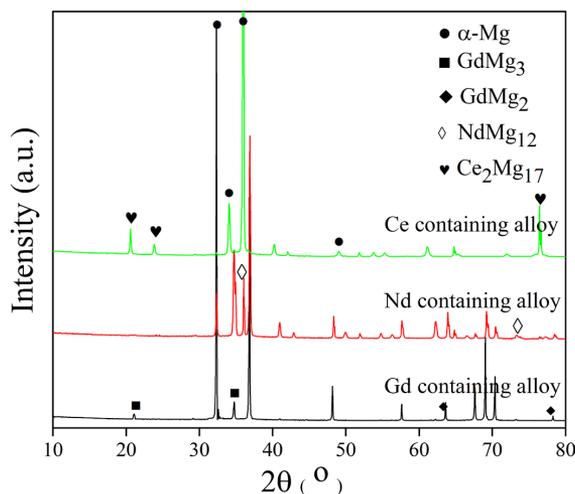
3.1 Densities and microstructures of as-cast Mg-9Li-5RE-0.4Zr alloys.

Densities of three as-cast Mg-9Li-5RE-0.4Zr alloys ranged from 1531 to 1548 kg/m³ (Table 1). Compared with the density of pure Mg (1738 kg/m³) and AZ31 alloy (1780 kg/m³), Mg-9Li-5RE-0.4Zr alloys proposed in this work still have significant ultra-light property. Hence, these alloys are possible to be used as a kind of ultra-light structural material as long as their mechanical properties are acceptable.

Microstructures of as-cast Mg-9Li-5RE-0.4Zr alloys were shown in Figure 1. All microstructures consisted of α -Mg, gray β -Li and small black disperse precipitates. Since the Li contents of the experimental alloys were within the range between 5.5 and 10.3%, β -Li phase then formed and transformed Mg-9Li-5RE-0.4Zr alloys to dual phase alloys. XRD patterns shown in Figure 2 suggested that GdMg₃ and GdMg₂ formed in Gd-containing alloy, NdMg₁₂ formed in Nd-containing alloy and Ce₂Mg₁₇ formed in Ce-containing alloy. Constituent phases observed by SEM were identified by EDS and shown in Figure 3, from which it can be seen that the intermetallic compounds were of fishbone-like distribution at grain boundaries and β -Li phase showed typical dendritic morphology and distributed on the α -Mg matrix in three RE-containing alloys.

3.2 Microstructures and mechanical properties of as-extruded Mg-9Li-5RE-0.4Zr alloys.

Microstructures of as-extruded Mg-9Li-5RE-0.4Zr alloys were shown in Figure 4. Nd and Ce-containing alloys presented complete dynamic recrystallization (DRX)


Figure 2. XRD patterns of RE-containing alloys.

microstructures with crushed precipitates along the extrusion direction (Figure 4b and c). DRX was less complete in Gd-containing alloy (Figure 4a), in which, elongated α -Mg and typical deformation band structure can be observed. It was interesting to see that, unlike Figure 4b and c, most particles in Figure 4a were found unbroken and still retained their original shape and size after extrusion. This phenomenon possibly because, on the one hand, intermetallic compounds of GdMg₃ and GdMg₂ formed in Gd-containing alloy had high hardness and intensity; on the other hand, the extrusion ratio of 17:1 adopted in this work was too low to crush those intermetallic compounds during extrusion. For Nd and Ce-containing alloys, precisely because many crushed and fine particles probably acted as nucleation sites during DRX, these two alloys showed more complete DRXed microstructures than Gd-containing alloy.

The mechanical properties of as-extruded RE-free and RE-containing alloys were given together in the form of a histogram in Figure 5. By comparison, Gd, Nd and Ce additions improved ultimate strength by 21~27 MPa,

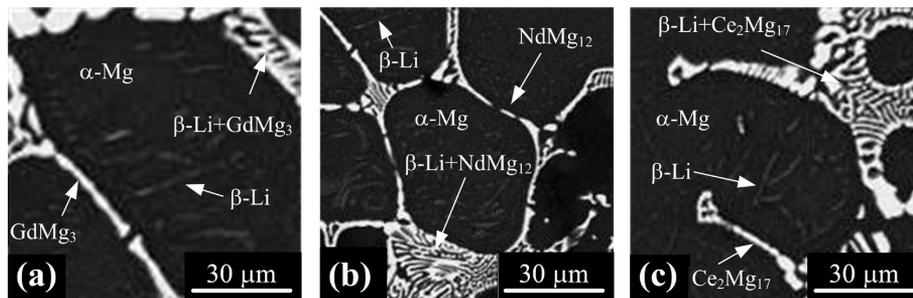


Figure 3. SEM images of as-cast (a) Gd-containing, (b) Nd-containing and (c) Ce-containing alloys.

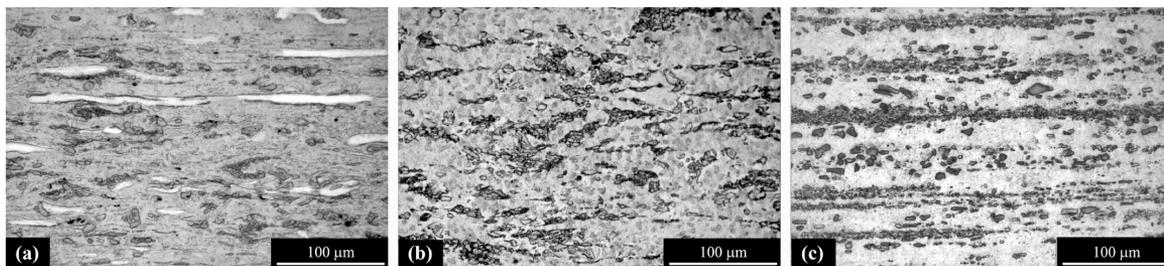


Figure 4. Microstructures of as-extruded (a) Gd-containing, (b) Nd-containing and (c) Ce-containing alloys.

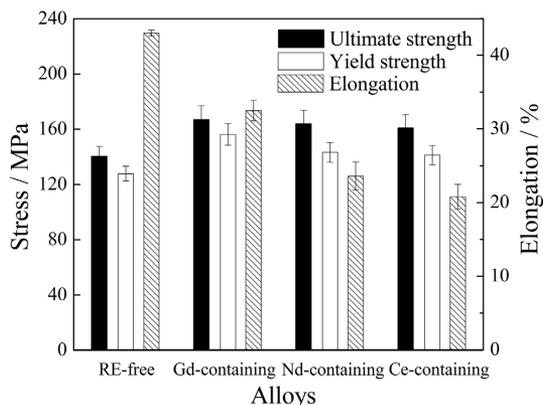


Figure 5. Mechanical properties of as-extruded RE-free and RE-containing alloys.

yield strength by 14~29 MPa, but decreased elongation by 10.5~22.2%. It could be concluded that 5% additions of Gd, Nd and Ce obviously enhanced the strength properties of as-extruded Mg-9Li-0.4Zr alloy. Nevertheless, the final ultimate strengths were 167 MPa, 164 MPa and 161 MPa in Gd, Nd and Ce-containing alloys respectively, which were still relatively low to be used as structural material.

The strength properties enhancement by extrusion was not significant probably because of the low extrusion ratio adopted in this work, which resulted in limited deformation of α -Mg. ¹⁵ reported that, for dual phase Mg-Li alloys, with the increasing of extrusion ratio, strength properties increased while ductility showed a tendency of decreasing. Only when the extrusion ratio reached 79:1 could the best strength properties be achieved in their investigations. Therefore, the low extrusion ratio should be the main cause of the low strength properties enhancement obtained in this work.

Strengthening effects of RE in dual phase Mg-Li alloys resulted from multi strengthening mechanisms, such as solid solution, grain refinement and second phase dispersion¹⁶. From Figure 4, it could be seen that massive RE-containing intermetallic compounds distributed between deformation bands, hence it was reasonable to deduce that the main role of RE played was formation of intermetallic compounds rather than dissolution in matrix. Also proved that the solid solution strengthening effect of Gd in Mg-Li alloys might be negligible.¹⁷

The fractographies of the as-extruded Mg-9Li-5RE-0.4Zr alloys were shown in Figure 6. All the fracture morphologies exhibited ductile fracture with massive dimples which agreed with the report¹⁸. Particles could be seen at the bottom of dimples in all the three alloys (as marked in Figure 6). Normally, dispersed intermetallic compounds could strengthen wrought Mg alloys effectively. However, in this work, most crushed intermetallic compounds were found aggregated within deformation bands regions as shown in Figure 4, and these aggregated particles probably became crack sources during extrusion and led to the deterioration of ductility.

3.3 Microstructures and mechanical properties of heat-treated Mg-9Li-5RE-0.4Zr alloys.

The eutectic temperature (T_e) of Mg-9Li binary system is at 588°C, and then the solution temperature for Mg-Li alloys should be at around 373°C ($0.75T_e$). High aging temperature and long aging time lead to Li losses and severe oxidation to Mg-Li alloys. To find the optimal ageing time for Mg-9Li-5RE-0.4Zr alloys, the HV hardness of alloys for 0-60h aging time at 110°C were examined and shown by curves in Figure 7. The trends of curves for Nd and Ce-containing alloys were similar on the whole. The peak values were 51.7 and 51.2 at 52h. For Gd-containing alloy, the peak value of 53.2 appeared at 4h.

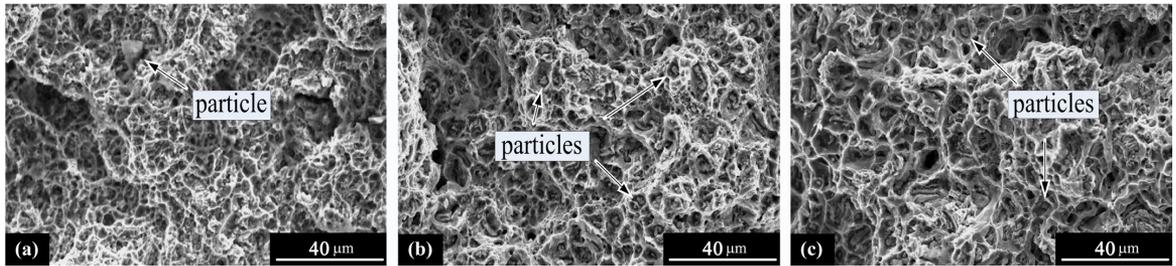


Figure 6. Tensile fracture surfaces of as-extruded (a) Gd-containing, (b) Nd-containing and (c) Ce-containing alloys.

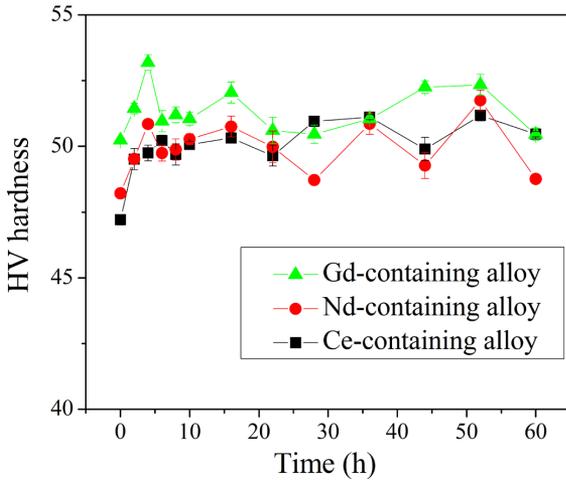


Figure 7. Curves of HV hardness-aging time of RE-containing alloys.

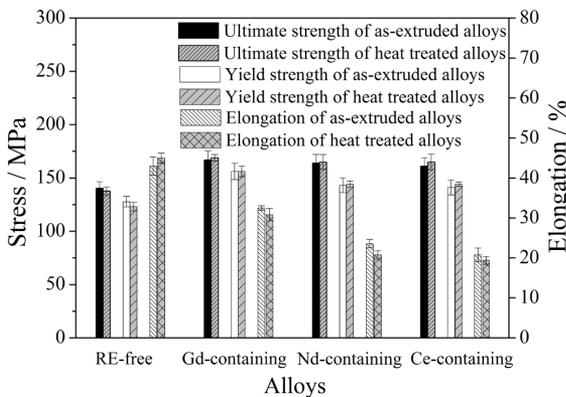


Figure 8. Comparison of mechanical properties between as extruded and heat treated RE-containing alloys.

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Based on the HV hardness curves, 373°C×1h solution-treated, subsequently water quenching and 110°C×4h aging-treated were adopted for Gd-containing alloy; 373°C×1h solution treated, subsequently water quenching and 110°C×52h aging-treated were adopted for Nd and Ce-containing alloys. For easy comparison, the mechanical properties of as-extruded and heat-treated alloys were shown together in Figure 8. Clearly it can be seen that there was almost no change in mechanical properties between as-extruded and heat-treated Mg-9Li-5RE-0.4Zr alloys.

4. Conclusions

Microstructures and mechanical properties of as-extruded and heat-treated Mg-9Li-5RE-0.4Zr alloys (RE: Gd, Nd and Ce) were studied in this paper, which led to the following conclusions:

- (1) Mg-9Li-5RE-0.4Zr alloys exhibited α -Mg, β -Li and RE-containing intermetallic compound structures.
- (2) 5% additions of Gd, Nd and Ce enhanced the strength of as-extruded Mg-9Li-0.4Zr alloy, but greatly deteriorated the ductility, which could be attributed to the low extrusion ratio and aggregated intermetallic compounds.
- (3) Heat treatment was hardly able to improve the mechanical properties for Mg-9Li-5RE-0.4Zr alloys.

Acknowledgements

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