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Effect of oxide and fluoride addition on electrolytic preparation of Mg−La alloy in chloride molten salt

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Abstract: Mg−La alloys were prepared by constant voltage electrolysis in the molten salt system of $MgCl_2$−$LaCl_3$−KCl at 750 °C, with a graphite crucible as the anode and a tungsten rod as the cathode. The effect of oxide and fluoride addition on the electrolysis was investigated comprehensively. X-ray diffraction (XRD) was used to characterize some of the Mg−La alloy products and the sludges. As the content of MgO or La_2O_3 in the electrolyte increased, both the current efficiency and the mass of alloy product decreased, indicating that both MgO and La_2O_3 may take part in the reactions in the electrolyte. When the same mass of the oxide was added, compared with La_2O_3, MgO had a more pronounced effect on both the current efficiency and the mass of alloy product. XRD studies confirmed the formation of LaOCl when MgO or La_2O_3 was added into the electrolyte. The formation of LaOCl sludge would be the main reason for the negative effect of the oxide addition on both the current efficiency and the mass of alloy. In the electrolytic system, the addition of CaF_2 was not helpful to suppress the negative effect of MgO on the electrolysis, probably due to the complex reactions of the La compounds in the electrolyte.

Key words: Mg−La alloy; molten salt; electrolysis; oxide; fluoride; current efficiency

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1 Introduction

Due to the high specific strength, high dimensional stability, high thermal conductivity, high damping capacity, good castability and machinability, good electromagnetic shielding characteristic, good recycling property, etc [1,2], Mg alloys have been used in: 1) automobiles, aircrafts, and spacecrafts; 2) computers and mobile phones; 3) microelectronics; 4) sporting goods, handheld tools, and household equipments; etc [2−5].

During applications of Mg alloys, the improvement of their corrosion resistance properties is of critical importance. Rare earth (RE) elements are effective alloying elements for the improvement of the corrosion resistance properties of Mg alloys [1,6]. Mg−RE master alloys are basic materials for the preparation of corrosion−resistant and high temperature−resistant magnesium alloys [3,7]. The improved performance is commonly due to three effects of grain refinement, precipitation hardening, and solid solution strengthening [8−10]. Therefore, the preparation and applications of Mg−RE alloys have drawn more and more attention [11].

Mg−RE alloys are mainly produced by the vacuum metallurgical technique and the molten salt electrolysis process [11,12]. Compared with the former technique, the later process is more attractive due to the homogeneity of alloy composition, simplicity in technology, and continuous or semi-continuous manufacturing process [11,12]. Up to now, there have been some reports on the electrolytic preparation of Mg−RE alloys, including Mg−Y [11], Mg−Yb [6], Mg−Gd [13], Mg−LaPrCe [7,14], Mg−Li−La [12] alloys.

Usually, the electrolytic production of Mg−RE alloys from fused chloride requires the production of anhydrous Mg chloride and anhydrous RE chloride as charging material. The preparation of anhydrous chlorides of Mg and RE is not easy, and in some cases, a certain amount of water remains in the chlorides, and/or

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some oxide impurities exist due to hydrolysis of the metal ions. It is known that water in the electrolysis cell reduces the current and power efficiency. Oxides are common impurities in anhydrous chlorides that are highly undesirable in the electrolyte bath. Because these oxides are only slightly soluble in the conventional electrolytes, they remain suspended throughout the process, causing sludge to form within the electrolytes. As a result, some elemental Mg and RE are lost during the process as sludge, which must be periodically removed from the electrolytic cell [5]. Therefore, it is very necessary to study the influence of oxides on the electrolysis and to find an effective method to minimize or avoid this influence.

The cost of Mg alloys is relatively high, limiting their usage. The cost of Mg is high compared with Al. When anhydrous chlorides are used for the electrolytic preparation of Mg−RE alloys, much of the cost results from the preparation of the anhydrous chlorides. When magnesium is produced by electrolysis of the molten chloride in an electrolyte consisting of alkali and alkaline earth metal chlorides, the majority of these processes require anhydrous magnesium chloride as the feed, and it is reported that 50% of the total energy input required is expended in the production of the anhydrous magnesium chloride [15]. There remains a substantial need for Mg alloy production processes that can utilize oxides or partially dehydrated chlorides as feed materials [15,16].

Based on the above statements, it is readily apparent that when Mg−RE alloys are prepared in chloride molten salts, using chlorides as feeding materials, the influence of water and oxide still remains to be a problem. And in order to reduce the total cost for the preparation of Mg−RE alloys, it is necessary to investigate the possibilities of using oxides or hydrous chlorides as feeding materials to prepare the alloys. In this work, electrolytic preparation of Mg−La alloys in chloride molten salt was studied, with the emphasis on the influence of oxides on the electrolysis. The effects of oxide and fluoride addition on the average electrolysis current, current efficiency, elemental and phase composition of the alloy products were investigated comprehensively.

2 Experimental

2.1 Electrolytic cell

Schematic diagram of the cell assembly is shown in Fig. 1. Electrolyte was held in a graphite crucible with 100 mm in inside diameter and 150 mm in height, which was used as the anode. A tungsten rod (15 mm in outside diameter and 380 mm in length) was used as the cathode. Tungsten was chosen as the cathode because it can maintain a good stability in molten salt at high temperature. The graphite crucible was placed in an electric furnace. The electric furnace was used to heat the cell assembly, and the furnace temperature was adjusted using a controller. Temperature measurements were made with a thermocouple placed into the molten salt electrolyte. A KXN-15150D DC power supply that had a capacity of providing 150 A current at maximum of 15 V was used for the electrolysis experiments.

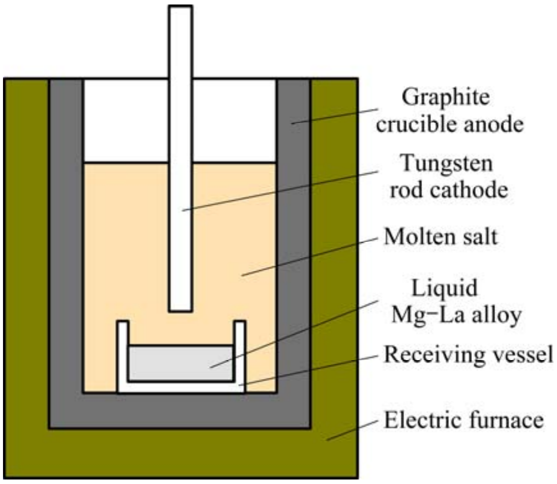

Fig. 1 Schematic diagram of electrolytic cell

2.2 Electrolytic preparation of alloys

Analytically pure KCl, $MgCl_2$, $LaCl_3$, La_2O_3, MgO, and CaF_2 were used for the electrolysis experiments. Commercially pure NaOH was used for the absorption of the produced Cl_2 gas. In all the electrolysis experiments, the total amount of the electrolyte together with the oxide and fluoride was 1.4 kg. The mass ratio of KCl to $LaCl_3$ to $MgCl_2$ was fixed at 13:4:3. In the experiments with oxide and fluoride added, the amount of the oxide and fluoride added is listed in Tables 1 and 2. The

Table 1 Effect of oxide addition on electrolysis

No.	Oxide added	w(Oxide)/%	I/A	S/cm^2	η/%	m/g	w(Mg)/%
1	−	0	44.6	35.4	90.5	46.0	72.8
2	La_2O_3	1	45.9	35.6	87.2	46.2	71.5
3	La_2O_3	3	44.1	35.1	82.8	43.5	68.1
4	La_2O_3	5	43.6	34.8	79.1	41.5	67.1
5	MgO	1	45.4	35.7	85.2	43.5	74.3
6	MgO	2	44.4	35.0	73.6	35.6	77.8
7	MgO	3	42.5	34.5	66.6	30.6	78.5

w(Oxide) is the content of the oxide added into the electrolytes; I is the average electrolysis current; S is the active electrode surface area in each experiment; E is the current efficiency of the electrolysis; m is the mass of Mg−La alloy products obtained in the experiments; w(Mg) is the Mg content in the Mg−La alloy products

Table 2 Effect of MgO and CaF_2 co-addition on electrolysis

No.	$w(MgO)$/%	$w(CaF_2)$/%	I/A	S/cm^2	η/%	m/g
8	1	0	45.4	35.7	85.2	43.5
9	1	0.3	41.9	35.6	83.9	39.5
10	1	0.5	43.6	35.5	83.9	41.2
11	1	1	44.8	35.3	82.7	41.7
12	2	0	44.4	35.0	73.6	35.6
13	2	0.5	46.1	34.8	62.2	31.3

$w(MgO)$ and $w(CaF_2)$ are the contents of MgO and CaF_2 added into the electrolytes, respectively; I is the average electrolysis current; S is the active electrode surface area in each experiment; E is the current efficiency of the electrolysis; M is the mass of the Mg−La alloy products obtained in the experiments

compounds needed were weighed, mixed, and loaded into the graphite crucible. Connections to the auxiliary apparatus were all made. The heating process was started. After fusion of the mixture, the electrolyte temperature was allowed to stabilize at 750 °C. The cathode and the anode contacted, and the electrolysis commenced.

Constant voltage electrolysis was performed at 4.5 V for 2 h. The current was recorded every 10 min. Mg−La alloy, heavier than the electrolyte, was collected in a 100 mL porcelain crucible (alloy receiving vessel) placed at the bottom of the graphite crucible, while chlorine gas evolved from the graphite anode. Therefore, the interaction of Mg and La with chlorine gas in inter-electrode region was minimized. During electrolysis, the distance between the bottom of the cathode and the bottom of the porcelain crucible was fixed at 28 mm. The chlorine gas produced was ventilated and absorbed with NaOH solution before the exit gas was admitted to the atmosphere. After electrolysis, the cathode was lifted up. The porcelain crucible was taken out from the molten salt by a clamp and was allowed to cool down to room temperature naturally. The obtained alloy was cleaned and polished.

The current efficiency was calculated by the following equation:

$$\eta=\frac{w(\mathrm{La})m/E_{\mathrm{La}}+w(\mathrm{Mg})m/E_{\mathrm{Mg}}}{It}\times 100\% \qquad (1)$$

where m is the mass of the Mg−La alloy; w(La) and w(Mg) are the La and Mg contents in the Mg−La alloys; E_{La} and E_{Mg} are the electrochemical equivalents of La and Mg, respectively; I is the average electrolysis current, and t is the electrolysis time.

2.3 Analyses and characterization of alloys

Hydrochloric acid was used to dissolve the alloy samples. The content of Mg was determined by potentiometric titration after the precipitation separation of La. Part of the alloys were mechanically crushed and ground into powders of about 75 μm for X-ray diffraction (XRD) analysis. The XRD analysis of the alloy samples were collected on an X' Pert PRO diffractometer with Cu K_α radiation.

3 Results and discussion

3.1 Effect of oxide addition on current efficiency

The effect of oxide addition on the average electrolysis current is shown in Fig. 2. It shows that the oxide added only has a slight effect on the average electrolysis current. The effect of oxide addition on current efficiency is shown in Fig. 3. As the content of oxide in the electrolyte increases, the current efficiency decreases gradually. When the same mass of the oxide is added, compared with La_2O_3, MgO has a more pronounced effect on the current efficiency. When the content of MgO in the electrolyte reaches 3%, the current efficiency drops to 66.6 % from 90.5% when no oxide is

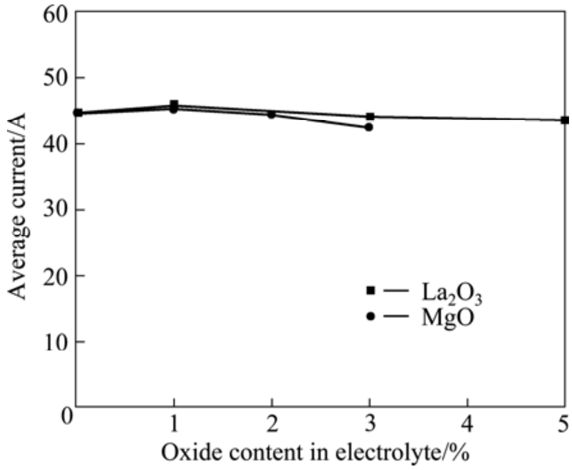

Fig. 2 Effect of oxide content in electrolytes on average electrolysis current

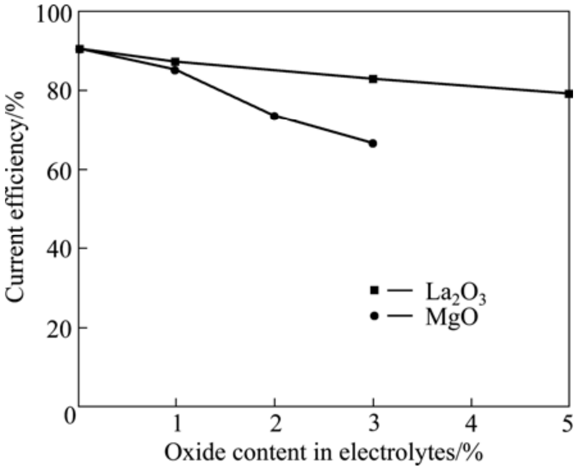

Fig. 3 Effect of oxide content in electrolytes on current efficiency

added. In the electrolysis preparation of magnesium, a high current efficiency requires that the cathode is well wetted by the liquid magnesium and that the liquid magnesium is well wetted by the electrolyte. Oxide impurities may form a passivation layer on the cathode surface, and may also concentrate on the surface of Mg droplets in such a way that these droplets become dispersed in the melt instead of coalescing with the Mg pool. One way to increase the current efficiency will obtain better control over the oxides dissolved in the bath [17]. In this work, the cathode passivation by the oxides or their insoluble reaction products may also be one of the reasons for the decrease of current efficiency with increasing content of the oxides in the electrolyte.

3.2 Effect of oxide addition on alloy products

The effects of oxide addition on the Mg−La alloy products are shown in Figs. 4 and 5. It is found that the mass of alloy decreases with the increase of oxide content in the electrolytes. When the same mass of the oxide is added, compared with La_2O_3, MgO has a more pronounced effect on the mass of alloy. The Mg content in the alloy gradually increases with the increase of MgO content in the electrolytes, but decreases with the increase of the La_2O_3 content in the electrolytes, indicating that both MgO and La_2O_3 may take part in the reactions in the electrolytes.

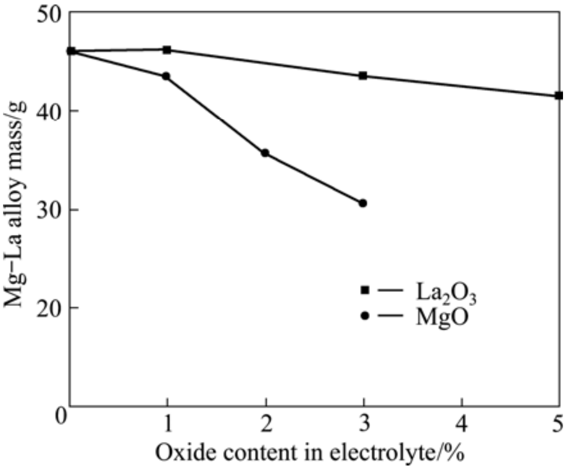

Fig. 4 Effect of oxide content in electrolytes on mass of Mg−La alloy

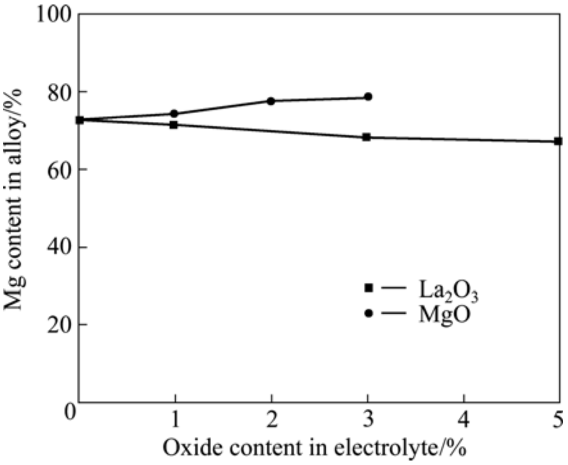

Fig. 5 Relationship between Mg content in alloys and oxide content in electrolytes

The solubility of MgO in pure $MgCl_2$ is very low; however, MgO readily dissolves in $NdCl_3$ [18]. MgO has been reported to react with a neodymium chloride/ magnesium chloride melt to form neodymium oxychloride and magnesium chloride, according to the following reaction [16,18]:

$$MgO+NdCl_3=\!=NdOCl+MgCl_2 \quad (2)$$

Pure molten $NdCl_3$ forms distorted octahedral species, $NdCl_6^{3-}$, with Cl^- anions shared. The formed network is to some extent broken when NdOCl exists in the melt. NdO^+ cations loosely connect with $NdCl_6^{3-}$ in the network [18].

NdOCl can also form when Nd_2O_3 dissolves in $NdCl_3$-containing melt [18]:

$$Nd_2O_3+NdCl_3=\!=3NdOCl \quad (3)$$

Reactions (2) and (3) tend to be spontaneous in that each has a negative free energy change above 750 °C. The MgO solubility in pure $MgCl_2$ is much lower than that in pure $NdCl_3$. When NaCl is added to the $NdCl_3$−$MgCl_2$ melt, the solubility of NdOCl decreases further. The solubility of MgO or NdOCl is found to be very limited in $NdCl_3$−$MgCl_2$−NaCl melt containing sufficient NaCl to give a reasonable electrical conductivity [18].

Similar to Nd compounds, La compounds may take place similar reactions:

$$MgO+LaCl_3=\!=MgCl_2+LaOCl \quad (4)$$

$$La_2O_3+LaCl_3=\!=3LaOCl \quad (5)$$

With the addition of MgO or La_2O_3, LaOCl forms in the electrolytes. Unfortunately, the solubility of LaOCl is very limited in the electrolytes, leading to the formation of the sludge. The sludges formed in No. 4 and No. 7 experiments (Table 1) are checked by XRD technique (Fig. 6). In No. 4 experiment, 5% La_2O_3 is added into the electrolyte, while in No. 7 experiment, 3% MgO is added. As shown in Fig. 6, the sludges obtained in both No. 4 and No. 7 experiments contain LaOCl. No peaks for other La compounds or Mg compounds are detected, indicating that all the added MgO transforms into $MgCl_2$, together with the formation of LaOCl according to reaction (3). And all the added La_2O_3 reacts with $LaCl_3$ to form LaOCl according to reaction (4).

Figures 7(a)−(c) show the XRD patterns of the Mg−La alloy products obtained in experiments No. 1, 3 and 4, respectively. According to Mg−La diagram [19],

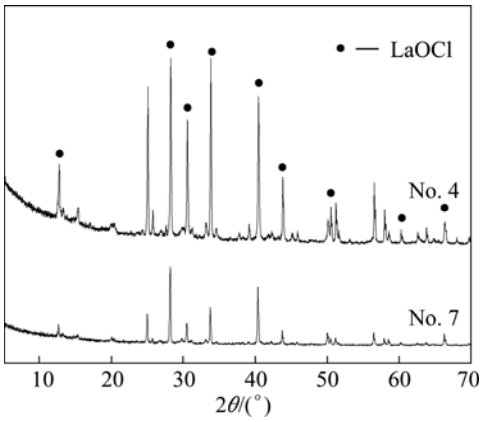

Fig. 6 XRD patterns of sludges formed in No. 4 and No. 7 experiments

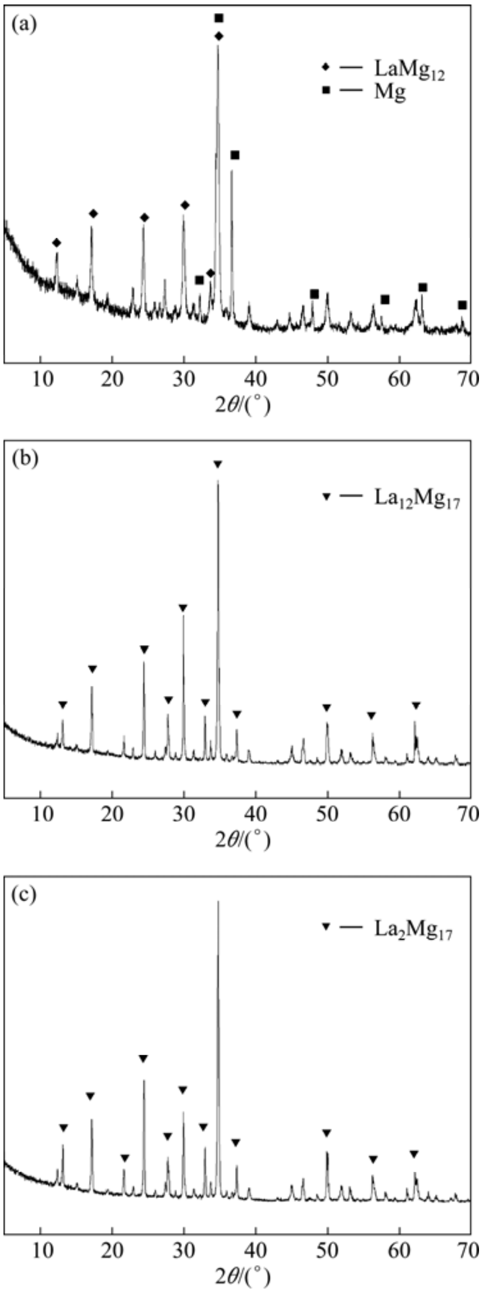

Fig. 7 XRD patterns of Mg−La alloys

the intermetallic compounds of $LaMg_{12}$ and Mg are formed in alloys containing magnesium more than 70%, which is consistent with the results, as shown in Fig. 7(a). The alloy shown in Fig. 7(a) has a Mg content of 72.8%, with $LaMg_{12}$ and Mg phases coexisted. As shown in Figs. 7(b) and (c), the main phase of the alloys obtained in No. 3 and 4 experiments is La_2Mg_{17}. In the thermodynamic assessment of the La−Mg system, La_2Mg_{17} is also found to be one of the Mg-rich phases [4,20].

After the addition of MgO and La_2O_3, $LaCl_3$ reacts with the two oxides according to reactions (3) and (4). In order to maintain the constant composition of the Mg−La alloy products, the corresponding amount of $LaCl_3$ consumed in reactions (3) and (4) should be supplemented.

The byproduct of reaction (2) and the product of reaction (3), neodymium oxychloride (NdOCl), will presumably react according to the following two reactions [5]:

$$NdOCl+C+Cl_2 == NdCl_3+CO \tag{6}$$

$$2NdOCl+C+2Cl_2 == NdCl_3+CO_2 \tag{7}$$

Each of these reactions has a negative standard free energy change, such that the neodymium oxychloride spontaneously reacts with carbon (provided by the carbon-based anode) and the chlorine gas (formed during electrolysis) to reform the rare earth chloride [5].

In this work, the reactions similar to reactions (6) and (7) may take place:

$$LaOCl+C+Cl_2 == LaCl_3+CO \tag{8}$$

$$2LaOCl+C+2Cl_2 == 2LaCl_3+CO_2 \tag{9}$$

Reactions (8) and (9) are helpful for the removal of the sludges. However, in the experimental conditions, such helpful effects are not obvious. Reactions (8) and (9) should be enhanced by improving the experimental techniques.

3.3 Effect of oxide and fluoride co-addition on current efficiency

CaF_2 addition to $MgCl_2$−NaCl melt has been reported to improve the technical electrolysis of magnesium if the $MgCl_2$ feed contains oxide impurities [17]. And the addition of 0.3−0.5% CaF_2 into the melt is reasonable. Therefore, in this work, CaF_2 is added into the electrolyte to try to suppress the bad effect of MgO.

The effects of oxide and fluoride co-addition on average electrolysis current and current efficiency are shown in Figs. 8−10. The co-addition of oxide and fluoride into the electrolytes does not have any obvious effect on the average electrolysis current. When the electrolyte contains 1% MgO, with the addition of CaF_2, the current efficiency slightly decreases, as shown in Fig. 8. When the electrolyte contains 2% MgO, after the

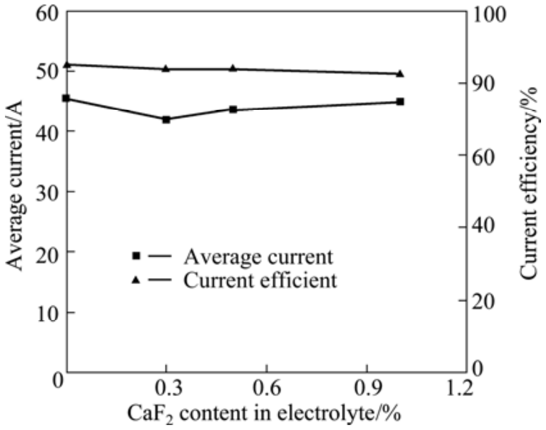

Fig. 8 Effects of CaF_2 content in electrolytes with 1% MgO coexisted on average electrolysis current and current efficiency

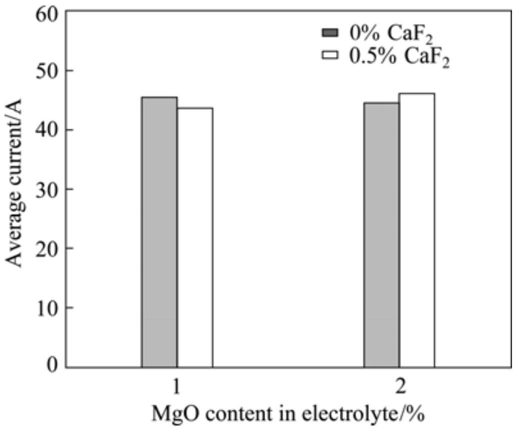

Fig. 9 Comparison of average electrolysis current under different conditions

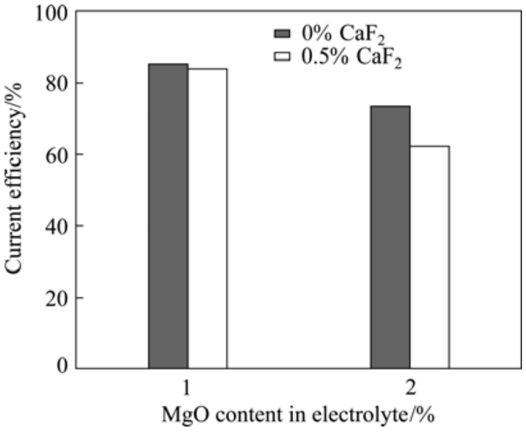

Fig. 10 Comparison of current efficiency under different conditions

addition of 0.5% CaF_2, the current efficiency decreases from 73.6% to 62.2% (Table 2 and Fig. 10).

For the Dow process, in which hydrous Mg chloride is used as the feed and some MgO formed in the melt, the maximum current obtained with 1.0%−1.4% CaF_2 added. The beneficial effect of CaF_2 is attributed to its fluxing action on the surface MgO on the produced magnesium (especially the Mg droplets), leading to increased rate of coalescence of small magnesium droplets dispersed in the melt. Another reason for the increased current efficiency may be that CaF_2 enhances the surface tension of the electrolyte at the boundary between the fused magnesium and the solid cathode, thereby favoring the persistence and growth of magnesium metal on the cathode [17]. In this work, however, the addition of CaF_2 is not helpful for the improvement of the current efficiency. The reason remains to be further investigated.

3.4 Effect of oxide and fluoride addition on alloy products

The effects of oxide and fluoride co-addition on the alloy products are shown in Figs. 11 and 12. When the electrolyte contains 1% MgO, with the addition of CaF_2, the mass of alloy does not change obviously. When the electrolyte contains 2% MgO, after the addition of 0.5% CaF_2, the mass of alloy decreases from 35.6 to 31.3 g (Table 2 and Fig. 12).

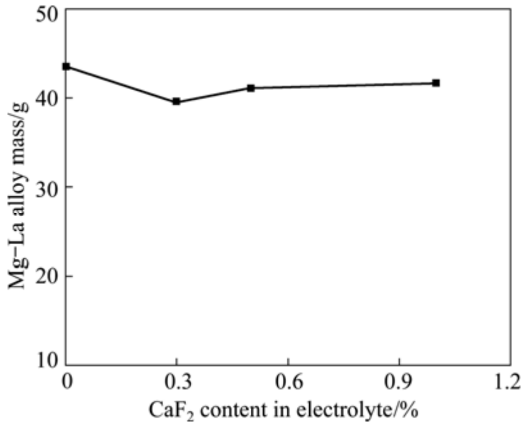

Fig. 11 Effect of CaF_2 content in electrolytes with 1% MgO coexisted on mass of Mg−La alloy

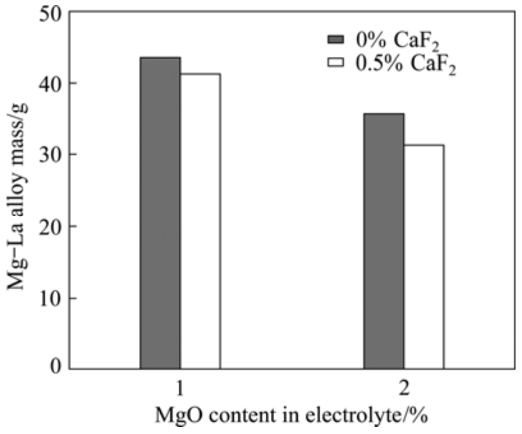

Fig. 12 Comparison of mass of Mg−La alloys obtained under different conditions

In study about the solubility of MgO in mixed chloride-fluoride melts containing $MgCl_2$, an increase of MgO solubility with increasing fluoride content of the melt is expected since the solubility of MgO in MgF_2 is much higher than in $MgCl_2$ (8.5% in mole fraction) in MgF_2 at 1228 °C and 0.36% (mole fraction) in $MgCl_2$ at 730 °C). The following reaction has a very negative Gibbs energy change [17]:

$$MgCl_2+2NaF=\!=MgF_2+2NaCl \tag{10}$$

This means that in the system of $KCl-MgCl_2-LaCl_3$ used in this work, when MgO and CaF_2 are added, together with reaction (4), the following reactions may take place:

$$MgCl_2+CaF_2=\!=MgF_2+CaCl_2 \tag{11}$$

$$2LaCl_3+3CaF_2=\!=2LaF_3+3CaCl_2 \tag{12}$$

In the electrolytic system for the preparation of Mg metal, in which the positive effect of CaF_2 addition is obtained, there is no $RECl_3$ in the system [17]. In this work, the negative effect of CaF_2 addition may be due to the complex reactions of the La compounds in the electrolyte.

4 Conclusions

1) The oxide addition only has a slight effect on the average electrolysis current. As the content of MgO or La_2O_3 in the electrolyte increases, the current efficiency decreases gradually. When the same mass of the oxide is added, compared with La_2O_3, MgO has a more pronounced effect on the current efficiency. When the content of MgO in the electrolyte reaches 3%, the current efficiency drops to 66.6 % from 90.5 % when no oxide is added.

2) The mass of alloy decreases with the increase of oxide content in the electrolytes. When the same mass of the oxide is added, compared with La_2O_3, MgO has a more pronounced effect on the mass of alloy. The Mg content in the alloy gradually increases with the increase content of MgO in the electrolytes, but decreases with the increase of the La_2O_3 content in the electrolytes, indicating that both MgO and La_2O_3 may take part in the reactions in the electrolytes.

3) XRD analyses confirme the formation of LaOCl when MgO or La_2O_3 is added into the electrolyte. The formation of LaOCl sludge will be the main reason for the negative effect of the oxide addition on both the current efficiency and the mass of alloy.

4) The addition of CaF_2 together with MgO into the electrolyte does not have any obvious effect on the average electrolysis current. When the electrolyte contains 1% MgO, with the addition of CaF_2, the current efficiency slightly decreases, but the mass of alloy does not obviously change. When the electrolyte contains 2% MgO, after the addition of 0.5% CaF_2, the current efficiency decreases from 73.6% to 62.2%, and the mass of alloy decreases from 35.6 to 31.3 g. In the electrolytic system used in this work, the addition of CaF_2 is not helpful to suppress the negative effect of MgO on the electrolysis, probably due to the complex reactions of the La compounds in the electrolyte.

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氧化物与氟化物的加入对氯化物熔盐体系电解制备 Mg−La 合金的影响

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摘 要：以石墨坩埚为阳极，钨棒为阴极，在 750 °C 的 $MgCl_2$−$LaCl_3$−KCl 熔盐体系中，采用恒电位电解制备 Mg−La 合金。研究氧化物和氟化物的加入对电解的影响，通过 XRD 对部分 Mg−La 合金产物和电解渣进行表征。随着 MgO 或 La_2O_3 在熔盐电解质中加入量的增加，电流效率和所得合金产物的质量都减小，表明 MgO 和 La_2O_3 参与电解质中的反应。在加入的氧化物质量相同的情况下，MgO 与 La_2O_3 相比对电流效率和合金产物质量的影响更明显。XRD 研究结果表明：MgO 或 La_2O_3 加入到熔盐电解质中后，有 LaOCl 生成，LaOCl 电解渣的生成是氧化物对电解消极影响的主要原因。在本实验的的熔盐体系中，CaF_2 的加入对消除 MgO 的负面影响没有积极意义，这可能和镧化合物在熔盐电解质中的复杂反应有关。

关键词：Mg−La 合金；熔盐；电解；氧化物；氟化物；电流效率

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