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JOURNAL OF RARE EARTHS
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JOURNAL OF RARE EARTHS, Vol. 27, No. 6, Dec. 2009, p. 1046

Preparation of Mg-Li-Sm alloys by electrocodeposition in molten salt

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Received 26 November 2008; revised 4 August 2009

Abstract: Electrocodeposition of Mg-Li-Sm alloys was investigated in molten KCl-LiCl-$MgCl_2$-$SmCl_3$-KF system. The effects of electrolytic temperature and cathodic current density on current efficiency were studied and optimal electrolysis parameters were obtained. The optimum electrolysis condition was a molten salt mixture of LiCl: KCl =50:50 (wt.%), electrolytic temperature: 660 ºC, cathode current density: 9.5 A/cm^2 and electrolysis time of 40 min. The current efficiency reached 77.3%. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses of the deposits indicated that Mg-Li-Sm alloys, having Mg, βLi and $Mg_{41}Sm_5$ phases, were obtained by electrocodeposition in molten system. The content and distribution of elements in Mg-Li-Sm alloys were analyzed by ICP-MS and EPMA, respectively. The results showed that the distribution of Mg and Sm was homogeneous in the alloys. ICP analyses of samples obtained by electrolysis showed that lithium contents in Mg-Li-Sm alloys could be controlled by $MgCl_2$ concentration and electrochemical parameters. It was proved that preparation of Mg-Li-Sm alloys by electrocodeposition in molten salt was feasible.

Keywords: Mg-Li-RE alloys; electrodeposition; current efficiency; molten salt; rare earths

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Mg-Li alloys, having a density of 1.35–1.65 g/cm^3, are ultra-light structural metallic materials. Their density is 1.5–2.0 times less than that of aluminum alloys and similar to that of structural plastics. Mg-Li alloys also have high specific stiffness, and high electrical and thermal conductivities. Based on these advantages, Mg-Li alloys are widely used in aerospace and weapon industry[1–4].

Pure Mg has hexagonal closed-packed (hcp) structure. The Mg-Li phase diagram[5] shows that Li is soluble in hcp magnesium up to 5 wt.%. As the content of Li exceeds 11.5 wt.%, Mg-Li alloys become body-centered cubic (bcc, β) structure. With the increase of lithium content, the density of Mg-Li alloys decreases, and the ductility increases. The addition of rare earth element can significantly improve high temperature strength, anti-creep capacity and corrosion resistance of Mg-Li alloys.

At present, the production method of Mg-Li-RE alloy is metal casting. It has many disadvantages such as inhomogeneous alloy composition, complex production process, serious problem with metal burning, and high-energy consumption. Consequently, preparation of Mg-Li-RE alloys by electrochemical process in molten salts is proposed. Molten salt electrocodeposition process has been successfully applied to prepare many rare earth-transition metal alloy films[6–9].

In order to prepare homogeneous alloys, save energy consumption and simplify the process, preparation of Mg-Li-Sm alloys by electrocodeposition in molten salts was investigated. The effects of experimental parameters and cathodic current density on current efficiency were also studied.

1 Experimental

The LiCl-KCl eutectic (LiCl:KCl=50:50 wt.%) was placed in a high purity alumina crucible (99.5 wt.% Al_2O_3) and dried under vacuum for more than 24 h at 300 °C to remove water. The salts $MgCl_2$, KF and $SmCl_3$ were dehydrated under vacuum for more than 24 h at 130 °C. The temperature of the electrolysis bath was controlled by CONTROLLOR AL808 with an accuracy of ±1 ºC. The cathode was molybdenum wire (Φ=1 mm). Graphite rod (Φ=10 mm) was used as anode. Fig. 1 showed the experimental apparatus.

The phases, contents and element distribution of Mg-Li-Sm alloys were analyzed by XRD (TTR-III Rigako X), ICP-MS(IRIS Intrepid II) and SEM (SM-6360LV) respectively.

Foundation item: Project supported by 863 project of Ministry of Science and Technology of China (2006AA03Z510) and the National Natural Science Foundation of China (50871033)

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DOI: 10.1016/S1002-0721(08)60386-5

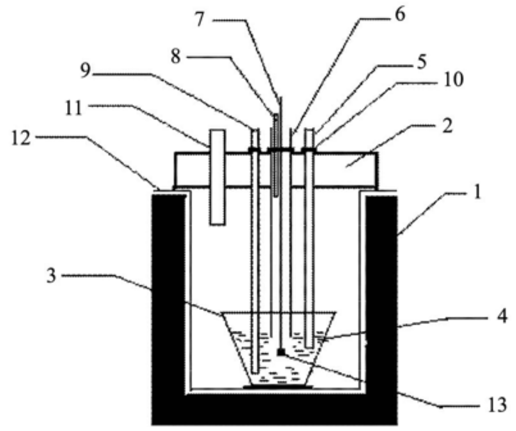

Fig. 1 Apparatus of electrolysis

1-Resistance furnace; 2-Firebrick; 3-Crucible; 4-Electrolyte; 5-Thermocouple; 6-Corundum tube; 7-Cathode (Mo); 8-Ar gas inlet; 9-Anode (graphite rod); 10-Iron clip; 11-Chlorine gas export; 12-Stainless steel sleeve; 13-Alloy

Pre-electrolysis was carried out in order to remove residual water and some metal impurities. All experiments were performed under argon atmosphere. Anhydrous $SmCl_3$ was added directly into the melts as Sm (III) ion source.

The electrolyte composition: $LiCl:KCl:MgCl_2:SmCl_3:KF=44.5:44.5:5.9:0.2:4.9$, wt.%.

The current efficiency was calculated using the equation:

$$\eta=\frac{Q_{Mg}+Q_{Li}+Q_{RE}}{It}\times 100\%$$

where: I is current intensity, A; t is electrolysis time, h; Q_{Mg}, Q_{Li}, Q_{RE} represent electrical quantity of deposited Mg, Li and RE respectively according to Faraday's Law:

$$Q=nzF$$

where: n is the amount of metal material deposited, mol; z is number of electrons transferred in the reaction; F is Faraday's constant, 26.801 A·h/mol.

2 Results and discussions

2.1 Electrocodeposition of Mg-Li alloys

The deposition potential of Li is more negative than that of Mg; it is difficult to codeposit Mg and Li at the same time. Therefore, at first the experimental conditions of electrocodeposition of Mg-Li alloys were investigated.

In the molten $MgCl_2$-LiCl-KCl-$BaCl_2$-KF (KCl:LiCl:$MgCl_2$:$BaCl_2$:KF=32:32:12.5:21:2.5, wt.%) system, electrolysis temperature was 660 ºC and cathodic current density was 22.3 A/cm^2. The change of composition of Mg-Li alloys during electrolysis is shown in Fig. 2.

It can be seen that Mg was deposited only during the interval of 0–60 min in the form of Mg layer on Mo cathode. After 60 min Li^+ began to deposit on the surface of Mg cathode. For the Mg electrode, the electroreduction of Li^+ took place at more positive potential values than that at inert electrode and then Mg-Li alloys formed[10–12]. In this case the codeposition of Mg and Li occurred at 60 min.

ICP-MS was used to analyze content of the electrolyte at 60 min, and the concentration of $MgCl_2$ in the electrolyte was just 5–6 wt.%. Similar results were found in Ref. [12].

2.2 Electrocodeposition of Mg-Li-Sm alloys

Based on the experimental results mentioned above, KCl-LiCl-$MgCl_2$-$SmCl_3$-KF (KCl:LiCl=50:50 wt.%) system was chosen as the electrolyte. The concentration of $MgCl_2$ in the electrolyte was 5 wt.%. For optimum electrolysis the temperature was 660 ºC and the cathodic current density 9.5 A/cm^2.

The change of composition of Mg-Li alloys during electrolysis is shown in Fig. 3. It shows that the quantity of Mg and Li in Mg-Li-Sm alloys increased with the increase of electrolysis time. It means that Mg and Li were codeposited during the interval of 20–80 min. This new method for the

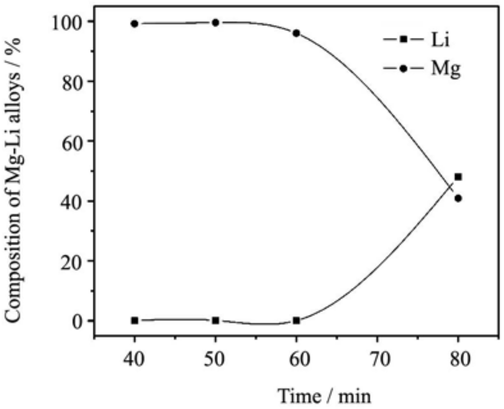

Fig. 2 Relationship of the composition of Mg-Li alloys with electrolytic time

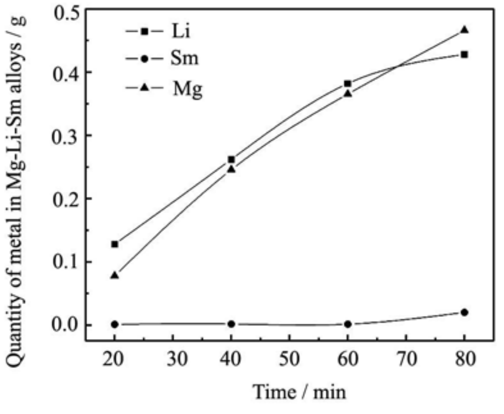

Fig. 3 Effect of electrolytic time on composition of Mg-Li-Sm alloys