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Preparation of Magnesium-Rare Earth Master Alloy Using Electrowinning method with Subsidence Cathode

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Abstract. A new series of magnesium-rare earth master alloys have been developed by the electrowinning method with subsidence cathode in the KCl•NaCl-$RECl_3$ system. The electrolysis conditions were studied. Experimental results showed that the optimum for electrolyte at 850°C and 10~20wt% $RECl_3$ content in the molten salt system. The current efficiency of electrolyte increased with increasing the rare earth content and reach the maximum at the content of 20% $RECl_3$. The current efficiency gradually decreased with increasing cathode current density. The component of master-alloys was analyzed using ICP-MS and chemical method. A series of magnesium-rare earth master-alloy, Mg-Y, Mg-Nd, Mg-Ce, Mg-La, Mg-Nd-rich and Mg-LPC were successfully prepared and the content of rare earth is adjustable between 5 – 20%.

Introduction

Mg alloys are being used in a broad variety of structural applications in automotive, aero-space, electronics and consumer products industries. The rare earth metals (RE) are well-known as effective alloying elements for magnesium alloys, especially in creep resistance up to high temperatures [1, 2]. There are a few kinds of rare earth magnesium alloys, for example, AE42, AE41, WE43, WE54 etc. It is very difficulty to directly form the especial magnesium alloy contained rare earth because there are a large difference between magnesium (1.78g/cm^3) and rare earths (~ 7.8g/cm^3) in density. Also it is very difficulty to alloy because their molten point is very different, which magnesium is about 650°C and rare earths are above 1100°C. Because of the lack of rare earth magnesium alloys their application in high temperature, creep resistance, high strength and corrosion resistance is deeply limited.

Lanthanide has 16 elements including Y and Sc. A specific feature of the rare earth metals is significant difference between them as they are added to magnesium. The magnesium alloys contained neodymium, for instance, shows higher strengthening effect than that contained cerium. And yttrium shows higher strengthening effect and creep resistance effect than neodymium in magnesium alloys [3]. The strength properties of Mg alloys with rare earth metals are connected at a great extent with the content of RE in magnesium, especially, solubility of the rare earth metals in solid Mg. Therefore, the success in developing a series of rare earth magnesium master-alloys will be very important for wide application of magnesium alloys.

In this paper, a new series of magnesium-rare earth master-alloys have been developed through the electrowinning method with subsidence cathode in the molten salt system.

Experimental

The raw materials of NaCl and KCl are A.R. purity. The rare earth chloride was prepared by previous method.[4, 5] The 99.8% pure magnesium was melted in a graphite crucible and the KCl•NaCl-$RECl_3$ mixture salt also was added. The molybdenum rod was used as cathode. The electrolyte apparatus was controlled by the programming temperature controller. The eutectic temperature and weight loss of mixture molten salt were measured by the SDT 2960(TA Instruments) at 10^{o}C/min.

Results and Discussion

Electrolyte Selection. There are interaction between mixture molten salt and alloy at high temperature and the thermal mass loss was accompanied. The thermal mass loss of mixture molten salt was measured and the results were listed in Table 1.

Table 1 the thermal weight loss of molten salt at different temperature

Mixture system	Temp.[^{o}C]	$RECl_3$ content in molten salt [wt]%					
		0	10	20	30	40	50
$RECl_3$-KCl·NaCl	750	0.2	0.5	0.7	0.8	0.9	2.0
	850	0.5	0.8	1.6	1.9	2.7	3.2
$LaCl_3$-KCl·NaCl	750	0.2	0.3①	0.5	0.6	1.0②	
	850	0.5	1.0①	1.5	1.7	2.4②	
$NdCl_3$-KCl·NaCl	750	0.2	0.6	0.7	0.8	1.0	1.7
	850	0.5	1.2	1.6	1.8	2.3	3.1

①:$LaCl_3$ content 15%, ②: $LaCl_3$ content 14%

From Table 1, the thermal weight loss at 850^{o}C is two and four times than that at 750^{o}C. Considering system stability and higher electrolyte efficiency it is better for electrolyze molten salt to prepare the master-alloys.

In order to select the suitable molten salt the eutectic temperature and density of mixture molten salt were investigated. The experimental results are listed in Table 2 and Table 3.

Table 2 the eutectic temperature of mixture molten salt

$RECl_3$ content in molten salt %	Temp.(^{o}C) $RECl_3$	Temp. (^{o}C) $LaCl_3$	Temp. (^{o}C) $NdCl_3$
0	661	661	661
10	650	641	652
20	637	631	640
30	631	615	621
40	615	614	617
50	536	603	543

Table 3 density of molten salt

Mixture system	$RECl_3$%	ρ 750^{o}C	ρ 800^{o}C	ρ 850^{o}C
$RECl_3$-KCl·NaCl	10	1.704	1.625	1.565
	20	1.850	1.741	1.660
	40	1.882	1.831	1.791
$LaCl_3$-KCl·NaCl	10	1.67	1.63	1.60
	20	1.74	1.72	1.69
	40	1.89	1.88	1.83
$NdCl_3$-KCl·NaCl	10	1.68	1.63	1.58
	20	1.73	1.69	1.67
	40	1.92	1.90	1.87

From Table 2 and 3, it is obvious that the eutectic temperatures of molten salt are lower than the melt point of magnesium (650^{o}C) range 5 ~ 15% $RECl_3$ content. But the density of molten salt increases with increasing $RECl_3$ content. [6, 7] This requires the content of $RECl_3$ in lower level in the mixture molten salt system. The 10 ~ 20% $RECl_3$ content in mixture molten salt system is considered.

Electrolyte conditions. The electrolyte process is very complicated in the mixture molten salt system. In order to get high quality RE-Mg master-alloys the technologic conditions were studied carefully and respectively. Fig.1 shows the relationship between current efficiency and $RECl_3$ content. Current efficiency dependence of electrolyte temperature and cathode current density was shown in Fig.2 and Fig.3, respectively.

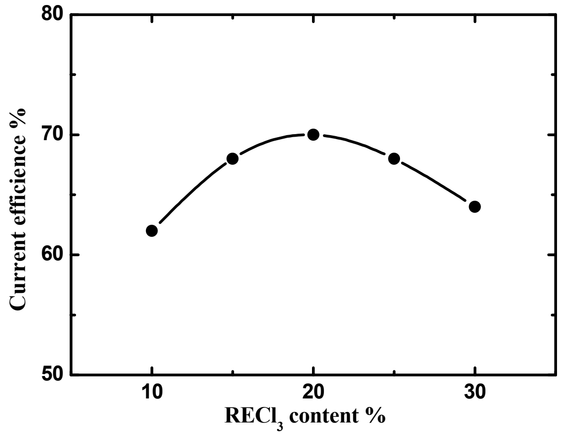

Fig.1 the relationship between current efficiency and $RECl_3$ content

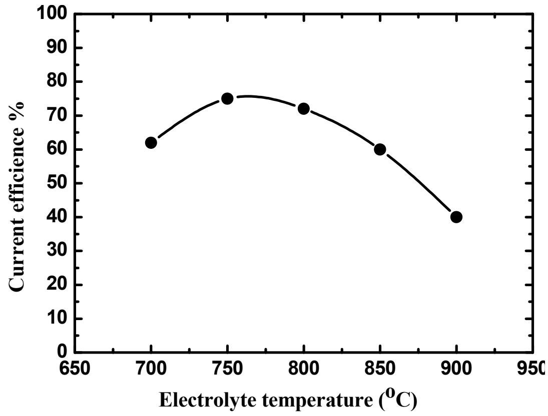

Fig.2 the relationship between current efficiency and electrolyte temperature

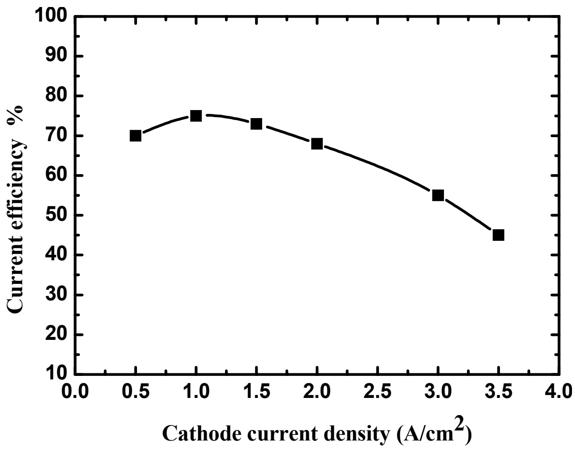

Fig.3 Current efficiency dependence of cathode current density

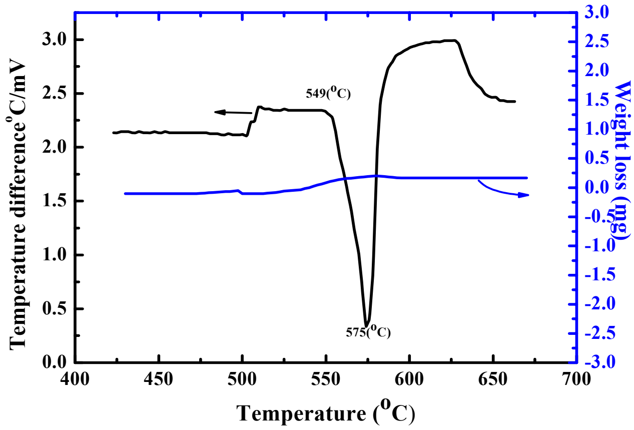

Fig.4 the TG/DTA result of Mg-Ce master-alloy

It is obvious from Fig.1 that current efficiency of electrolyte increases with increasing the rare earth content and reaches the extremum at 20% $RECl_3$ content. When the $RECl_3$ content continue to increase the current efficiency of system gradually decrease. It reveals that increasing $RECl_3$ content in the mixture molten salt will lead to decrease the move speed of the mobility [8, 9]. Meanwhile, this also results to the depression of conductivity in the mixture molten salt system. It is too bad to get homogenous RE-Mg master-alloys. From Fig.2, it is seen that the 750°C seems the most suitable temperature for electrolyte. If temperature is higher than that the volatilization of Mg and molten salt will increase. If temperature is lower than that the fluidity of molten salt system became no good. The $RECl_3$ content and molten salt density of the system plays an important role in the electrowinning process.

Composition analysis.

A new series of magnesium-rare earth master-alloys (rare earth =Y, Nd, Ce, Ce-rich and LPC) have been developed by the electrowinning method with subsidence cathode in the KCl•NaCl-$RECl_3$ system. In order to demonstrate the quality the TG/DTA analysis of selective Mg-Ce master-alloy (Ce content 15.4%) was performed and the results are given in Fig.4. From Fig.4, it is obvious that the weight loss is nearly no change in the measurement temperature up to 680°C. The DTA curve shows that there is an endothermic peak at 575°C. It indicates that the melt point of Mg-Ce master-alloys are at 575°C. It is coincide with the co-crystallized point in the Mg and Ce ternary phase diagram. The alloy composition of three RE-Mg master-alloys were analyzed by ICP-MS equipment and the results were given in Table 4.

Table 4 alloy composition analysis

Elements	Mg-Nd	Mg-Y	Mg-Ce
La	0.12	0.09	0.57
Ce	0.022	0.006	154
Pr	0.35	0.02	0.13
Nd	211	4.5	23
Y	0.027	196	0.034
Fe	0.35	0.48	0.26
Cu	<0.005	0.18	<0.002
Si	0.12	0.33	0.13
Ni	<0.005	<0.005	0.04

From Table 4, the RE-Mg master-alloys have homogenous Nd 21.1%, Y 19.6% and Ce 15.4%, respectively, and much lower impurity content.

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