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### Preparation of Mg-Li-La alloys by electrolysis in molten salt

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**Abstract:** An electrochemical method was used to prepare Mg–Li–La alloys in a molten LiCl–KCl–KF–MgCl<sub>2</sub> containing La<sub>2</sub>O<sub>3</sub> at 943 K. The results showed preparation of Mg–Li–La alloys by electrolysis is feasible. The Mg–Li–La alloys were analyzed by means of X-ray diffraction (XRD), optical micrograph (OM) and scanning electron microscopy (SEM). XRD analysis indicates that  $\alpha$ +Mg<sub>17</sub>La<sub>2</sub>,  $\alpha$ + $\beta$ +Mg<sub>17</sub>La<sub>2</sub> and  $\beta$ +LaMg<sub>3</sub> Mg–Li–La alloys with different lithium and lanthanum contents were obtained via galvanostatic electrolysis. The microstructures of typical  $\alpha$ +Mg<sub>17</sub>La<sub>2</sub> and  $\beta$ +LaMg<sub>3</sub> phases of Mg–Li–La alloys were characterized by optical microscopy (OM) and scanning electron microscopy (SEM). The analysis of energy dispersive spectrometry (EDS) shows that the element of Mg distributes homogeneously in the Mg–Li–La alloy and the element of La mostly exists at grain boundaries to restrain the grain growth rate due to the larger ionic radius and lower electronegativity compared with Mg. Key words: Mg–Li–La alloys; La<sub>2</sub>O<sub>3</sub>; electrolysis; microstructure

### **1** Introduction

Mg-Li alloys have excellent mechanical properties, corrosion resistance and castability for the applications in the military and automotive industry [1, 2]. However, the application of Mg-Li alloys is limited due to their low strength, poor creep resistance and thermal stability [3, 4]. As a result, the development of Mg-Li alloys has focused on improving specific mechanical properties at high temperatures. Rare earths (REs) are important alloying elements to Mg-Li binary alloys to improve their performance [5]. At present, the standard way to produce Mg alloys is vacuum metallurgical technique, using argon gas. This method is inferior to the molten salt electrolysis process with respect to the homogeneity of alloy composition, simplicity in technology, and continuous or semi-continuous manufacturing process. Recently, in our laboratory [6, 7] attempts were made to prepare Mg-Li alloys from LiCl-KCl-MgCl<sub>2</sub> melts and the cost for the production of Mg-Li alloys via electrolysis following by thermal treatment is reduced greatly, therefore it is necessary to prepare Mg-Li-RE. The solubility of light RE, such as La and Pr elements in Mg–Li alloys is very limited and abundant RE elements can react with Mg, leading to the formation of many kinds of intermetallic compounds [8]. The influence of La and Pr elements on AZ91 was studied by TONG et al [9] and LU et al [10]. Their results indicate that the intermetallic (La, Ce)Al<sub>4</sub> can be formed with the additions of La and Pr to AZ91. In addition, at present, La is abundant and its price is relative lower in China. Thus it would have great significance to try to use La<sub>2</sub>O<sub>3</sub> as sources of La(III) species to prepare Mg–Li–La alloys.

Herein, an approach is proposed for direct preparation of Mg–Li–La alloys via electrochemical codeposition of Mg and Li from LiCl–KCl–MgCl<sub>2</sub> melts by adding  $La_2O_3$  powders directly. The questions under study in this investigation are as follows.

1) Is the La<sub>2</sub>O<sub>3</sub> able to provide La<sup>3+</sup> in our experimental condition? To our knowledge, there has been no report on its solubility in molten LiCl-KCl-MgCl<sub>2</sub>-KF. Several studies on the redox system of RE ions have reported in various media, such as LiF-CaF<sub>2</sub>, LiF-NaF and CaCl<sub>2</sub>-NaCl. GAO [11] et al proposed a reduction process of LaCl<sub>3</sub> into La metal in one single step exchanging three electrons (La(III)+3e→La(0)) at

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an inert electrode in the LiCl–KCl melts. The result shows that the value of the cathodic peak positon is about -2.2 V (versus Ag/AgCl couple). The electrochemical codeposition of Mg–Li–La alloys will be feasible due to the relative negative deposition potential of La to Mg. At the same time according to Ref. [12], MgCl<sub>2</sub> can react with La<sub>2</sub>O<sub>3</sub> at high temperature as follows:

$$MgCl_2 + La_2O_3 = 2LaOCl + MgO$$
(1)

$$LaOCl+MgCl_2=LaCl_3+MgO$$
 (2)

2) The present work focuses on the possibilities of producing Mg–Li–La alloys by molten salt electrolysis. But if the intermetallic compounds were obtained by electrolysis, since the growth of grains can be restricted, subsequently their performance is improved due to the formation of intermetallic compounds, a series of Mg–Li–La alloys were prepared and their microstructure were analyzed and discussed.

### 2 Experimental

The experiments were carried out under purified Ar atmosphere. The electrolytic bath was prepared by LiCl-KCl melts with 8% KF in an Al<sub>2</sub>O<sub>3</sub> crucible in an electric furnace. The chlorides of LiCl and KCl with mass ratio of 1:1 (analytical grade) used in experiment were dehydrated at 873 K and 573 K for 24 h to remove residual water before electrolysis, respectively. Lanthanum and magnesium ions were introduced into the bath in the forms of  $La_2O_3$  ( $\geq 99.0\%$ ) and dehydrated MgCl<sub>2</sub> powder. The working temperature was measured with a thermocouple protected by an alumina tube inserted into the melt. The working electrode was Mo wire (d=1 mm, 99.99% purity) which was fixed in an alumina tube. The lower end of the Mo working electrode was polished thoroughly using SiC paper, and then cleaned in ethanol using ultrasonic cleaning. The immersion depth of the electrode in the molten salts was described as the active electrode area and in this study it was 0.322 cm<sup>2</sup>. A spectrally pure graphite rod (d=6 mm) was served as the anode electrode.

Auxiliary techniques such as X-ray diffraction (Rigaku TRR III), scanning electron microscopy (SEM JSM-6480A; JEOL Co., Ltd.), optical micrograph (DFC320, Leica microsystems) and inductively coupled plasma atomic emission spectrum (ICP-AES, IRIS Intrepid II XSP, Thermo Elemental) analyses were also used.

#### **3** Results and discussion

# 3.1 Relationship between electrolytic time and cell voltage

The cell voltage at temperature of 943 K was

measured at current density of 6.37, 9.55, 12.74 and 15.92 A/cm<sup>2</sup>, respectively. The relationship between cell voltage and time is shown in Fig. 1. According to the curves, the cell voltage is nearly constant during the entire electrolysis process at corresponding current density. At the beginning of the deposition, all the curves have the slightly higher voltage. Taking the curve at 6.37  $A/cm^2$  for example, the cell voltage is 6.15V at the very beginning, and the average value is 5.75 V. It can be explained that when the Mo wire was dipped into the molten salt of higher temperature, it caused the solidification of the molten salt surface and led to a decrease in conductivity, consequently resulting in the increase in cell voltage in the Mo wire. The ohmic resistance of the electrolyte was considered constant at the temperature of 943 K. The cell voltage was performed using the following relationship:

$$E = R_{\rm e} I \tag{3}$$

where *E* is the cell voltage,  $R_e$  is the resistance between the graphite and the Mo wire and *I* is the applied current. It can be seen from Fig. 1 that the current increases, which corresponds to an increase of the cell voltage, until reaches a stabilized value.



Fig. 1 Relationship between cell voltage and electrolysis time

## **3.2** Relationship between electrolytic temperature and cell voltage

Equation (4) shows the relationship between the conductivity ( $\rho$ ) of LiCl-KCl and temperature (*T*).

$$\rho = a + bT + cT^2 \tag{4}$$

where *a*, *b* and *c* are constants.

For 50% LiCl-50% KCl, a=-5.65,  $b=1.37 \times 10^{-2}$ ,  $c=-5.18 \times 10^{-6}$ . It can be seen from Eq. (4), although the conductivity increases with an increase in electrolytic temperature, it is not obvious at high temperature. And in this report, the cell voltages at electrolytic temperature of 923 and 983 K were measured at cathodic current densities of 6.37, 9.55, 12.74 and 15.92 A/cm<sup>2</sup>,

respectively. The shape of the curves presented in Fig. 2. Since the results show that the cell voltage mainly depends on the conductivity and the temperature in this report is high. It can be explained that when the current density increases, the cell voltage increases, but when the temperature increases, its increase is not obvious.



Fig. 2 Relationship between electrolytic temperature and cell voltage

### 3.3 Galvanostatic electrolysis and characterization of deposits

Galvanostatic electrolysis was carried out in a KCl-LiCl-MgCl2-La2O3-KF molten system on molybdenum electrodes at 943 K. For comparison, the molybdenum electrodes with the same active area  $(S=0.322 \text{ cm}^2)$  were used in electrolysis. In the beginning stage of electrolysis, compared with the higher concentration of LiCl in the melts, MgCl<sub>2</sub> reached limited diffusion current density and deposited first. The temperature of 943 K was higher than the melting point of metal magnesium (923 K). So, the liquid magnesium cathode was around the molybdenum wire. And then Li<sup>+</sup> and La<sup>3+</sup> began to deposit on the surface of the pre-coated liquid magnesium cathode.

From Table 1, the lower the MgCl<sub>2</sub> concentration in the LiCl-KCl-KF melts, with equivalent La2O3 concentration at a constant current intensity, the higher the lithium content of the Mg-Li-La alloys. In the case of neglecting La deposition (the concentration of  $La_2O_3$ in the melts is very low), the molar ratio of deposited Mg and Li is proportional to the ratio of their current densities. The limited diffusion current density of MgCl<sub>2</sub> is proportional to its concentration in the melts. Therefore, Mg content in the alloy decreases with decreasing MgCl<sub>2</sub> concentration in the melts. We can also find the lanthanum contents of Mg-Li-La alloys increase with increasing the La2O3 concentrations in LiCl-KCl-8%MgCl<sub>2</sub>-La<sub>2</sub>O<sub>3</sub>-KF melts. The lithium contents of Mg-Li-La alloys also increase with increasing La<sub>2</sub>O<sub>3</sub> concentrations. The increase of lithium content is caused by the formation of  $Mg_3La$  and leads to the positive shift of deposition potential of Li (I) ions. The potential shift is due to a lowering of activity of the deposited metal (Li) in other foreign substrates ( $Mg_3La$ deposits). Based on these results, it can be concluded that the lithium and lanthanum contents of Mg-Li-La alloys can be adjusted by changing the  $MgCl_2$  and  $La_2O_3$ concentrations.

**Table 1** ICP analyses of samples obtained by galvanostaticelectrolysis on Mo electrodes (S=0.322 cm<sup>2</sup>) fromLiCl-KCl-MgCl<sub>2</sub>-La<sub>2</sub>O<sub>3</sub>-KF melts at 943 K

Sample No.	w(MgCl <sub>2</sub> )/ %	w(La <sub>2</sub> O <sub>3</sub> )/ %	w(Li)/ %	w(La)/ %	w(Mg)/ %
1	12	1	0.2	3.9	Bal.
2	10	1	9.6	4.22	Bal.
3	8	1	16.82	4.8	Bal.
4	8	0.5	61.48	2.4	Bal.

Figure 3 shows the complicated XRD patterns of Mg-Li-La alloys obtained by galvanostatic electrolysis from the LiCl-KCl-KF-1.0% La<sub>2</sub>O<sub>3</sub> melts containing 8%-12% MgCl<sub>2</sub> at 12.7 A/cm<sup>2</sup> for 2 h, respectively. The results show the  $\alpha$ +Mg<sub>17</sub>La<sub>2</sub>,  $\alpha$ + $\beta$ +Mg<sub>17</sub>La<sub>2</sub> and  $\beta$ +LaMg<sub>3</sub> in Mg-Li-La alloys were observed. In the previous study, the formation of Mg<sub>17</sub>La<sub>2</sub> was also confirmed by LE et al [13]. In sample 1, most of strong peaks are identified from  $\alpha$ , while some of the weak peaks are from the crystal Mg<sub>17</sub>La<sub>2</sub> phase. Sharp  $\beta$  phase peak is identified with a small amount of Mg<sub>3</sub>La phase except for  $\alpha$  phase in sample 3. The presence of the relatively weak  $\alpha$  phase diffraction peak to sample 1 and the relatively sharp  $\beta$  phase peak to sample 3 with small amounts of Mg<sub>17</sub>La<sub>2</sub> phase was shown in sample 2. In addition, the lithium contents of Mg-Li-La alloys decrease (from  $\alpha$  to  $\beta$  phase) with the increase of MgCl<sub>2</sub> concentrations in the LiCl-KCl melts at constant current intensity. Perhaps Mg<sub>3</sub>La/Mg<sub>17</sub>La<sub>2</sub> is easy to be found when the content of Li/Mg is higher. The result is in good agreement with the one obtained in the analysis of ICP analyses.

#### 3.4 Microstructure analysis of alloys

The optical microstructures of the samples by galvanostatic electrolysis on Mo electrodes in the LiCl-KCl-KF-1.0%La<sub>2</sub>O<sub>3</sub> melts containing 12.0% MgCl<sub>2</sub> and 10.0% MgCl<sub>2</sub> are presented in Fig. 4. According to above result, due to the increase of Li content in Mg-Li-La alloys, the major difference between the two samples is the appearance of  $\beta$ -phase in the latter. It is seen from Fig. 4, the  $\alpha$  phase was abundant in white lamellar phase in sample 1, while smaller  $\alpha$  phase in lath form located on the gray  $\beta$  phase is observed in sample 2.



Fig. 3 XRD patterns of deposits obtained by galvanostatic electrolysis on Mo electrodes in LiCl-KCl-KF-1.0%  $La_2O_3$  melts containing 12.0% MgCl<sub>2</sub> (a), 10.0% MgCl<sub>2</sub> (b) and 8.0% MgCl<sub>2</sub> (c)

According to the fundamentals of solidification and the binary phase diagram of Mg–La system [14], the distribution coefficient of solute La is less than 1 and consequently during the solidification process, could result in the reduction of diffusion rate of atoms, subsequently the number of nuclei is increased and the growth of grains is restricted. On the other hand, La acts as a surface active element with Mg to the formation of Mg–La phases, which mainly distributes in the grain boundary area, thus the grain growth is further inhibited.



Fig. 4 Optical micrographs of Mg–Li–La alloys by galvanostatic electrolysis on Mo electrodes in LiCl–KCl–KF– 1.0% La<sub>2</sub>O<sub>3</sub> melts containing 12.0% MgCl<sub>2</sub> (a) and 10.0% MgCl<sub>2</sub> (b)

In conclusion, addition of La brings certain effect on grain refinement. The results of optical micrograph are the same as those observed in the XRD and ICP.

To examine the uniformity of elements of Mg and La distributed in the Mg-Li-La alloys, a mapping analysis of the elements was employed. Figure 5 shows SEM and EDS mapping analyses of sample 1. The black zone in lath form in the SEM corresponds to the bright  $\alpha$ phase in lath form in the optical micrograph [15]. The element of Mg distributes homogeneously throughout the Mg-Li-La alloy, as presented in Fig. 5. However, La distribution is not uniform and mainly disperses along the grain boundaries, which is in agreement with the results obtained previously by ZHANG et al [16]. A SEM equipped with EDS quantitative analysis was applied to further investigating the distribution of the element La. Figure 6 shows the SEM and EDS quantitative analyses of sample 1. The EDS result of the points of labeled A, B and C taken from matrix, grain boundaries and the white pot indicates that the deposits are composed of the elements of Mg and La. At the same time, the result of the EDS demonstrates that the grain boundary dissolves more La than the matrix (19.75% at point B and 0.34% at point A). Sample 3 shows a distinctly different microstructure from both samples due to the higher Li content in the Mg-Li-La alloy. Figure 7 shows the SEM images and EDS mapping analyses of



Fig. 6 SEM image (a) and EDS mapping analyses (b, c, d) of Mg–Li–La alloys by galvanostatic electrolysis from LiCl–KCl– $MgCl_2$ –KF–1.0% La<sub>2</sub>O<sub>3</sub> melts containing 10% MgCl<sub>2</sub>



**Fig. 7** SEM image (a) and EDS mapping analyses (b, c) of Mg–Li–La alloys by galvanostatic electrolysis from LiCl–KCl–MgCl<sub>2</sub>–KF–1.0% La<sub>2</sub>O<sub>3</sub> melts containing 8% MgCl<sub>2</sub>

the sample 3. From Fig. 7, it is known that  $\beta$  phase dissolves more La than  $\alpha$  phase (2.74% at point *E* and 0.34% at point *A*).

#### **4** Conclusions

1)  $\alpha$ +Mg<sub>17</sub>La<sub>2</sub>,  $\alpha$ + $\beta$ +Mg<sub>17</sub>La<sub>2</sub> and  $\beta$ +LaMg<sub>3</sub> phases in Mg–Li–La alloys with different lithium contents (0.2%–61.48%) were prepared by galvanostatic electrolysis from LiCl–KCl–KF–MgCl<sub>2</sub>–La<sub>2</sub>O<sub>3</sub> melts on molybdenum electrode. The Li content and La content of Mg–Li–La alloys can be adjusted by changing the concentrations of La<sub>2</sub>O<sub>3</sub> and MgCl<sub>2</sub> in LiCl–KCl–KF melts.

2) The EDS results show that enough La atoms concentrate at the grain boundaries to react with Mg to form compound Mg<sub>17</sub>La<sub>2</sub> or LaMg<sub>3</sub> phase and  $\beta$  phase dissolves more La than  $\alpha$  phase.

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### 熔盐电解制备 Mg-Li-La 合金

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**摘 要:** 在温度为 943 K 的 LiCl-KCl-KF 熔盐体系中添加不同浓度的 La<sub>2</sub>O<sub>3</sub>和 MgCl<sub>2</sub>直接电解制备 Mg-Li-La 合金。运用 X 射线衍射分析、扫描电子显微镜及能谱分析和金相显微镜对所得合金进行分析。结果表明,在熔盐 体系中通过添加 La<sub>2</sub>O<sub>3</sub>直接制备 Mg-Li-La 合金的方法是可行的。在电解过程中,温度不变,槽电压随着电流密 度的增加而增加,而改变温度对于槽电压影响不大。X 射线衍射分析结果表明,通过恒电流电解可以得到 α+Mg<sub>17</sub>La<sub>2</sub>, α+β+Mg<sub>17</sub>La<sub>2</sub>和 β+LaMg<sub>3</sub>三种不同镁、镧含量的 Mg-Li-La 合金。能谱分析结果表明,Mg 元素在合 金中分布均匀,然而 La 元素主要分布在晶界处与 Mg 形成金属间化合物。

关键词: Mg-Li-La 合金; La<sub>2</sub>O<sub>3</sub>; 电解; 微观组织

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