Original Article

Electrolytic preparation of Mg-Al-La alloys in KCl-MgCl$_2$-AlF$_3$ molten salts

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A B S T R A C T

A KCl-MgCl$_2$-AlF$_3$ ternary system containing La$_2$O$_3$ was investigated for the preparation of Mg-Al-La master alloy by electrodeposition technique. The cyclic voltammetry and chronopotentiometry indicated that the co-reduction of Mg, Al and La occurs at cathode-current densities more negative than ~0.29 A cm$^{-2}$. Lanthanum under-potential deposited on pre-reduced Al and it formed Al-La alloy. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) and X-ray diffraction (XRD) analyses were used to consider the contents of components in the alloy, the supernatant composition of molten salt after dissolution of La$_2$O$_3$ and the composition of the alloy, respectively. The galvanostatic electrolysis results showed that the optimum electrolysis conditions were the electrolytic temperature of 800°C, the cathode-current density of 6.92 A cm$^{-2}$, and the electrolysis time of 60 min. The XRD and SEM analysis results showed that the main phases of the obtained alloy sample were a-Mg, a-Mg + β-Al$_{12}$Mg$_{17}$ and a-Mg + Al$_{11}$La$_3$. The content of magnesium in the Mg-Al-La alloy reach with the increase of the cathode-current density.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses of Mg-Al-La alloy samples showed that aluminum and Lanthanum contents of Mg-Al-La alloys could be controlled under the several cathode-current density.

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1. Introduction

Mg-Al family alloys have a low density and high strength-to-weight, good corrosion resistance as well as are convenient for manufacturing, therefore they are widely used building so on several field [1].

According to the different matrix, the master alloy can be classified into an aluminum-based, a copper-based, an iron-based, a magnesium-based, and a nickel-based master alloy.

Rare earth metal is one kind of important substances to improve the properties of Mg-Al binary alloys [2]. Rare-earth metals have high activity so that a low content of it has high metamorphism effects and impurity refining effects in Al alloy, Mg alloy, and Zn alloy (e.g., AM60 alloy [3], Al-Zn-Mg-Cu based alloy [4–7], Al-7Si-0.7 Mg alloy [8], AZ91 alloy [9] and so on). Rare-earth metal can improve successfully alloy’s abilities such as intensity, hardness, conductivity, corrosion

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resistance [10–12]. In general, the main production methods of the alloys include mixed melting method, metal heating reduction method, molten salt electrolysis method, and so on.

In the previous works, the reduction of Mg, Li and other ions in LiCl-KCl molten salts was investigated (e.g., and Mg-Li-Zn [13], Mg-Li-Al [14] and Mg-Li [15] alloys on inert electrodes were prepared) and Mg-Al-RE (RE: Ho, Gd, Er, Dy) ternary system [16,17] already was published.


Zhang [22] studied to make foam of Al-2 wt. % Mg-RE that had comparatively tiny abscess by melt solution foam method.

Han [23] studied to make Mg-Li-Sm alloy in KCl-LiCl-MgCl2-SmCl3-KF system by fused salt electrolysis method. Han [24] made Al-Li-La alloy in LiCl-KCl-AlCl3-La2O3 system. However, there is not report on preparation of Mg-Al-La master alloy by fused salt electrolysis method in KCl-MgCl2-AlF3-(La2O3) molten salt.

In this work, the Mg-Al-La master alloy was prepared by fused salt electrolysis in KCl-MgCl2-AlF3-La2O3 molten salts. Electrochemical co-reduction of Mg, Al, and La ions in KCl-MgCl2-AlF3-La2O3 molten salts on Mo electrode is proposed for direct preparation of Mg-Al-La alloys at 800 °C. The microstructure of the obtained alloy sample was analyzed and discussed.

2. Experimental procedures

2.1. Preparation of the molten salts

AlF3 and La2O3 (≥99.0%), MgCl2 and potassium chloride (KCl, 99.9%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the reagents were dehydrated under vacuum at 673 K (400 °C) for 24 h to remove the moisture before use. The metal molybdenum line was used as the cathode and spectroscopic pure graphite was used as the anode. The manufacturing method of anhydrous AlF3 is as follows. AlF3-3H2O and ammonium bifluoride (NH4HF2) were mixed to the mass ratio of 7:3 evenly and made vacuum dehydration for two hours at 150 °C and 250 °C each other and constant temperature maintenance for three hours at below 500 °C.

Chloride mixture (KCl:MgCl2 = 50:50 (in mol. %), analytical grade) was melted in graphite crucible placed in a quartz cell inside an electric furnace. Al (III) and La (III) ions were introduced into the bath in the form of dehydrated AlF3 and La2O3 powder. All experiments were performed under an argon atmosphere.

2.2. Experimental apparatuses

The schematic diagram of experimental apparatus is shown in Fig. 1.

All potentials were referred to the Ag/AgCl couple.

The working electrode was molybdenum (99.99% purity) wire with a diameter of 1mm, which was fixed in alundum tube and was polished thoroughly using SiC paper, and then cleaned in the ultrasonic ethanol bath. A spectrally pure graphite rod (d = 6 mm) was used as the counter electrode.

2.3. Measurement and characterization

Autolab electrochemical workstation (Metrohm Co., Ltd.) was used for all electrochemical measurements. ICP-OES (Optima 8300 DV; Perkin Elmer Corp., Waltham, MA) was used for the quantitative analysis of the components contents in the alloy.

X-ray diffraction (XRD; PW3040/60; PANalytical Corp., Almelo, the Netherlands) analysis was used for the qualitative analysis of the Mg-Al-La alloy composition and the supernatant composition of molten salt after dissolution of La2O3.

SEM and EDS (JSM-6610A; JEOL Co., Ltd.) analysis was used for the microstructure analysis of Mg-Al-La master alloy.

3. Results and discussion

3.1. Interaction between the molten salts compositions

When the content of KCl is 50 mol. %, the compound KMgCl3 exists and its melting point is low comparatively [25]. In the eutectic point neighborhood the composition curve of MgCl2-KCl molten salts is destroyed monotonously [26]. As can be seen from this, the compound KMgCl3 is dissociated into the
molten salts as well as following.

\[ \text{K,MgCl}_3 \rightarrow K^+ + \text{MgCl}_3^- \rightarrow K^+ + \text{MgCl}_3^{+} + 2\text{Cl}^- \rightarrow K^+ + \text{Mg}^{2+} + 3\text{Cl}^- \]  \hspace{1cm} (1)

The interaction between the molten salts compositions at 700–850 °C as follows.

\[ \text{MgCl}_2 + \text{La}_2\text{O}_3 = 2\text{LaOCl} + \text{MgO} \text{[Ref. 27]} \]  \hspace{1cm} (2)

\[ \text{LaOCl} + \text{MgCl}_2 = \text{LaCl}_3 + \text{MgO} \text{[Ref. 27]} \]  \hspace{1cm} (3)

From the above equations, the formed LaCl₃ is able to provide La³⁺ in our experimental condition.

The anodic reaction is 2Cl⁻ → 2e− → Cl₂. The formed Cl₂ gas can react with LaOCl on the surface of anode and form CO gas [28].

\[ \text{LaOCl} + \text{C} + \text{Cl}_2 = \text{LaCl}_3 + \text{CO} \]  \hspace{1cm} (4)

The cathodic reactions are as follows.

\[ \text{Al}^{3+} + 3\text{e} \rightarrow \text{Al} \]

\[ \text{Mg}^{2+} + 2\text{e} \rightarrow \text{Mg} \]

\[ x\text{Al} + \text{La}^{3+} + 3\text{e} \rightarrow \text{Al}_x\text{La} \]

\[ x\text{Al} + \text{Mg}^{2+} + 2\text{e} \rightarrow \text{Al}_x\text{Mg} \]

3.2. Cyclic voltammetry curve in KCl-MgCl₂-AlF₃-La₂O₃ system at Mo electrodes

To study the mechanism of electrodeposition, cyclic voltammetry measurement was performed as shown in Fig. 2. The cyclic voltammetry curves were scanned for the Mo cathode (S = 0.31 cm²) from −1.8 V (vs. Ag/AgCl) at 800 °C with scanning rate of 100 mV s⁻¹.

All potentials were referred to the Ag/AgCl couple.

As shown in Fig. 2, a pair of oxidation-reduction signals (C’ and C) appeared in the curve-1, which corresponds to the oxidation-reduction process of Mg.

After adding AlF₃ into the MgCl₂-KCl system, the other peaks (A’ and A) and (B’ and B) appeared on curve 2. The peak potential of A is about −0.95 V (vs. Ag/AgCl). The peak A was corresponding to deposition of Al on electrode surface. This peak potential of A is similar to the peak in Ref. [24]. The pair of signals (B’ and B) correspond to oxidation-reduction signals for alloy AlₓMg. Curve 3 is cyclic voltammetry curve in system KCl-MgCl₂-AlF₃-La₂O₃.

As known from curve 3, after adding 1 wt.% La₂O₃ in the molten salt, another oxidation-reduction signal (D’ and D) was observed. This would be the signal related with production of compounds.

The peak D that was detected at −1.55 V corresponds to the formation of AlₓLa. The reduction signal D for AlₓLa also could be concordant with the signal for AlₓLa reported by Han et al. [24] in LiCl-KCl-AlCl₃-La₂O₃ system.

3.3. Square wave voltammetry for the KCl-MgCl₂-AlF₃-La₂O₃ system on the Mo cathode

The square wave voltammogram (SWV) is another analytical technique to determine the electron transfer number (n) in an electrode process. The width of the half-peak, \( W_{1/2} \), depends on n and on the temperature (T) as follows [29].

\[ W_{1/2} = 3.52RT/nF \]  \hspace{1cm} (5)

Using the half peak (\( W_{1/2} \)) of Gaussian wave, the number of exchanged electrons can be calculated.

The relationship between the half peak of Gaussian wave and the number of exchanged electrons is the same as the Eq. (5).

Fig. 3 shows the square wave voltammogram (SWV) for the reduction of Mg²⁺ on the Mo cathode.

By measuring \( W_{1/2} \) of this peak and using the Eq. (5), the average number of electrons transferred was calculated as \( n = 1.983 \). The number of electrons transferred is close to two.
Fig. 4 – Net-current square wave voltammogram on Mo electrode (S = 0.31 cm$^2$) in KCl-MgCl$_2$ system at 1073 K (800 °C) and 20 Hz.

Fig. 4 shows the SWVs for the reduction of Mg, Al and La on the Mo electrode in the KCl-MgCl$_2$ molten salts at frequency of 20 Hz.

In curve 1 (Fig. 4), there were three peaks A, B and C corresponding to the deposition of Al and Mg on the Mo electrode. After adding 1 wt.% La$_2$O$_3$ in the molten salt, the another peak D appeared in curve 2. In consideration with Fig. 2, the cathodic peak D was identified as the reduction of La(III) ion on Al substrate forming intermetallic compounds.

Fig. 5 shows the results observed by the square wave voltammetry corresponding to the mentioned peak D on Mo electrode in KCl-MgCl$_2$-AlF$_3$-La$_2$O$_3$ at the various frequencies and 1073 K (800 °C). The scan frequency varied from 5 to 35 Hz. As shown in Fig. 5, the square wave voltammograms exhibit the peak current in the same potential range, and then, the peak current is increasing with the increase of the scan frequency.

The average number of electrons transferred was calculated as $n = 2.94$ by measuring $W_{1/2}$ and using Eq. (5). The number of electrons transferred is close to 3, which confirm that the reduction La(III)$\rightarrow$La(0) on Al substrate is a single step with three electrons exchanged.

3.4. Chronopotentiometry of KCl-MgCl$_2$-AlF$_3$-La$_2$O$_3$ system at Mo electrodes

Chronopotentiometry was employed to further investigate the electrochemical formation of Mg-Al-La alloys via co-reduction of Mg, Al and La. Fig. 6 presents that the chronopotentiograms were measured in KCl-MgCl$_2$-6 wt.% AlF$_3$-1 wt.% La$_2$O$_3$ melts at different current densities. The first plateau marked by curve (1) at the cathode current up to 20 mA ($i = 0.06$ A·cm$^{-2}$) is associated with the reduction of Al (III) ion.

Fig. 6 – Chronopotentiograms at different currents on the Mo electrode (S = 0.31 cm$^2$) in KCl-MgCl$_2$- AlF$_3$-La$_2$O$_3$ molten salt at 800 °C.
Table 1 – ICP-OES analysis results of some alloys prepared under the different electrolysis conditions from KCl-MgCl₂-AlF₃-1 wt.%La₂O₃ molten salt.

<table>
<thead>
<tr>
<th>№</th>
<th>Tem. (°C)</th>
<th>Time (min)</th>
<th>i (A cm⁻²)</th>
<th>Al (wt. %)</th>
<th>La (wt. %)</th>
<th>Mg (wt. %)</th>
<th>Current efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700</td>
<td>60</td>
<td>6.92</td>
<td>6.90</td>
<td>2.64</td>
<td>Bal.</td>
<td>42.45</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>60</td>
<td>6.92</td>
<td>12.88</td>
<td>2.99</td>
<td>Bal.</td>
<td>51.25</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>30</td>
<td>6.92</td>
<td>62.01</td>
<td>1.57</td>
<td>Bal.</td>
<td>47.89</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>60</td>
<td>3.46</td>
<td>81.10</td>
<td>7.38</td>
<td>Bal.</td>
<td>53.24</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>60</td>
<td>5.19</td>
<td>60.30</td>
<td>5.05</td>
<td>Bal.</td>
<td>57.4</td>
</tr>
<tr>
<td>6</td>
<td>800</td>
<td>60</td>
<td>6.92</td>
<td>27.00</td>
<td>3.17</td>
<td>Bal.</td>
<td>71.2</td>
</tr>
<tr>
<td>7</td>
<td>800</td>
<td>90</td>
<td>6.92</td>
<td>9.88</td>
<td>4.20</td>
<td>Bal.</td>
<td>62.88</td>
</tr>
<tr>
<td>8</td>
<td>800</td>
<td>120</td>
<td>6.92</td>
<td>8.17</td>
<td>2.63</td>
<td>Bal.</td>
<td>67.58</td>
</tr>
<tr>
<td>9</td>
<td>850</td>
<td>60</td>
<td>6.92</td>
<td>27.10</td>
<td>5.40</td>
<td>Bal.</td>
<td>66.52</td>
</tr>
<tr>
<td>10</td>
<td>800</td>
<td>60</td>
<td>8.65</td>
<td>6.57</td>
<td>1.56</td>
<td>Bal.</td>
<td>64.5</td>
</tr>
</tbody>
</table>

Fig. 7 – Chronopotentiogram of La(III) in KCl-MgCl₂-AlF₃-La₂O₃ (ClLa(III) = 1.23 × 10⁻⁴ mol/cm³) molten salt at 800 °C. I = 80 mA (i = 0.258 A/cm²). Working electrode area of 0.31 cm². Reference electrode: Ag/AgCl.

Under the applied current 30 mA (i = 0.10 A cm⁻²) and more, the plateaus marked by curve (2) are associated with the formation of Al₃Mg.

When the applied current is 60 mA (i = 0.194 A cm⁻²) to 80 mA (i = 0.258 A cm⁻²), the curve (3) is corresponding to the formation of Al₂La.

At the cathode current higher than 90 mA (i = 0.29 A cm⁻²), the curve (4) is ascribed to the deposition of Mg on Mo electrodes.

According to Sand’s law, the Eq. (6) demonstrates the relationship between the current density and the transition time [29,31].

\[ I^{1/2} = 0.5nFAC_0D^{1/2}r^{1/2} \]  \[ (6) \]

where I is the current, A; r is the transition time, s; C₀ is the concentration of La³⁺ ion, mol/cm³; n is the electron charged number; F is the Faraday constant (96500 C/mol); A is electrode area (0.31 cm²); D is diffusion coefficient, cm²/s. The transition time was determined by measuring the duration of the first part in the chronopotentiograms according to methodology indicated in Ref. [30]. The chronopotentiogram presented in Fig. 7 exhibits an transition time (r = 0.24 s). By using the average value I√₂, the diffusion coefficient was calculated using the Eq. (6) as 1.82 × 10⁻⁵ cm²/s (±10 pct).

Fig. 8 – XRD pattern of the Mg-Al-La alloy after electrolysis from KCl-MgCl₂-6 wt.%AlF₃-1 wt.%La₂O₃ molten salt at 800 °C for 60 min (cathode-current density of 6.92 A cm⁻²).

3.5. Galvanostatic electrolysis of Mg-Al-La alloys and characterization

Cyclic voltammetry curves and chronopotentiograms show that electrochemical co-reduction occurred when the potentials are negative than −1.8 V or the cathode current densities are negative than −0.29 A cm⁻². The limiting cathode-current density is too small to deposit enough alloys in a short time for SEM and XRD analyses. So the galvanostatic electrolysis were carried out at more negative current densities in KCl-MgCl₂-6 wt.%AlF₃-1 wt.%La₂O₃ molten salts with different electrolysis temperature and electrolysis time, using a molybdenum electrode.

The current efficiency is able to calculate according to following equation. [23]

\[ \eta = \frac{Q_{Mg} + Q_{Al} + Q_{La}}{I \cdot t} \]  \[ (7) \]

where Qₘ₉₉, Qₐ₉ and Qₖ₉ are the electrical quantities of the deposited Mg, Al and La, respectively, A h⁻¹; t is the electrolysis time, h; I is current intensity, A.

According to Faraday’s Law, Q = nzF.
Fig. 9 – (a) Sample image and (b) Microstructure of the Mg-Al-La alloy obtained by galvanostatic electrolysis from KCl-MgCl$_2$-6 wt.%AlF$_3$-1 wt.%La$_2$O$_3$ molten salt at 800°C for 60 min. (cathode-current density of 6.92 A·cm$^{-2}$).

Where: $n$ is the amount of the deposited metal, mol; $z$ is number of the transferred electrons; $F$ is Faraday’s constant, 26.801 A·h/mol.

ICP-OES analyses of samples obtained by galvanostatic electrolysis are listed in Table 1. Under the same electrolysis time, with increase of the cathode current density, the content of Mg among the alloy was increased continuously, and then the contents of Al and La were decreased. The contents of Al and La in the alloy are increased while the content of Mg in the alloy is continuously decreased with the increase of electrolysis temperature. At the same electrolysis temperature, the content of Mg in the alloy was continuously increased and La content was decreased with the increases of cathode-current density and electrolysis time.

Fig. 8 shows the XRD pattern of Mg-Al-La alloy sample obtained by galvanostatic electrolysis from KCl-MgCl$_2$-6 wt.%AlF$_3$-1 wt.%La$_2$O$_3$ molten salt at 800°C for 60 min under the cathode current density of 6.92 A·cm$^{-2}$. As shown in Fig. 8, the sample consists of Al$_{12}$La$_3$, β-Al$_{12}$Mg$_7$, and α-Mg phase. Fig. 9 shows the sample image (a) and microstructure (b) of

Fig. 10 – EDS mapping analysis of the Mg-Al-La alloy according to Fig. 9(b).
4. Conclusions

Electrochemical techniques showed that the co-reduction occurred when the current densities are more negative than $-0.29 \text{ A cm}^{-2}$.

Under the conditions having the maximum current efficiency, Mg-Al-La alloys with $\alpha$-Mg, $\beta$-Al$_{12}$Mg$_{17}$ phase and Al$_{11}$La$_3$ phase were successfully prepared via galvanostatic electrolysis co-reduction of Mg, Al and La on inert molybdenum electrodes in KCl-MgCl$_2$-$\alpha$F$_3$-$\beta$F$_3$ molten salts. An analysis of microstructures shows that the banding eutectic structure of ($\alpha$-Mg + Al$_{12}$La$_3$) phase and the flaky crystal of ($\alpha$-Mg + $\beta$-Al$_{12}$Mg$_{17}$) phase are distributed in Mg-Al-La alloy sample obtained by galvanostatic electrolysis from KCl-MgCl$_2$-$\alpha$F$_3$-$\beta$F$_3$ molten salt at $800^\circ\text{C}$ for 60 min. The contents of Al and La in the alloy are increased while the content of Mg in the alloy is decreased continuously with the increase of electrolysis temperature. At the same electrolysis temperature, the content of Mg in the alloy was increased continuously and La content was decreased with the increases of cathode-current density and electrolysis time.

Conflicts of interest

The authors declare no conflicts of interest.

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References


