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REVIEWS ON THE INFLUENCES OF ALLOYING ELEMENTS ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Mg-Li BASE ALLOYS

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Abstract. Mg-Li base alloys are the lightest metallic structural materials with a density of 1.35-1.65 g/cm^3. They also possess many other advantages, such as high specific strength, high specific stiffness, et al. However, the usages of Mg-Li alloy are often limited by the insufficient properties, of which the poor strength is the most obvious aspect. Accordingly, many literatures reported the alloying process of Mg-Li alloy. In this regards, this paper reports the influences of some alloying elements on the microstructures and mechanical properties of Mg-Li alloys.

1. INTRODUCTION

Magnesium alloys possess many advantages, such as light weight, high specific strength, good vibration resistance, good electromagnetic shielding property. Furthermore, magnesium alloys can be reused. Therefore, they are called as the Green Engineering Materials of 21th Century, which have wide application prospects in the fields of arospace, automobile, 3C products, et al.

However, the crystal lattice of magnesium possesses few slip systems during deformation because it is close-packed hexagonal structure. Accordingly, magnesium alloys show the poor plasticity property in the process of extrusion, rolling, forging and punching. To obtain all kinds of magnesium alloys products, die-cast technology is always used. Compared with the processes of deformations, this technology has some disadvantages, such as low production effeciency, high production cost, and relatively poor properties, et al. Therefore, the International Magnesium Association (IMA) specified that the development of wrought magnesium alloys should be the long-term target in the strategic frame for the development of magnesium alloys in the year of 2000 [1,2].

Based on the backgrounds of magnesium alloys mentioned above, Mg-Li alloys are attracting more and more interests from researchers. Mg-Li alloys are the lightest metallic materials with the density of 1.35-1.65 g/cm^3. Besides with the advantages of normal magnesium mentioned above, Mg-Li alloys also possess their specific characters comparing with normal magnesium alloys, such as lower density by 1/4-1/3, better plasticity property, et al. [3,4].

However, in the engineering application, Mg-Li alloys still have some problems that need to be solved urgently, such as relatively low strength, unstable mechanical properties, relatively high production cost, et al. To solve these disadvantages, alloying is one of the most commonly used methods to obtain Mg-Li base alloys with good properties. In this paper, the influences of alloying elements, Al, Zn, misch metal(RE), Y, Ce, Nd, Ag, Ca, on the microstructures and mechanical properties of Mg-Li base alloys are reviewed.

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2. INFLUENCES OF Al AND Zn ON Mg-Li BASE ALLOYS

Al and Zn are two most common alloying elements in Mg-Li base alloys. The solubilities of them in Mg-Li alloy are both high. The Al added in Mg-Li alloys mainly dissolves in solid solutions. When the Al content is larger than 3 wt.%, AlLi compound forms in the alloys. The addition of Al in Mg-Li alloys brings about the improvement of strength and the little increase of density(the density of Al is close to that of Mg), but it causes the decrease of elongation. When the addition is larger than 6 wt.%, the deterioration of elongation is serious. The addition of Zn has the similar effects in Mg-Li base alloys. The deterioration of elongation is less serious than that for the addition of Al, but the increase of density is larger than that for the addition of Al. Therefore, Al and Zn are always used as alloying elements in Mg-Li base alloys simultaneously to make them display their own advantages and avoid their disadvantages [5].

T.C. Chang et al. [6] compared the mechanical properties of the alloys of LZ91, LZM910, LZAM9110, and LAZM9310. All the alloys studied contain the same Zn content (1 wt.%) with/without the addition of Mn or/and Al. The results are shown in Fig. 1. The 0.2 wt.% Mn addition causes the decrease of strength of alloys, while the addition of Al improves the strength of alloys. The elongations of these alloys are all high, larger than 45%. The addition of Al somewhat decreases the elongation of alloys. Fig. 2 shows the comparisons of these alloys after equal channel angle extrusion(ECAE). After the process of ECAE, the strengths of all the alloys are improved, while the elongations of them decrease sharply. Comparing the results of them, the increase of the strength of LZ91 is the largest, 41.8 MPa, and the decrease of the elongation of LZ91 is the least, 25%.

H.C. Lin et al. [7] also studied the effects of Al in LZ91 alloy. The addition of 0.6 wt.% Al improves the strength and the corrosion resistance of alloy without the decrease of elongation and electromagnetic shielding property. However, the impact resistance value at lower than 150 °C decreases.

With the different Li content in Mg-Li alloys, the influence of Al in alloys is different [8]. With the increase of Al content, the exterior shrinkage decreases in spite of Li content. However, as for the interior shrinkage, in the alloys with different Li content, the influence of Al content differs. In Mg-(1-5)Li alloys, Al content has no effect on the interior shrinkage of them. The interior shrinkage of Mg-(8-20)Li base alloys decreases with the increase of Al content. As for the gas pores, Al content also has influence on it. In Mg-Li alloys with the Li content less than 14 wt.%, the amount of gas pores in alloy increases with the increase of Al content. When the Li content is larger than 16 wt.%, the increase of Al content will decrease the amount of gas pores in alloy.

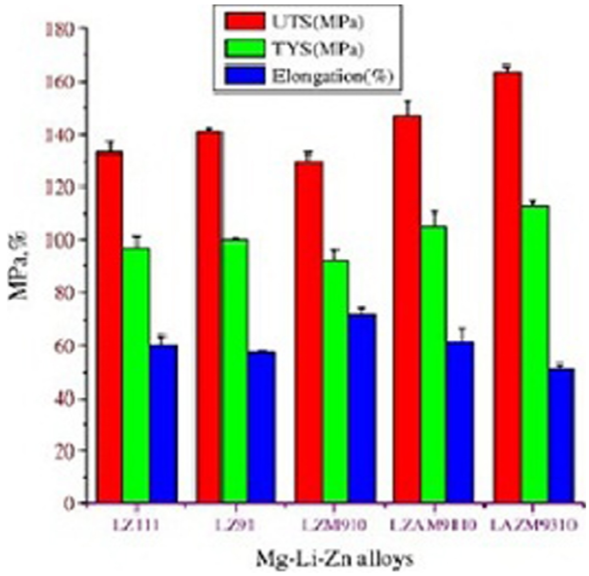

Fig. 1. Room temperature tensile strengths and elongations of the original five Mg-Li-Zn alloys(the initial strain rate is $2\times10^{-4}s^{-1}$).

3. INFLUENCES OF RARE EARTH ELEMENTS ON Mg-Li BASE ALLOYS

Whether in Li or in Mg, the solubility of rare earth elements is both very low. Therefore, rare earth elements mainly exist in the form of compounds in Mg-Li base alloys, which strengthens the alloys. The compounds containing rare earth elements always possess good thermostability, improving the elevated temperature properties of alloys. Furthermore, the refining effect is the one of the most obvious influences of rare earth elements in Mg-Li alloys, which can improve both the strength and elongation.

3.1. Influences of Nd on Mg-Li base alloys

In Mg-8Li binary alloy, the addition of Nd can not improve the mechanical properties and thermostability [9]. The reason is as follow: although Nd ex-

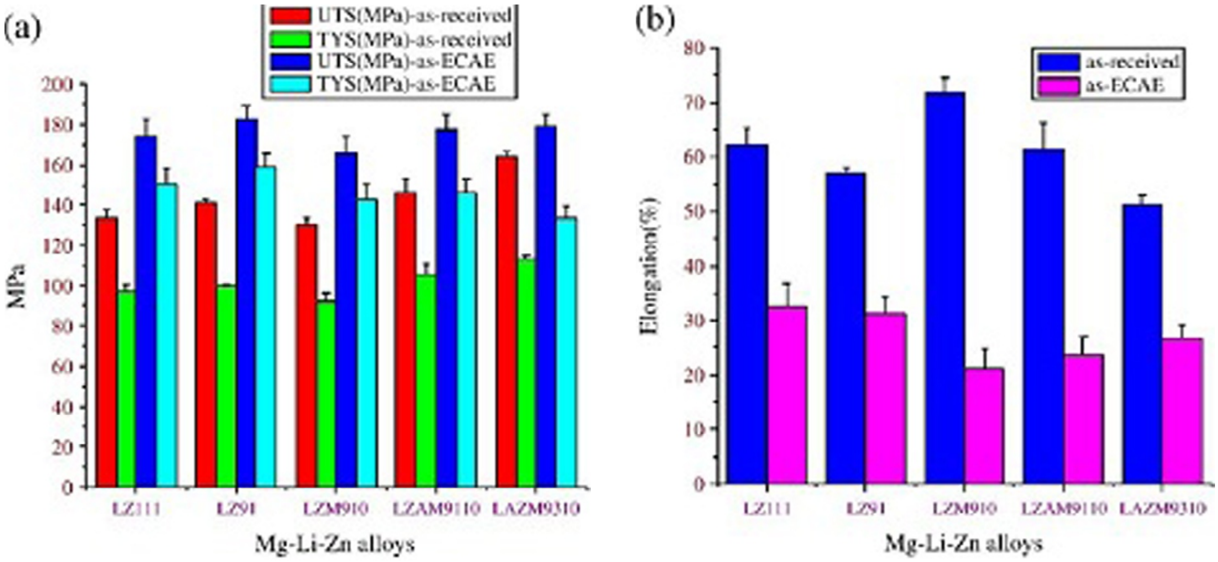

Fig. 2. Room temperature mechanical properties of the ECAE processed five Mg-Li-Zn alloys(the initial strain rate is $2\times10^{-4}s^{-1}$).

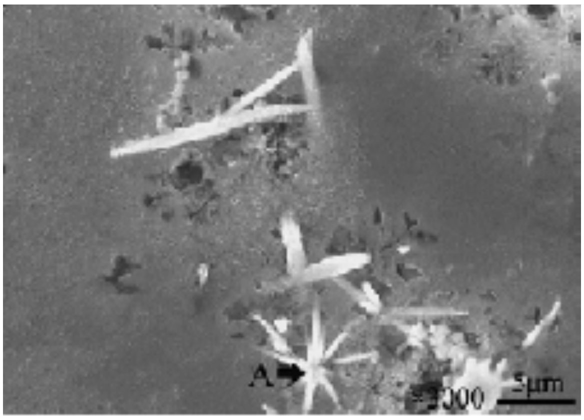

Fig. 3. Microstructure of LA141-0.6Nd.

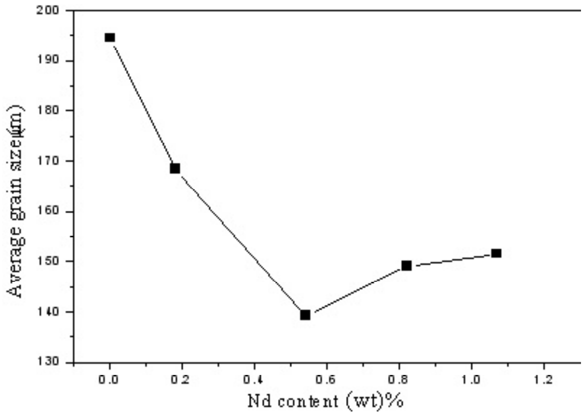

Fig. 4. Effect of Nd on the grain size of LA141 alloys.

ists in the form of Mg_3Nd compound, which improves the mechanical properties and thermostability, the addition of Nd decreases the amount of α(Mg) phase, and makes the mechanical properties and thermostability become poor. However, the addition of Nd can increase the recrystallization temperature of Mg-8Li alloy and make the alloy have aging harden phenomenon.

In the Mg-Li-Al alloys, Nd exists in the form of Al_2Nd phase whose shape is intercrossing rod-like(as shown in Fig. 3) [10]. Fig. 4 shows the refining effect of Nd on LA141. When the addition of Nd is 0.6 wt.%, the grain size of alloy is the least. The existance of Al_2Nd and the refining effect of Nd can both improve the strength of alloy, and the strength is the highest when Nd content is 0.6 wt.%(as shown in Fig. 5).

W. Xu et al. [11] studied the existing form of Y and Nd in Mg-(0-6)Li-2Al-Zn alloy. The compounds in the alloy are Nd_3Zn_{11} and Al_2Y. With the increase of Li content, the amount of Nd_3Zn_{11} phase decreases, while the amount of Al_2Y phase does not change.

3.2. Influences of Ce on Mg-Li base alloys

In the Mg-Li-Al alloys, Ce exists in the form of Al_2Ce phase. In the alloy of LA81-1Ce, the Al_2Ce phase is rod-like and distributes evenly [12]. After extrusion, the rod-like Al_2Ce becomes short rod and distributes in the extruding direction. The mechanical properties are improved accordingly(strength from 160 MPa to 187 MPa, elongation from 16% to 33%).

In the alloys of Mg-16Li-5Al-(0.2-1)Ce, with the increase of Ce content, the amount of Al_2Ce phase increases, while the amount of $Mg_{17}Al_{12}$ and AlLi

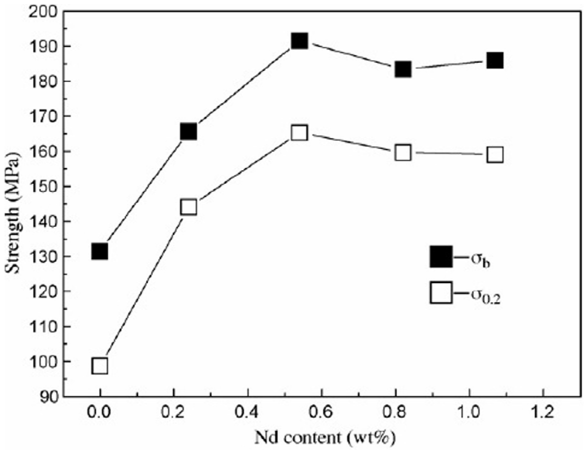

Fig. 5. Effect of Nd on the strength of LA141 alloys.

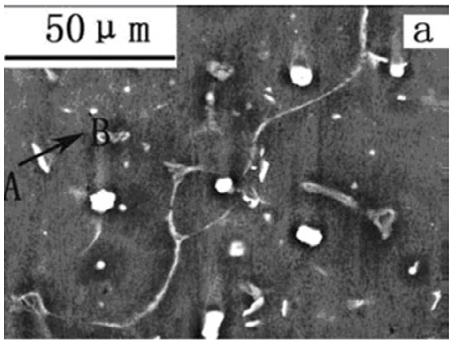

Fig. 6. SEM of as-cast $Mg_{83.75}Li_{10.5}A_{l3.54}Ce_{1.23}Ca_{0.94}$ specimen.

phases decreases [13]. The grains of the alloys are also refined. Al_2Ce phase distributes at grain boundary, making the fracture of alloys change from intergranular type to cleavage type. The Al_2Ce phase hinders the slip of grain boundary at elevated temperature(150 °C), and the thermostability of alloy is improved accordingly. However, when the Ce content is larger than 0.6 wt.%, the Al_2Ce becomes blocky and has dissevering effect on the matrix alloy, leading to the poor mechanical properties.

The addtion of Ce in Mg-8.5Li alloy leads to the decrease of α phase content and the formation of $Mg_{12}Ce$ compound in the microstructure of alloys [14]. Ce also has refining effect on the microstructure of alloys and the refining effect is the most obvious when Ce content is 2%.

3.3. Influences of Y on Mg-Li base alloys

Ninomiya [15,16] compared the superplasticity property of as-rolled Mg-8.5Li and Mg-8.5Li-1.0Y. The tensile strength of Mg-8.5Li-1.0Y is higher than that of Mg-8.5Li at the strain rate of 4×10^{-3} s^{-1}. At the tensile temperature of 350 °C and the strain rate of 2×10^{-4} s^{-1}, the elongation of Mg-8.5Li is 600%. At the same temperature, the elongation of Mg-8.5Li-1.0Y is 400%. Though the elongation of Mg-8.5Li-1.0Y is less than that of Mg-8.5Li, the strain rate is 4×10^{-3} s^{-1}, 20 times larger than that of Mg-8.5Li alloy. This can obviously improve the production efficiency.

In Mg-Li binary alloys, Y exists in the form of $Mg_{24}Y_5$ phase [17]. The $Mg_{24}Y_5$ phase distributes at grain boundary in the shape of reticular. In the quenching process, with the increase of quenching temperature, the solubility of Mg and $Mg_{24}Y_5$ in Li increases and the $Mg_{24}Y_5$ is spheroidized, leading to the increase of hardness and strength of alloy. In the aging process(150 °C) after quenching, the strength and elongation of alloy both decrease. The reasons are sumarized as two aspects. One is the coarsen of grain during aging, and the other is that the aging process makes the solubility of Mg and $Mg_{24}Y_5$ in Li decrease, and they precipitate at the grain boundary of Li phase, leading to the poor mechanical properties.

R.Z. Wu et al. [18] researched the effect of Y in Mg-8Li-(1,3)Al alloys. The addition of Y refines and spheroidizes the microstructure of alloys, and the AlY phase that forms during the solidification distributes both in α and β phases. The addition of Y also restrains the formation of α phase. These effects result in the improvement of mechanical properties of alloys, and the improvement of elongation is much more obvious than that of strength.

3.4. Influences of Sc on Mg-Li base alloys

Microcontent of Sc in Mg-Li-Al alloys has influence on the aging characters of alloys. Fig. 6 shows the effects of 0.01 wt.% Sc on the aging curves of LAZ1010 [19]. In LAZ1010, when the temperature is larger than 100 °C, the aging softening happens. In LAZ1010Sc, when the temperature is 50 °C, the aging softening happens. The reason for the decrease of aging hardening temperature because of Sc addition is that, the addition of Sc promotes the transfermation from $MgAlLi_2$ to AlLi. The microcontent of Sc in LAZ1010 has small influence on mechanical properties. After the addition of 0.01 wt.% Sc, the yeilding strength increases from 154.8 MPa to

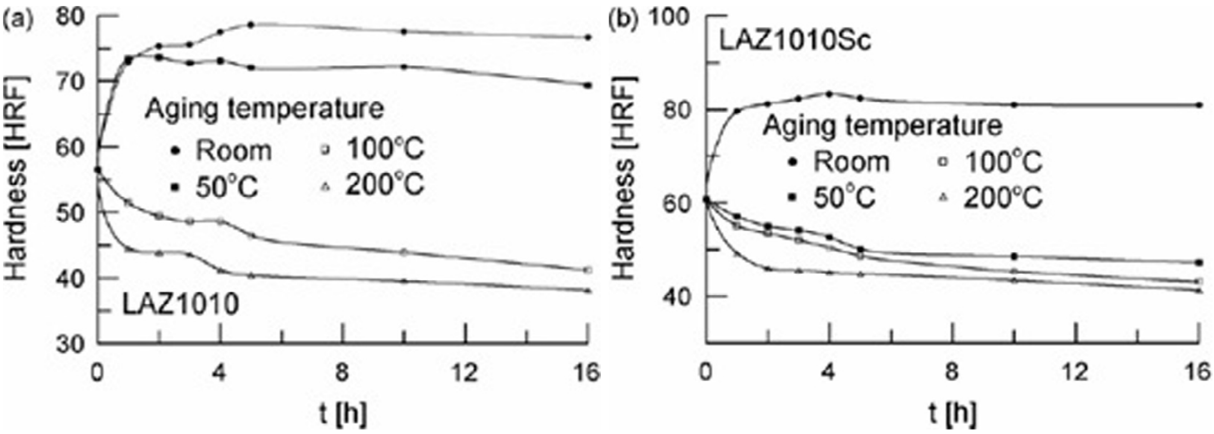

Fig. 7. Aging curves of alloys under different temperature.

Table 1. Comparation of properties of Mg-8Li base alloys under different alloying conditions.

Alloy	*E*(GPa)	Y.S.$_{0.2\%}$(MPa)	U.T.S.(MPa)	Elongation(%)	Density(g/cm^3)
L8	40	93	132	52	1.51
LA87	39	184	239	33	1.53
LAS871	44	145	225	20	1.59
LAS871-4.5RE	53	200	260	14	1.60

172.1 MPa, the tensile strength from 172.5 MPa to 186.4 MPa, elongation from 28.9% to 25.2%.

3.5. Influences of misch metal on Mg-Li base alloys

Misch metal (RE) is much cheaper than pure rare earth. The alloying with misch metal in Mg-Li base alloys has more industrial value. Therefore, the influence of misch metal on Mg-Li base alloys has been being paid more and more attention [20].

The addition of 1-2 wt.% RE has effect of refinment on Mg-8Li alloy [21]. When the RE content is 2 wt.%, RE reacts with Mg to form compound and makes the elongation of alloy decrease. The compound consumes some Mg atoms and makes the amount of α(Mg) decrease. Accordingly, the strengthening effect of α(Mg) is weakened, causing the decrease of strength. However, the elevated temperature thermostability of the alloy is improved because of the existance of compound.

The addition of 4.5 wt.% RE in Mg-8Li-7Al-Si brings about the formation of large amount of blocky $REAl_3$, $REAl_4$, and REAlSi phases [22]. The addition of RE also makes the amount of blocky $MgAlLi_2$ and Mg_2Si decrease(as shown in Fig. 7). RE improves the elastic modulus obviously. The strength of the alloy is also somewhat improved. However, the elongation decreases and the density of the alloy increases. The data of alloys properties are listed in Table 1.

T. Wang et al. [23] reported that, in Mg-7Li-6Al-6Zn-*x*LPC (in which *x* is 0-1.0 wt.%, and LPC stands for the mixture of La, Pr and Ce, the weight ratio of them is 85:10:5), the stable $LaAl_2Zn_2$ compound exists at the grain boundaries. The compound restrains the formation and growth of $Mg_{17}Al_{12}$, which is a phase with poor thermal stability. The $LaAl_2Zn_2$ compound also pins the dislocations, and restrains the grain boundaries slipping and deformation. All these effects improve the room temperature strength and elevated temperature strength. In the alloys of Mg-7Li-Al-0.5LPC, the rare earth elements can not be dissolved in matrix entirely. Some Al_3La precipitates from matrix. The addition of LPC makes the microstructure become somewhat coarser. It also improves the hardness and strength. However, in the alloy of Mg-9Li-5Al-Zn-0.6LPC, the rare earth elements are dissolved completely [24].

In the alloys of Mg-10Li-4Al-(0-1.2)LPC, rare earth elements enrich at the frontior of boundary between liquid and solid, producing the constitutional supercooling which refines the grains of alloys. The finest grains can be obtained when LPC content is 0.6

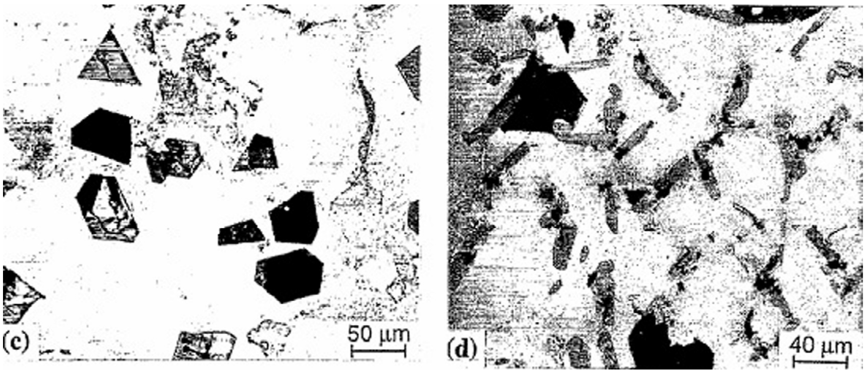

Fig. 8. Optical microstructure of Mg-8Li-7Al-Si alloy with and without RE.

wt.% [25]. The compounds in the alloys are Al_3La, which makes the amount of the phases of $Mg_{17}Al_{12}$, α and AlLi decrease. With the increase of LPC content, the strength and elongation both increase. The increasing rate of strength decreases with the LPC content. When the LPC content is larger than 0.9 wt.%, the elongation begins to decrease with the increase of LPC content.

The investigation about the effects of different rare earth elements on the alloy of Mg-7Li-4Zn indicates that, the effects of Nd, Ce, and La on the mechanical properties decrease sequentially and the optimal additions of them are 1.1-1.3 wt.%, 0.4-0.6 wt.%, 0.8-1.0 wt.%, respectively [26]. Nd in the alloy exists in the form of solid solution. Ce and La exist in the form of Mg_3Ce, $Mg_{17}Ce_2$, $Mg_{17}La_2$.

In the alloy of Mg-8.16Li-4.10Zn-0.59Zr-2.68Y-2.14LPC, some reticular MgLiZnRE compound is found [27]. MgLiZnRE is a brittle phase, which makes the solid solubility of Zn in matrix decrease, and the solution strengthening effect becomes poor. Therefore, the strength of the alloy decreases because of the MgLiZnRE compound. After the alloy is heated in the atmosphere of hydrogen (0.1 MPa) at the temperature of 480 °C for 24 hours, the samples with the diameter of 12 mm can be hydrogenized fully. The reticular MgLiZnRE disappears, and the granular compound with H and RE forms in the alloy. The Zn from MgLiZnRE previously is solid soluted in matrix again, making the improvement of strength.

In LAZ532 alloy, RE has refining effect on the microstructure, and the microstructure of LAZ532-2RE is the finest [28]. The amount of AlLi also decreases with the addition of RE. Besides α phase and AlLi, Al_3La precipitates exist in the alloys. The shapes of Al_3La precipitates in alloys are shown in Fig. 8. In LAZ532-1RE and LAZ532-2RE, Al_3La precipitates are granular particles. They are rod-like in LAZ532-3RE and pearlite-like eutectic microstructure in LAZ532-6RE. With the addition of RE, the mechanical properties of alloys increase and they reach the peak values in LAZ532-2RE.

4. INFLUENCES OF Ca ON Mg-Li BASE ALLOYS

In magnesium base alloys, Ca has the advantages of grain refinement, melt fire-retarding, improvement of elevated temperature creep, et al. Ca also has the characters of cheapness and light-weight [29,30]. Therefore, in Mg-Li base alloys, Ca also has many favorable influences.

The isothermal section of Mg-Li-Ca ternary phase diagram at 150 °C is obtained through thermodynamic calculation, as shown in Fig. 9 [31]. When the Ca content reaches a specific value, the phases of $CaMg_2$ and $CaLi_2$ exist in alloys.

The microstructure of Mg-12Li is a β single phase. After it is added with 5 wt.% Ca, the microstructure of it is a lamellar eutectic of β + $CaMg_2$, as shown in Fig. 10. After cold rolling, the lamellar eutectic can be crashed. During the oxidization of the alloy, the β single phase is oxdized firstly, and the eutectic is hard to be oxidized. This demonstrates that the Ca in Mg-Li base alloys has the effects of fire-retarding and oxidization-retarding.

R. Chandran et al. [33] researched the effects of Ca on the semi-solid state Mg-Li-Al alloys with the microsturcture of α, α + β, β, respectively. Fig. 11 shows that, Ca has refining effect on the alloys of Mg-5Li-3Al, Mg-9Li-3Al, Mg-14Li-3Al. In the alloy of Mg-9Li-3Al, Ca also has the spheriodizing effect on the α phase. When the Ca content is 2 wt.%, some particular compounds, Al_2Ca phase, exist at the grain boundary in all the three alloys. Liquid-solid temperature spans of Mg-Li-Al alloys can be ex-

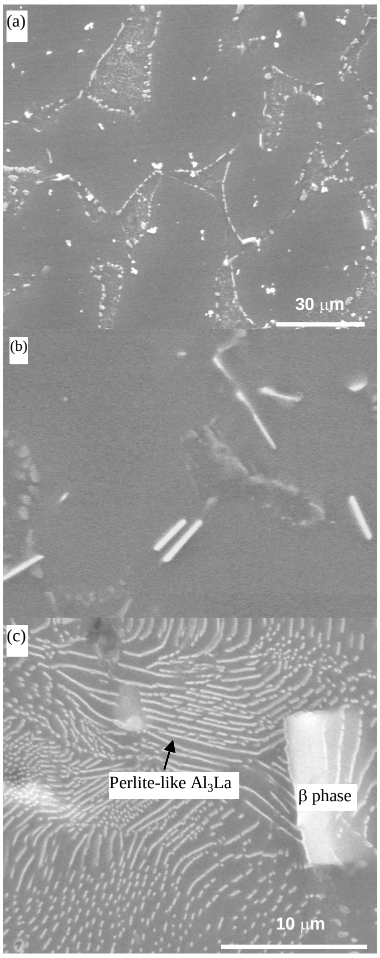

Fig. 9. SEM pictures of alloys (SEI images): (a) LAZ532-2RE; (b) LAZ532-3RE; (c) LAZ532-6RE.

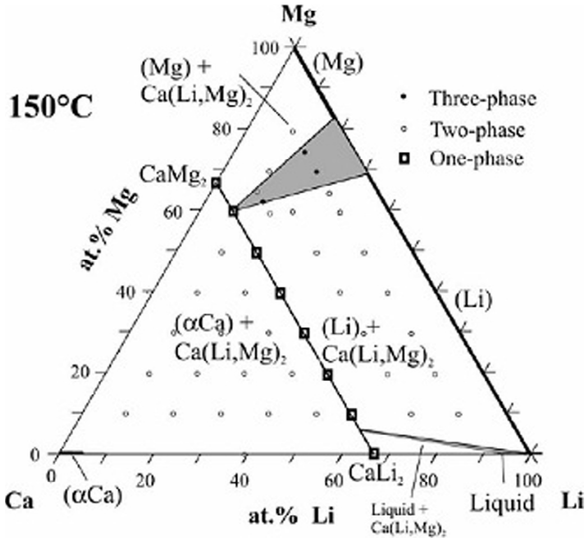

Fig. 10. Ca-Li-Mg phase diagram at 150 °C: calculated isothermal section.

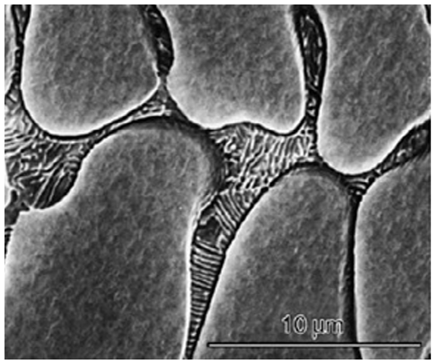

Fig. 11. Microstructure of Mg-12Li-5Ca alloy.

tended because of the addition of Ca, as shown in Fig. 12. The expansion of liquid-solid temperature span is favorable for the semi-solid forming.

Ca also has refining effect on the alloys of LZ series and improves the mechanical properties [34,35]. In the alloy of LZ92, when Ca content is 0.1 wt.%, the refining effect is the best, and the strength and elongation increase by 19% and 6%, respectively. Further increasing the Ca content makes the strength increase further, but the elongation somewhat decreases [36,37].

In the alloy of Mg-6Li-3Al, the addition of Ca makes the AlLi phase disappear, and it has refining effect on the microstructure [38]. The disappearance of AlLi phase is unfavourable for strength, and the refining effect is favourable for strength. Both the disappearance of AlLi and the refining effect are favourable for elongation improvement. When the Ca content is larger than 2 wt.%, the bone-like Al_2Ca forms in β phase. The bone-like Al_2Ca is unfavourable for strength and elongation. After extrusion, the bone-like Al_2Ca can be crashed as fine particles, improving the strength and elongation of alloys.

5. INFLUENCES OF Ag ON Mg-Li BASE ALLOYS

Ag has a large solubility in both Mg and Li. Therefore, the strenghening effect of Ag in Mg-Li alloys is mainly solution strengthening [39]. Table 2 lists the mechanical properties of Mg-12Li base alloys with different Ag contents [40]. When Ag content is lower than 10 wt.%, the strength increases with Ag content linearly. But the increasing rate is little until the Ag content is larger than 10 wt.%. Accordingly, the strengthening effect of Ag is poorer than that of Al and Zn. The increase of Ag content makes the elongation decrease, but the decreasing rate is low. When the Ag content is 10 wt.%, the elongation is still as high as 38%. Additionally, Ag can also stablize the strengthening effects of Al, Zn and Cd on Mg-Li base alloys. The addition of 1 wt.% Ag

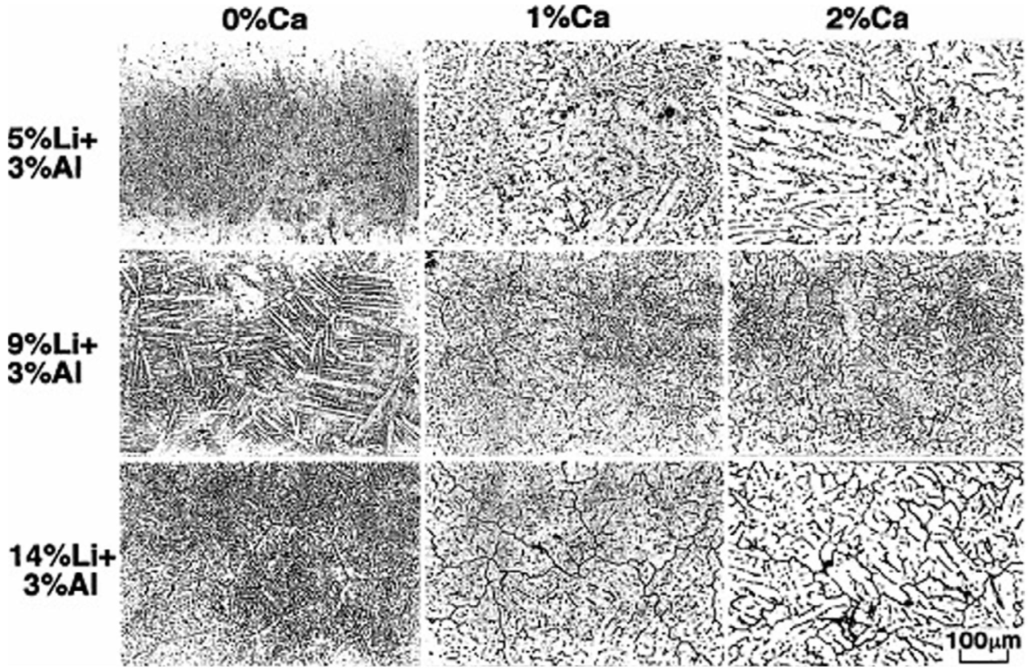

Fig. 12. Microstructure of Mg-Li-Al alloys with different Ca addition.

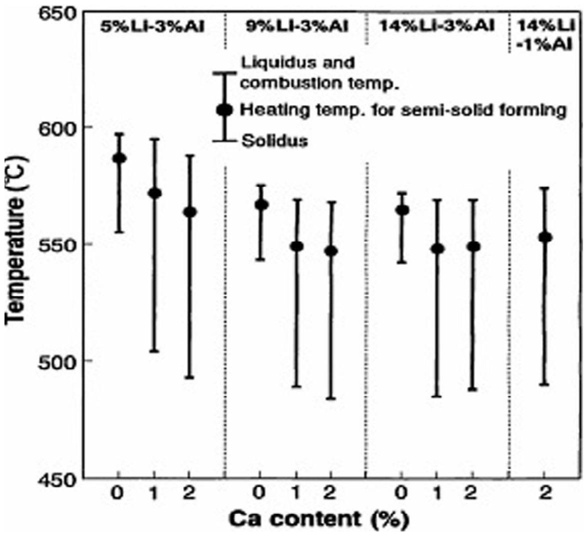

Fig. 13. Liquid-solid temperature spans of Mg-Li-Al alloys with different Ca addition.

can obviously retard or avoid the over-age of Mg-12Li-7.5Zn and Mg-12Li-18Cd.

However, the density of Ag is relatively large. The strengthening effect per weight of Ag is low, making the cost of alloys high. Therefore, Ag is always used as a stablizing element for Mg-Li base alloys, not a strengthening element.

In the alloys of Mg-5Li-3Al-2Zn-(0-0.6)Ag, the microstructure is composed of α, β, and AlLi. In the alloy of Mg-5Li-3Al-2Zn-1.2Ag, the microstructure is composed of α, β, and $MgAlLi_2$ [41]. In the as-cast alloys, AlLi or $MgAlLi_2$ phase exists in β phase.

Table 2. Influence of Ag content on the mechanical properties of Mg-12Li alloy.

	Ag content, wt.%				
	0.5	1.0	3.0	5.0	10.0
σ_b/MPa	100	108	120	138	182
σ_s/MPa	62	70	77	104	150
δ/%	51	43	54	43	38

In the solid solution state alloys, there are only α and β. During the aging treatment at 100 °C, $MgAlLi_2$ precipitates from matrix phase first. Then it decomposes as AlLi phase. In the alloy of Mg-5Li-3Al-2Zn-1.2Ag, the $MgAlLi_2$ does not decompose during the further aging treatment. In Mg-Li base alloys, the solid solution of Ag in matrix phases and the formation of $MgAlLi_2$ phase are both strengthening factors. While the AlLi phase is a softening factor. The $MgAlLi_2$ is a metastable phase which is easy to decompose as AlLi. Ag dissolves in matrix phases and it stabilizes the $MgAlLi_2$ phase. Accordingly, the over-aging can be restrained or avoided.

6. SUMARY AND CONCLUSIONS

In the alloying process for Mg-Li base alloys, the following aspects should be considered.

(1) Light weight is one of the most outstanding advantages of Mg-Li alloys. Therefore, the density of alloying element should not be too high.

(2) In the strengthening process, there are three factors that affect the strength of alloys. They are solution strengthening, refining strengthening, and secondary phase strengthening. To obtain good strengthening effects, all the three factors can be considered comprehensively.
(3) To obtain good comprehensive mechanical properties, during the strengthening process, the ductility of alloys should also be considered.
(4) In the alloying process, the influences of the alloying elements on the other properties of alloys, such as corrosion resistance, mechanical properties stability, should also be considered.

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