Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 21(2011) 778−783
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Effects of yttrium and strontium additions on as-cast microstructure of Mg-14Li-1Al alloys

LI Rui-hong[1, 2], PAN Fu-sheng[1, 2], JIANG Bin[1, 2], YIN Heng-mei[1, 2], LIU Ting-ting[1, 2]

1. National Engineering Research Center for Magnesium Alloys, Chongqing University, Chongqing 400044, China;
2. College of Materials Science and Engineering, Chongqing University, Chongqing 400044, China;

Received 25 September 2010; accepted 24 December 2010

Abstract: Mg-14Li-1Al (LA141), LA141-0.3Y, LA141-0.3Sr, and LA141-0.3Y-0.3Sr alloys were prepared in an induction furnace in the argon atmosphere. The microstructures of these alloys were investigated through scanning electron microscope (SEM), X-ray diffractometer (XRD) and energy dispersive spectrometer (EDS). The results show that yttrium and/or strontium additions produce a strong grain refining effect in LA141 alloy. The mean grain sizes of the alloys with addition of Y and/or Sr are reduced remarkably from 600 to 500, 260, 230 μm, respectively. Al_2Y, Al_4Sr and $Mg_{17}Sr_2$ phases with different morphologies are verified and exist inside the grain or at the grain boundaries, thus possibly act as heterogeneous nucleation sites and pin up grain boundaries, which restrain the grain growth.

Key words: Mg-14Li-1Al alloy; microstructure; grain refinement; second phase

---

1 Introduction

Mg-Li alloys are the lightest magnesium alloys and have much better plasticity than the general Mg-Al or Mg-Zn alloys[1−2]. Mg-14Li-1Al (LA141) alloy is a typical Mg-Li based alloy, containing full *β*-Li phase at room temperature. It possesses superior plasticity and ductility but relatively low strength, especially at high temperature, the tensile strength of LA141 alloy can reach 144 MPa at room temperature, but drops to about 50 MPa at 473 K[3]. Multi-element alloying[4] and composite reinforcement[5] can increase the strength of this alloy, but the lightness and ductility have to be devoted. Grain refinement can strengthen the alloy with the increase of strength and plasticity. Equal channel angular pressing[6] and rapid solidification method[7] are typical processes for grain refinement. Minor element addition[8], which is particularly suitable for mass production, is a simple and economical way to refine the microstructure. Some research results have been reported. CHEN et al[9] added zirconium to LA141 alloy and obvious grain refinement was offered. WU et al[10] used zinc addition to refine the microstructure of Mg-5Li-3Al alloy. When the mass fraction of Y in Mg-8Li-3Al alloys attained 1%, the microstructure was fine and Al_2Y phase occurred[11]. Although reduction of grain size was observed, unlike LA141 alloy, these alloys contained *α*-Mg (HCP) phase at room temperature. Both Sr and Y have good grain refinement effect on Mg-Al alloys. And it was also reported that Al_4Sr and $Mg_{17}Sr_2$ were found in Mg-Al-Sr system[12] as well as Al_2Y in Mg-Al-Y system [13]. Basically, the effect of Sr or Y on the microstructures of Mg-Al alloys containing *α*-Mg (HCP) has been investigated well[14−15]. However, there is little report about the effect of minor Sr and Y additions on the microstructure of LA141 alloy. In the present work, LA141 alloy containing full BCC *β*-Li phase was set up as the study alloy. Both growth restriction factor (GRF) and mismatch value were introduced to discuss the grain refining mechanism.

2 Experimental

The materials used in this investigation were magnesium, lithium and aluminum with commercial

---

Foundation item: Project (50725413) supported by the National Natural Science Foundation of China; Project (2010CSTC-BJLKR) supported by Chongqing Science and Technology Commission, China; Project (CDJXS10132203) supported by the Fundamental Research Funds for the Central Universities, China

Corresponding author: PAN Fu-sheng; Tel: +86-23-65112635; E-mal: fspan@cqu.edu.cn

DOI: 10.1016/S1003-6326(11)60780-2

purity. Mg-30Y, Mg-40Sr (mass fraction, %) master alloys were added to the alloys.

These materials were placed together with nominal composition shown in Table 1, and were heated to 720 °C in an induction melting furnace at an atmosphere of pure argon. After being melted, the liquid metal was held for 30 min and then dumped into a preheated steel mould with argon protection. Actual chemical compositions of the obtained ingots were determined by inductively coupled plasma spectrometer. The results are shown in Table 1.

Table 1 Chemical composition of experimental alloys (mass fraction, %)

Alloy No.	Nominal composition	Actual composition
1	Mg-14Li-1Al	Mg-14.31Li-1.11Al
2	Mg-14Li-1Al-0.3Y	Mg-13.61Li-0.96Al-0.1Y
3	Mg-14Li-1Al-0.3Sr	Mg-13.82Li-0.92Al-0.37Sr
4	Mg-14Li-1Al-0.3Y-0.3Sr	Mg-14.48Li-0.97Al-0.28Y-0.21Sr

The microstructures of these alloys were characterized by optical microscope (OM) and scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The phase constitution of these alloys was conducted by X-ray diffractometer (XRD).The samples for OM and SEM observation were grounded, polished and etched in the solution of 5 g picric, 10 mL acetic acid, 10 mL distilled water and 100 mL ethanol.

3 Results and discussion

3.1 Grain size of LA141 alloys containing Y and/or Sr

Figure 1 shows the optical microstructure of as-cast LA141 alloys. Equiaxed grains are obtained in all samples and no columnar structure is observed. Notable grain refinement occurs in the LA141-0.3Sr alloy, which reduces the grain size from 600 μm to 260 μm, as shown in Figs. 1(a) and (c).The finest grains with the average grain size of 230 μm are achieved in the LA141-0.3Y-0.3Sr alloy (Fig.1(d)). The variation of the average grain size with the additions is presented in Fig.2. Although the grain refining efficiency of the addition of Y and/or Sr in the present LA141 alloy is not as significant as that in Mg-Al alloys[14−15], the reduction of grain size is still remarkable.

3.2 Characteristics of intermetallic compounds in LA141 alloys

The XRD results of the LA141 alloys are demonstrated in Fig.3. It reveals that all the LA141 alloys contain both *β*-Li and $LiMgAl_2$. $MgLiAl_2$ phase is a stable phase at room temperature and comes from the transformation of metastable Li_2MgAl phase[16]. Meanwhile, Al_2Y phase appears in the LA141 alloys containing Y, $Mg_{17}Sr_2$ and Al_4Sr phases in the LA141 alloys containing Sr as well, although the peak intensity is lower. Because of the formation of these new phases containing Al, the content of $LiMgAl_2$ phase decreases with the addition of Y and/or Sr.

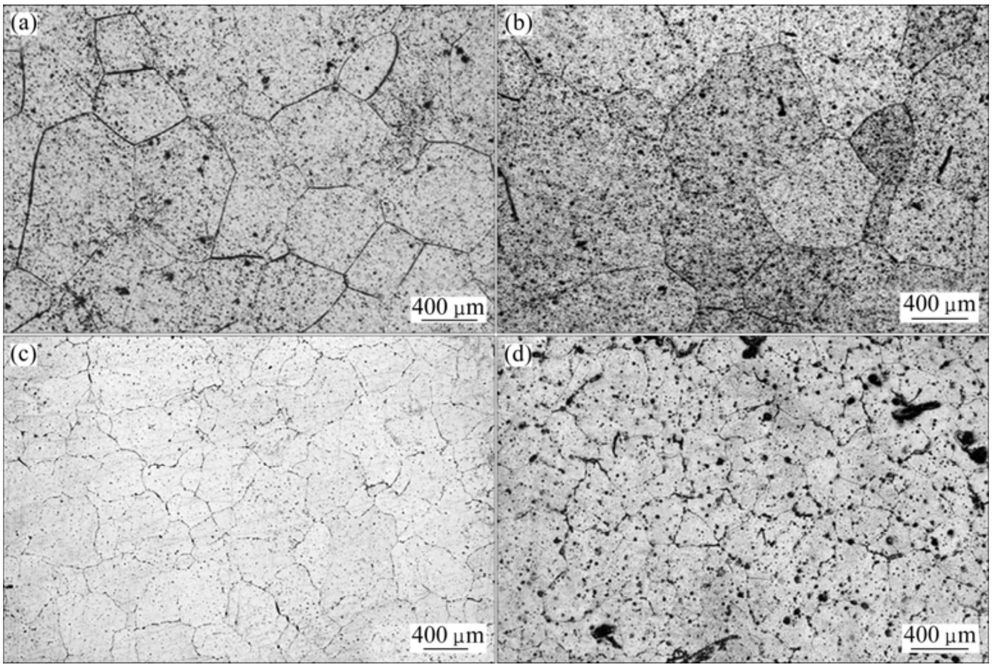

Fig.1 Microstructures of investigated alloys: (a) LA141; (b) LA141-0.3Y; (c) LA141-0.3Sr; (d) LA141-0.3Y-0.3Sr

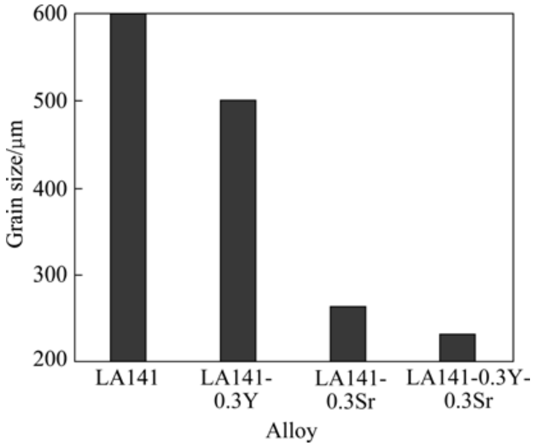

Fig.2 Mean grain size of LA141 alloys without or with additions

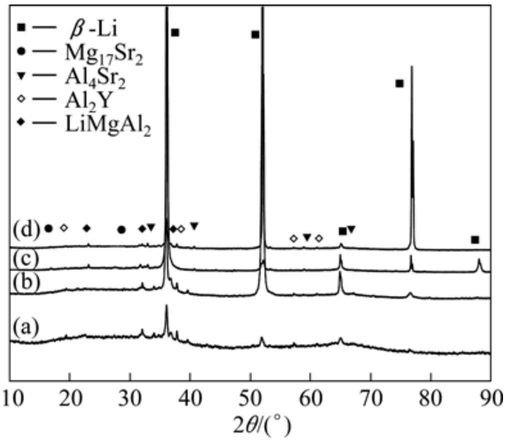

Fig.3 XRD patterns of LA141 (a), LA141-0.3Y (b), LA141-0.3Sr (c) and LA141-0.3Y-0.3Sr alloy (d)

SEM images and micro-area chemical composition analysis results of LA141 alloys are shown in Fig.4 and Table 2, respectively. As can be observed, the second phases locate within the grain or at grain boundary. Globular $MgLiAl_2$ particles exist in LA141 alloy and granular Al_2Y particles in LA141-0.3Y alloy. Mg, Al and Sr are detected by EDS in the compounds at point *C* (Fig.4(c)) and at point *D* or *E* (Fig.4(d)), which shows that these compounds consist of $Mg_{17}Sr_2$ and Al_4Sr because of the electronegativity difference between Mg and Sr or between Al and Sr larger than that between Li and Sr. Some locate inside grain, and the others locate at the boundary. Through comparison of Figs.4(c) and (d), the Y addition improves the morphology of the

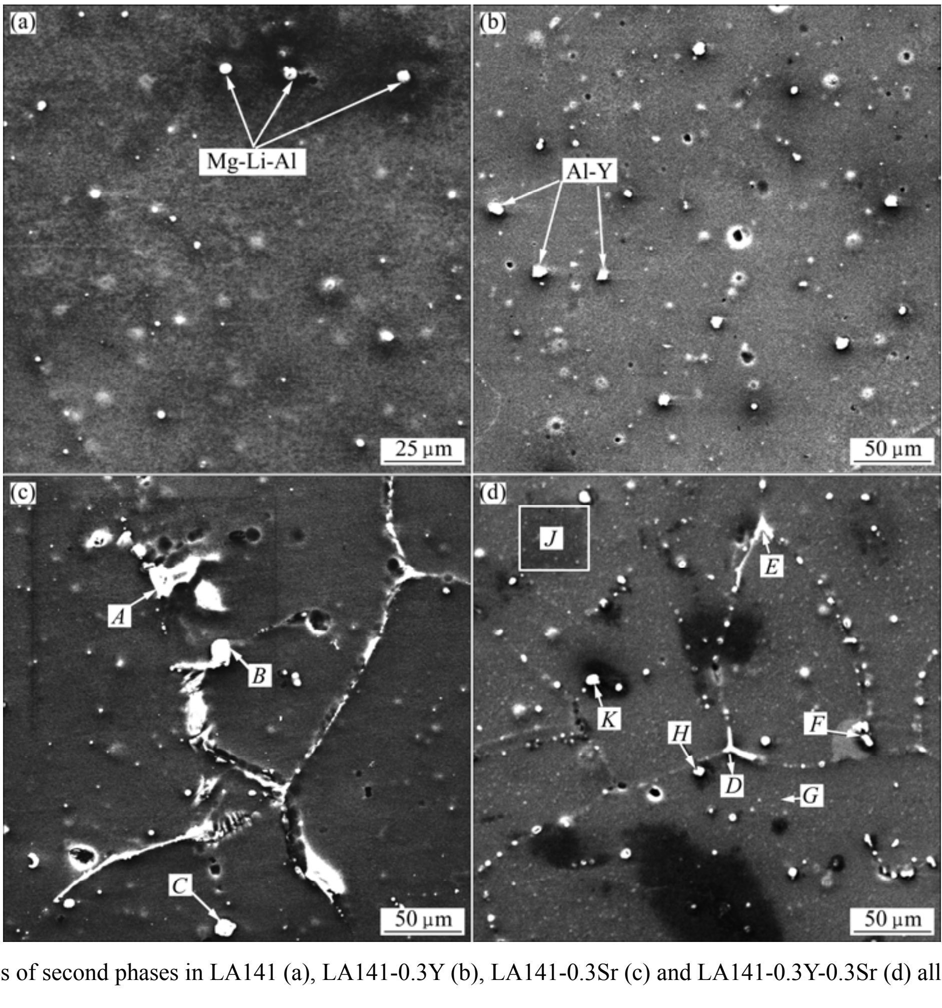

Fig.4 SEM images of second phases in LA141 (a), LA141-0.3Y (b), LA141-0.3Sr (c) and LA141-0.3Y-0.3Sr (d) alloys

Table 2 Micro-area chemical composition analysis results of alloys in Fig.4 (mole fraction, %)

Position	O	Mg	Al	Sr	Y
A	8.35	90.30	1.35		
B	24.67	68.81		6.51	
C	15.83	63.56	6.20	14.41	
D	58.17	31.21	2.7	7.93	
E	32.55	58.00	4.31	5.14	
F	55.72	39.30		4.97	
G	16.16	83.02	0.82		
H	47.48	49.43	1.71		1.02
J	16.80	82.50	0.70		
K	76.36	9.06	9.21		5.27

Content of O in LA141 alloys is high because this type alloy can be easily oxidized during sample preparation, which has no effect on mole ratio of Al to Sr or Y basically.

compounds at the boundary and makes it evolve from long plate-like to short or granular ones.

The results of EDS of LA141-0.3Y-0.3Sr alloy indicate that there are Mg, Al and Y elements in the granular compounds at point *H* or *K* of Fig. 4(d) and corresponding mole ratio of Al to Y is nearly 2:1. In addition, the electronegativity difference between Al and Y is larger than that between Mg and Al or between Mg and Y. Thus, these compounds can be identified as Al_2Y.

According Fig.4 and Table 2, the type, the morphology and the distribution of second phases in all the LA141 alloys are listed in Table 3.

3.3 Mechanism of grain refinement of LA141 alloys with Y and/or Sr

The addition of alloy element to metallic materials can reduce the grain size of the matrix, through the growth restriction of the grains due to the segregation power of solute elements in the matrix[17−18] and/or through heterogeneous nucleation[19] of the matrix grains on the metallic particles. The effect of solute elements on grain size has been explained in terms of the GRF, which can be calculated using binary phase diagrams. The larger the GRF value, the more powerful the growth restriction. According to the computation method of the GRF values for alloy elements in magnesium[20], the GRF value for Sr in β-Li is 0.74, much lower than that for Ca, Zn or Al, in Mg matrix. So far, the phase diagram of Y and Li is not known, the GRF value for Y in β-Li cannot be got by calculation. Furthermore, as shown in Table 2, no Y and Sr elements are observed in β-Li matrix from EDS results. Therefore, Y and Sr cannot refine the microstructure by their segregation in β-Li matrix, and the grain refinement of LA141 alloys containing Y and/or Sr may be caused by heterogeneous nucleation role of the metallic compounds, such as Al_2Y, $Mg_{17}Sr_2$ and Al_4Sr.

ZHANG et al[21] have reported that a metallic compound can be the potential grain refiner for the matrix alloy when the crystallography mismatch of the close to or nearly close to packed planes between the compound and the matrix is less than 10%. From the XRD results, the potential matching planes among Al_2Y, Al_4Sr, $Mg_{17}Sr_2$ and β-Li can be obtained. The mismatch values of these potential matching planes can be figured out through the definition method[1]. The mismatch values that are less than 10% and the corresponding matching planes are listed in Table 4. Therefore, there are certain crystallography orientation relationships among Al_2Y, Al_4Sr, $Mg_{17}Sr_2$ and β-Li that need to be further studied. From crystallographic point view, these compounds can be regarded as grain refiners for LA141 alloys. In addition, from the binary phase diagrams of Al-Y, Al-Sr, and Mg-Sr, the melt points of Al_2Y and Al_4Sr are 1 485 °C and 1 040 °C, respectively, while that of $Mg_{17}Sr_2$ is 606 °C. Thus, Al_2Y and Al_4Sr particles can stably stay in the alloy melt, those inside the grains of β-Li matrix are potential grain refiner for β-Li and are the main factors of the grain refinement of LA141 alloys

Table 3 Morphology and distribution characteristics of the second phases observed in LA141 alloys

Alloy	Phase	Morphology	Observed by SEM with EDS	Distribution
LA141	$LiMgAl_2$	Globular	Fig.4(a)	Inside grain
LA141-0.3Y	Al_2Y	Granular	Fig.4(b)	Inside grain
LA141-0.3Sr	$LiMgAl_2$	Erratic blocky	*A* in Fig.4(c)	At boundary
	Al_4Sr	Granular and long plate-like	*C* in Fig.4(c)	Inside grain and at boundary
	$Mg_{17}Sr_2$	Long plate-like	*B* in Fig.4(c)	At grain boundary
LA141-0.3Y-0.3Sr	Al_2Y	Granular	*H*, *K* in Fig.4(d)	Inside grain
	Al_4Sr	Granular and short plate-like	Fig.4(d)	At grain boundary
	$Mg_{17}Sr_2$	Short plate-like	*F* in Fig.4(d)	At grain boundary

containing Y and/or Sr. $Mg_{17}Sr_2$ phases, appearing during the solidification, cannot exist in the alloy melt at 720 °C and hardly have the heterogeneous nucleation effect on β-Li matrix, although the mismatch value between $Mg_{17}Sr_2$ and β-Li is less than 10%. On the other hand, $Mg_{17}Sr_2$ phase at the boundary can pin up the grain boundaries, restraining the grain growth. Especially, when $Mg_{17}Sr_2$ phase is changed to be granular morphology due to Y addition in LA141-0.3Sr alloy, it will block the grain growth in a more effective way.

Table 4 Mismatch values of potential matching planes for Li and compounds (%)

(110)Li/ $(302)Mg_{17}Sr_2$	(110)Li/ $(220)Mg_{17}Sr_2$	(110)Li/ $(200)Al_4Sr$	(110)Li/ $(311)Al_2Y$
5.63	6.12	10	4.55

4 Conclusions

1) The additions of Y and/or Sr have obvious grain refinement effect on the as-cast LA141 alloys. Addition of 0.3%Y and 0.3% Sr can reduce the as-cast grain size of the LA141 alloys from 600 μm to 230 μm.

2) Both β-Li and $MgLiAl_2$ phases are found in all the as-cast LA141 alloys. Granular Al_2Y phase appears in the as-cast LA141 alloys containing Y, plate-like $Mg_{17}Sr_2$ and granular Al_4Sr phases in the as-cast LA141 alloys containing Sr. Y addition makes the morphology of $Mg_{17}Sr_2$ change to be granular or short rod-like from long plate-like. These second phases are distributed within the grain or at grain boundary.

3) Al_2Y and Al_4Sr phases with high melt points have mismatches less than 10% with β-Li matrix and thus can act as heterogeneous nucleation sites for β-Li grains. $Mg_{17}Sr_2$ phases hardly have the heterogeneous nucleation effect on β-Li matrix due to the low melt point, although the mismatch value between $Mg_{17}Sr_2$ and β-Li is less than 10%. However, those $Mg_{17}Sr_2$ compounds distributed at the grain boundaries can pin up grain boundaries and restrain the grain growth of β-Li matrix during solidification.

References

[1] JIANG Bin, QIU Dong, ZHANG Ming-xing, DING Pei-dao, GAO liang. A new approach to grain refinement of an Mg-Li-Al cast alloy [J]. Journal of Alloys and Compounds, 2010, 492: 95−98.

[2] MA Chun-jiang, ZHANG Di, ZHANG Guo-ding, QIN Jin-ning. Mg-Li matrix composites [J]. Rare Metal Materials and Engineering, 1998, 27(3): 125−129.

[3] CHEN Zhen-hua, YAN Hong-ge, CHEN Ji-hua, QUAN Ya-jie, WANG hui-min, CHEN Ding. Magnesium alloy [M]. Beijing: Chemical Industry Press, 2004: 1−477.

[4] SONG G S, KRAL M V. Characterization of cast Mg-Li-Ca alloys [J]. Materials Characterization, 2005, 54: 279−286.

[5] TROJANOVÁ Z, DROZD Z, KÚDELA S, SZÁRAZ Z, LUKÁČ P. Strengthening in Mg-Li matrix composites [J]. Compos Sci Technol, 2007, 67: 1965−1973.

[6] MITSUAKI F, CHENG X, TETSUO A, MAKOTO I, HIROSHI A, TERENCE G. Improving the superplastic properties of a two-phase Mg-8%Li alloy through processing by ECAP [J]. Materials Science and Engineering A, 2005, 410−411: 439−442.

[7] AYMAN E, KATSUYOSHI K, HISASHI I, JUNKO U. Microstructure and mechanical properties of hot extruded Mg-Al-Mn-Ca alloy produced by rapid solidification powder metallurgy [J]. Materials and Design, 2010, 31: 2444−2453.

[8] GUANG S S, STAIGER M, KRAL M. Some new characteristics of the strengthening phase in β-phase magnesium-lithium alloys containing aluminum and beryllium [J]. Materials Science and Engineering A, 2004, 371: 371−376.

[9] CHEN B, FENG L P, ZHOU T T, LIU P Y LI H X. Effects of Zr on microstructures and properties of a beta matrix Mg-13Li-3Al-0.7Zr alloy [J]. Mater Science Forum, 2005, 488−489: 155−159.

[10] WU Rui-zhi, ZHANG Mi-lin. Microstructure, mechanical properties and aging behavior of Mg-5Li-3Al-2Zn-*x*Ag [J]. Materials Science and Engineering A, 2009, 520: 36−39.

[11] WU Rui-zhi, QUA Zhi-kun, ZHANG Mi-lin. Effects of the addition of Y in Mg-8Li-(1, 3)Al alloy [J]. Materials Science and Engineering A, 2009, 516: 96−99.

[12] PARVEZ M, MEDRAJ M, ESSADIQI E, MUNTASAR A, DÉNÈS G. Experimental study of the ternary magnesium-aluminium-strontium system [J]. Journal of Alloys and Compounds, 2005, 402: 170−185.

[13] ZOU Hong-hui. Effects of microstructure on creep behavior of Mg-5%Zn-2%Al(-2%Y) alloy [J]. Trans Nonferrous Met Soc China, 2008, 18: 580−587.

[14] NIU Jie-xin, CHENG Qiu-rong, XU Nai-xin, WEI Zhong-ling. Effect of combinative addition of strontium and rare earth elements on corrosion resistance of AZ91D magnesium alloy [J]. Trans Nonferrous Met Soc China, 2008, 18: 1058−1064.

[15] XU Chun-xiang, LU Bin-feng, LV Zheng-ling, LIANG Wei. Grain refinement of AZ31 magnesium alloy by Al-Ti-C-Y master alloy [J]. Journal of Rare Earths, 2008, 26: 604−608.

[16] LIU T, WU S D, LI S X, LI P J. Microstructure evolution of Mg-14% Li-1% Al alloy during the process of equal channel angular pressing [J]. Materials Science and Engineering A, 2007, 460−461: 499−503.

[17] EASTON M, STJOHN D. Grain refinement of aluminum alloys: Part I. The nucleant and solute paradigms-a review of the literature [J]. Metallurgical and Materials Transactions A, 1999, 30: 1613−1623.

[18] EASTON M, STJOHN D. Grain refinement of aluminum alloys: Part II. Confirmation of, and a mechanism for, the solute paradigm [J]. Metallurgical and Materials Transactions A, 1999, 30: 1625−1633.

[19] FU H M, QIU D, ZHANG M X, WANG H, KELLY P M, TAYLOR J A. The development of a new grain refiner for magnesium alloys using the edge-to-edge model [J]. Journal of Alloys and Compounds, 2008, 456: 390−394.

[20] LEE Y C, DAHLE A K, STJOHN D H. The role of solute in grain refinement of magnesium [J]. Metallurgical and Materials Transactions A, 2000, 31: 2895−2906.

[21] ZHANG Ming-xing, KELLY P M, EASTON M A, TAYTOR J A. Crystallographic study of grain refinement in aluminum alloys using the edge-to-edge matching mode [J]. Acta Materialia, 2005, 53: 1427−1438.

Y 和 Sr 的添加对 Mg-14Li-1Al 合金铸态组织的影响

李瑞红 [1,2], 潘复生 [1,2], 蒋 斌 [1,2], 殷恒梅 [1,2], 刘婷婷 [1,2]

1. 重庆大学 国家镁合金工程技术研究中心，重庆 400044；
2. 重庆大学 材料科学与工程学院，重庆 400044

摘 要：在氩气保护气氛下，熔炼 Mg-14Li-1Al (LA141), LA141-0.3Y、LA141-0.3Sr 和 LA141-0.3Y-0.3Sr 合金。通过扫描电镜(SEM)、X−射线衍射(XRD)和能谱分析研究这几种合金的组织。结果表明：单独添加 Y 或 Sr 或复合添加 Y 和 Sr，对 LA141 的组织细化有明显的效果；添加 Y，Sr,和复合添加 Y 和 Sr 的 LA141 合金的晶粒尺寸从原始尺寸 600 μm 分别减小到 500、260 和 230 μm；不同形貌的 Al_2Y, Al_4Sr 和 $Mg_{17}Sr_2$ 相存在于晶粒内部或晶界处，提供了异质形核质点、阻碍了晶界的滑移，从而抑制了晶粒的长大。

关键词：Mg-14Li-1Al 合金；组织；晶粒细化；第二相

(Edited by LI Xiang-qun)