Microstructure and mechanical properties of Mg–5Li–3Al–2Zn–*x*RE alloys

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Abstract Mg–5Li–3Al–2Zn–*x*RE alloys were prepared. The microstructure and mechanical properties of as-cast and wrought specimens were studied. RE elements in Mg–5Li– 3Al–2Zn alloy cause the microstructure refinement and the formation of Al₃La, which bring about the improvement of mechanical properties of alloys. The optimal RE content for Mg–5Li–3Al–2Zn alloy is 2 wt%, which makes the microstructure the finest and the mechanical properties the best. The further increase of RE content makes the microstructure be coarsened and the morphology of Al₃La change from particular to rod-like and pearlite-like eutectic shape, leading to the poor mechanical properties of alloys.

Introduction

Magnesium alloys are used more and more widely in the fields of aerospace, automobile, electron, etc. However, because of the close-packed hexagonal (HCP) lattice of magnesium, the plasticity property of magnesium alloys is relatively poor [1, 2]. Therefore, most of magnesium alloys parts are made by die-casting method. The process of diecasting is relatively low efficient and high costly.

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To avoid this shortcoming, lithium is added into magnesium alloys to form Mg to Li alloys. The addition of Li can make the c/a value of HCP lattice of magnesium solid solution decrease, improving the plasticity property of alloys. In Mg–Li binary system, when Li content is larger than 5.7 wt%, β phase (Li solid solution) forms in the alloys [3, 4]. The β phase is a soft phase which makes the strength of alloys decrease.

Al and Zn are two alloying elements that are used in Mg–Li alloys most commonly. The addition of them can strengthen Mg–Li alloys [5, 6]. RE elements are also favorable alloying elements in Mg–Li alloys [7, 8]. In previous research, the RE elements in LA141 and LA83 can improve the mechanical properties of alloys [9]. However, the effects of RE elements in the alloys in α single phase zone, whose Li content is less than 5.7 wt%, have not been reported in present literatures.

Accordingly, to obtain alloys with good comprehensive properties (both high strength and good plasticity property), LAZ532 (Mg–5Li–3Al–2Zn) alloy is chosen as base alloy in this study. In this base alloy, the Li content is close to the boundary Li content point (5.7 wt%) between single phase (α) zone and double phases ($\alpha + \beta$) zone, and the Al content and Zn content are the common values in literatures [10, 11]. The influence of RE on the microstructure and mechanical properties of LAZ532 alloy is studied.

Experimental procedure

The materials used in these experiments were commercial pure (CP) magnesium, CP lithium, CP aluminum, CP zinc, and Mg-30% RE master alloy in which the RE contains 85 wt% La, 10 wt% Pr, and 5 wt% Ce. The alloys of LAZ532-*x*RE were prepared in a pure graphite crucible by

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induction melting in the atmosphere of argon. After the uniform heat treatment (250 °C \times 12 h), the as-cast specimen was extruded as wrought alloy. The extrusion–reduction ratio was 15, and the extrusion temperature was 280 °C.

The chemical composition of alloys was measured with inductively coupled plasma mass spectrometry. The optical microstructure of as-cast and wrought alloys was observed with a Leica Optical Microscope (OM). The detailed microstructures of alloys were observed with a scanning electron microscope (SEM). The specimens for OM and SEM observation were etched with 2 vol.% nital. The microstructure of the as-extruded alloys was observed at the tangential direction. The phases of alloys were measured with X-ray diffraction (XRD), and the chemical composition of some phases in the microstructure was measured with energy dispersive X-ray (EDS). The mechanical properties of the alloys were measured with a tensile machine using a crosshead speed of 1 mm/min. In the tensile tests, the dimensions of specimens were designed according to the standard of ASTM E M8-08 (plate-type: 6 mm of width, rod-type: 6 mm of diameter).

Results

Chemical composition

Table 1 shows the chemical composition of alloys in these experiments. By and large, the contents of elements in alloys are close to the nominal composition. All the contents of alloying elements, except the Li content, are somewhat lower than those of nominal composition. Li content is higher than that of nominal composition. The Li content in LAZ532-6RE even reaches 6.506 wt%, which comes into the double-phase zone of Mg–Li alloy.

Microstructure

The optical microstructure of alloys investigated is shown in Fig. 1, and the phases of these alloys are shown in Fig. 2. From these results, LAZ532 alloy consists of α phase and AlLi. With the addition of RE, the AlLi phase is refined, and the amount of it decreases with the RE content. At the same time, some particles (Al₃La) distribute in α phase, and the size of it in LAZ532-2RE is the smallest. When the RE content is larger than 3 wt%, the Al₃La particles aggregate and form as rod-like shape. The α phase is also refined when RE is added into alloys. From Fig. 2, it can also be known that, some β phase exists in the alloy of LAZ532-6RE. This is because the actual Li content of the alloy comes into double-phase zone (as listed in Table 1).

The detailed microstructure of alloys is shown in Fig. 3. From the SEM pictures, the precipitates in LAZ532-2RE are granular particles, those in LAZ532-3RE are rod-like, and those in LAZ532-6RE are pearlite-like eutectic microstructure. In LAZ532-6RE, the blocky β phase can also be observed. The EDS analysis results show that, except the effect of matrix element (Mg), these precipitates are mainly composed of the elements of Al and La. The contents of Al and La are listed in Table 2. It shows that, in these precipitates, the molar ratios of Al to La are all about 3. This confirms that these precipitates are Al₃La phase.

Figure 4 is the optical microstructure of alloys after extrusion. It is known that, in LAZ532-RE alloys, the microstructure is mainly composed of deformation bands. The dynamic re-crystallization microstructure exists partially, while in LAZ532-2RE and LAZ532-3RE, the dynamic re-crystallization microstructure exists in the whole alloys. The grain size of LAZ532-3RE is larger than that of LAZ532-2RE. In LAZ532-6RE alloys, the microstructure is completely composed of deformation bands.

Mechanical properties

Figure 5 is the strength of alloys investigated in experiments. Both in as-cast alloys and in the alloys after extrusion, the ultimate strength of alloys increases with the addition of RE, and it reaches the peak value at the RE addition of 2 wt%. Further increasing the RE content makes the strength become poor. The extrusion process can improve the strength of alloys. The improvement in LAZ532-2RE alloy is the most obvious, and the second obvious improvement happens in LAZ532-3RE. The least obvious improvement happens in LAZ532-6RE. The elongation percentage of the alloys varies

 Table 1 Nominal composition and measured composition of alloys in experiments

Nominal composition	Measured composition, wt%							
	Li	Al	Zn	La	Pr	Ce	RE(La + Pr + Ce)	
LAZ532	5.615	2.885	1.656					
LAZ532-1RE	5.622	2.890	1.726	0.495	0.197	0.136	0.828	
LAZ532-2RE	5.628	2.876	1.537	0.967	0.358	0.287	1.612	
LAZ532-3RE	5.526	2.884	1.981	1.559	0.676	0.341	2.576	
LAZ532-6RE	6.506	2.758	1.922	2.771	0.816	0.636	4.223	



Fig. 1 Optical microstructure of alloys investigated. a LAZ532; b LAZ532-1RE; c LAZ532-2RE; d LAZ532-3RE; e LAZ532-6RE

with the same tendency as the strength of the alloys (as shown in Fig. 6). Figure 7 shows the stress-displacement tensile curves of LAZ532-2RE (as-cast and as-extruded).

Discussions

Chemical composition error during melting

Because of the melting loss, all the contents of alloying elements, except the Li content, are somewhat lower than

those of nominal composition. As for the phenomenon that Li content is higher than nominal composition, it can be explained as follows. The melting process was carried out under the atmosphere of argon, and the atmospheric pressure was kept low (0.02 MPa) in order to prevent air from coming into melting chamber. Therefore, the vaporization of Mg is somewhat more drastic than that under normal air ambient, which makes the actual Mg content in the alloys lower than that of nominal composition [10]. The Li content in the alloys increases accordingly.



Fig. 2 XRD patterns of alloys investigated. (*a*) LAZ532; (*b*) LAZ532-1RE; (*c*) LAZ532-2RE; (*d*) LAZ532-3RE; (*e*) LAZ532-6RE

Microstructure variation during the addition of RE

RE is a surface-active element which can form a surface film around the precipitates during the process of solidification. The surface film can restrict the growth of precipitates [11].

Table 2 EDS results for the corresponding precipitates in Fig. 3

Precipitates	Contents of elements, mol%		
	Al	La	
Granular particles	0.3	0.12	
Rod-like precipitates	6.84	1.97	
Blocky precipitates	23.37	6.65	

During the solidification in Mg–Li alloys, the equilibrium distribution coefficient (k) is less than 1 [12], which means the addition of RE can increase the constitutional supercooling. The increase of constitutional supercooling leads to the refinement of microstructure [13]. Therefore, the addition of RE in Mg–Li alloy has refining effect on the microstructure of alloy.

Because the electronegative difference between RE and Al is larger than that between RE and other elements in alloys investigated [14], Al₃La can prefer to form in the alloys. The Al dissolved in magnesium alloys is also a favorable element for the increase of constitutional supercooling [15]. Therefore, the formation of Al₃La consumes some Al atoms and makes the refining effect of Al decrease. This is the reason that the microstructure of alloys becomes coarser when the addition of RE is larger



Fig. 3 SEM pictures of alloys (SEI images). a LAZ532-2RE; b LAZ532-3RE; c LAZ532-6RE







Fig. 5 Strength of alloys investigated



Fig. 6 Elongation of alloys investigated

than 3 wt%. The consumption of Al in Al_3La also makes the amount of AlLi decrease.

With the increase of RE addition, the amount of Al_3La becomes larger and larger. They aggregate with each other, making the size of Al_3La precipitates become larger. Accordingly, the shape of Al_3La precipitates changes from granular particle to rod-like.

During the extrusion process, if the temperature and the stored energy of alloys produced during deformation are suitable, dynamic re-crystallization will take place in the alloys. The finer grain size has higher ability to restrict deformation and produces higher stored energy in the alloys. Therefore, the finer of the original grain size is more favorable for the process of dynamic re-crystallization



mm

during the hot-deformation [16, 17]. From the optical microstructure of as-cast specimens (Fig. 1), with the addition of RE, the grain size decreases and it reaches the finest when the content of RE is 2 wt%. When the content of RE is 1 wt%, the grain size is relatively coarse. Therefore, in LAZ532-1RE, the dynamic re-crystallization is not sufficient and the microstructure of the alloy after extrusion is the mixture of deformation bands and re-crystallization

grains. In LAZ532-2RE and LAZ532-3RE, because of the fine original grain size, the dynamic re-crystallization is sufficient during the process of deformation and the microstructure of them is completely composed of equiaxed grains. Because of the low extrusion speed, the recrystallization grains have sufficient time to grow after the dynamic re-crystallization process. During the process of grain growth, the precipitates can restrict the movement of

grain boundary. The size of precipitates is a main influencing factor for grain growth. The finer precipitates are more favorable for obtaining fine grain size [18]. Accordingly, the grain growth speed of LAZ532-3RE is higher than that of LAZ532-2RE because of the different Al₃La size in these alloys (as shown in Fig. 3).

In LAZ532-6RE alloy, there are a large amount of pearlite-like Al₃La precipitates because of high RE content. These precipitates can restrict the diffusion of atoms and the movement of grain boundary, which increase the dynamic re-crystallization temperature of the alloys during hot-extrusion process [18, 19]. Accordingly, the dynamic re-crystallization does not happen in LAZ532-6RE alloys under the extrusion parameters (as shown in Fig. 4d).

Mechanical properties

In the as-cast specimens, the refinement of microstructure (α phase, AlLi, and Al₃La) with the addition of RE leads to the improvement of strength and elongation of alloys [20]. Therefore, both the strength and the elongation of alloys increase with the addition of RE, and they both reach the peak values when the content of RE is 2 wt%.

The hot-extrusion process has three aspects of favorable effects on the mechanical properties [21, 22]. Firstly, through the extrusion process, some gas-pores and microcracks formed during solidification are removed from the alloys. Secondly, during the extrusion process, the large scale dendritic and columnar grains are crushed as finer grains. Lastly, the dynamic re-crystallization during the hot-extrusion also increases the mechanical properties. Among the three aspects, the last one is a main factor for mechanical properties of alloys. From Figs. 5 and 6, the mechanical properties of all the four alloys are improved after extrusion. The improvements of LAZ532-2RE and LAZ532-3RE are more obvious than those of LAZ532-1RE and LAZ532-6RE. As shown in Fig. 4, when RE content is 2 and 3 wt%, the dynamic re-crystallization happens sufficiently. However, only a small part of re-crystallization grains are observed in LAZ532-1RE and no re-crystallization grains in LAZ532-6RE. Accordingly, in LAZ532-2RE and LAZ532-3RE, all the three aspects mentioned above affect the mechanical properties of alloys. While in LAZ532-1RE and LAZ532-6RE, the extrusion process has no dynamic re-crystallization effect.

The mechanical properties and density of LAZ532-2RE and AZ31 are listed in Table 3. The ultimate strength of LAZ532-2RE is close to that of AZ31. The elongation percentage and specific strength of LAZ532-2RE are both much larger than those of AZ31, and the density of LAZ532-2RE is less than that of AZ31. The addition of Li not only decreases the density of alloy largely, but also

Table 3	Comparison	of mec	hanical	properties	and	density	between
AZ31 ar	nd LAZ532-21	RE					

	AZ31	LAZ532-2RE
Ultimate strength, MPa	280 [23]	290
Elongation percentage, %	14 [23]	25
Specific strength, MPa/(g/cm ³)	157.30	181.25
Density, g/cm ³	1.78 [24]	1.6 ^a

^a The density of Mg–Li base alloys is always less than 1.6 g/cm³. The density of LAZ532-2RE is assumed as 1.6 g/cm³

improves the plasticity of alloy. Suitable RE addition refines the microstructure of Mg–Li base alloys (Fig. 1) and strengthens the alloy. Accordingly, though the addition of Li and RE increases the cost of alloy, it improves the mechanical properties and decreases the density of alloy. Furthermore, the improvement of plasticity makes the yield of wrought LAZ532-2RE be larger than that of wrought AZ31. This makes the total cost of LAZ532-RE be not necessarily higher than that of AZ31.

Conclusions

In the as-cast alloys of LAZ532-*x*RE, Li content is larger than nominal content, and the contents of Al, Zn, and RE are all lower than nominal contents.

With the addition of RE, the microstructure is refined and the microstructure of LAZ532-2RE is the finest. The amount of AlLi also decreases with the addition of RE. Besides α phase and AlLi, Al₃La precipitates exist in LAZ532-xRE alloys. In LAZ532-1RE and LAZ532-2RE, Al₃La precipitates are granular particles. They are rod-like in LAZ532-3RE and pearlite-like eutectic microstructure in LAZ532-6RE. After the hot-extrusion, partial dynamic re-crystallization takes place in LAZ532-1RE, completely dynamic re-crystallization takes place in LAZ532-3RE and LAZ532-3RE, dynamic re-crystallization does not take place in LAZ532-6RE.

With the addition of RE, the mechanical properties of alloys increase and they reach the peak values in LAZ532-2RE. After the hot-extrusion, the mechanical properties of all the four alloys are improved. Because of the dynamic re-crystallization, the improvements in LAZ532-2RE and LAZ532-3RE are more obvious than those in LAZ532-1RE and LAZ532-6RE. The mechanical properties of LAZ532-2RE are better than those of AZ31.

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