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STUDY ON THE PROCESS OF PREPARING Al-Ce ALLOY BY ELECTRODEPOSITION

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The process of Al-Ce alloy prepared by electrodeposition was studied in molten LiF-KCl-CeF_3 salt at 820 °C. Several process parameters such as back electromotive force and current efficiency were measured by continuous pulse oscillograph. The results showed that the back electromotive force increased with the increase of the current intensity. With the addition of 2 *wt.*%Ce_2O_3, the back electromotive force decreased by 0,26 V on average, and increasing temperature could make the back electromotive force decrease as well. The back electromotive force changing period with feeding measured was 50 min. Finally, at 820 °C, the largest current efficiency (68.8 %) was obtained by electrolyzing for 2 h at 4 A.

Key words: Al-Ce alloy; electrodeposition; current efficiency; back electromotive force; molten salt

INTRODUCTION

Because of the low density, good plasticity, high durability, aluminum alloys become the most economical and practical materials used in the fields of industry, agriculture and so on [1,2]. At present, the main method of the production of aluminum alloys is the direct mixture method, but the problem of burning of pure metal used in the preparation process is more serious. Therefore, the spend of the aluminum alloys prepared by the direct mixture method is much higher.

Al-Li [3], Al-Er [4], Al-U [5], Al-La [6] and other aluminum alloys [7-11] have been produced directly in the electrolytic cell through the electrodeposition method, and the preparation of aluminum alloys by electrodeposition will be the main development direction in the near future. This paper presents the process of preparing Al-Ce alloy in LiF-KCl-CeF_3 fused molten melt with Ce_2O_3 as raw material. The graphite rod with the corundum protection tube is served as the anode and the liquid aluminum is served as the cathode. The process parameters such as the back electromotive force and the current efficiency are studied in detail.

EXPERIMENTAL

Experiment chemical and experiment equipment

Experiment chemicals: the LiF, KCl, CeF_3 and Ce_2O_3 used in the experiment were all produced by Sinopharm Chemical Reagent Co. Ltd. In order to avoid the influence of other factors such as the moisture on the electrolysis experiment, the salt mixture was pretreated before the start of the experiment. The experiment equipment used in this work is referring to the literature [3]. The temperature is controlled by two phase temperature control system, which temperature range is 0 ~ 1000 °C with the accuracy of 1 °C.

Experiment process

Firstly, the salt mixture was initially dried at 300 °C for 48 h to remove residual moisture and then added that into the corundum crucible tightly bonded with the graphite crucible. The liquid level can be increased to a certain height inside the corundum crucible as the salt mixture melted, and the graphite anode with the corundum protection tube is placed in an electric furnace. After preheating about 10 min, the position of the measuring equipment is adjusted so that the graphite anode is vertically aligned to the center of the corundum crucible. Then dropping down the graphite anode while observing the current representation, and the ammeter shows the current number when the graphite anode contacts with the molten salt. Then, dropping down the graphite anode 1 cm (lower 7~8 circles) and pretreating for 10 min under 1 A. When the parameters are stable, the electrolytic experiment is started.

RESULTS AND DISCUSSION

The effect of current intensity on the back electromotive force

The relationship between the applied current and the back electromotive force is obtained by changing the current intensity in molten LiF-KCl-CeF_3 salt at 820 °C. As shown by the dotted curve in Figure 1, the back elec-

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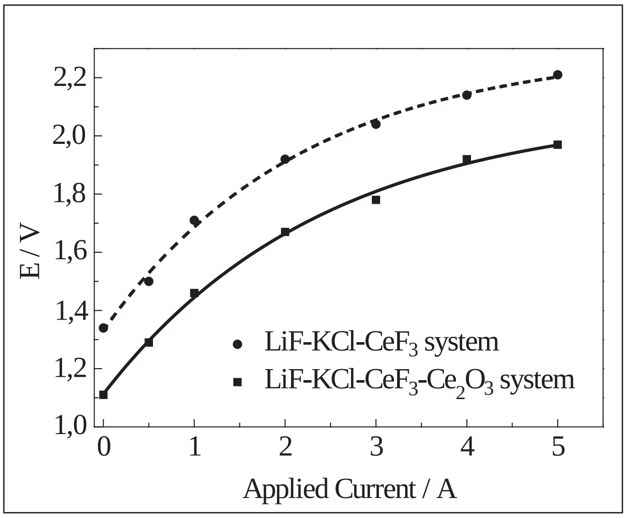

Figure 1 Relationship between applied current and back electromotive force (cathodic area: 32 cm^2)

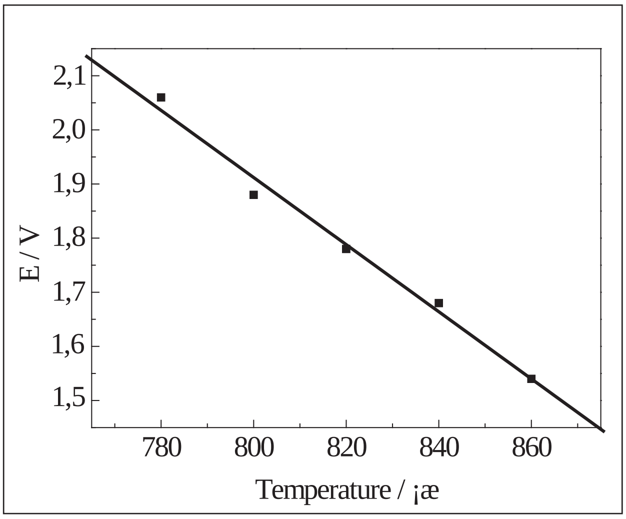

Figure 2 Relationship between temperature and back electromotive force

tromotive force exhibited a gradual increase over the increase of current intensity. When the applied current is 0 A, there is still a feedback to the potential difference of about 1,34 V, which is similar to the galvanic cell to the external feedback of back electromotive force, and it reflects the potential of the O^{2-} attached on the graphite anode to liquid aluminum cathode. Therefore, the molten salt needs to be pre-electrolyzed for 10 min at non-feeding stage, and the O^{2-} attached on graphite anode is consumed on the graphite anode.

When LiF-KCl-CeF_3-2 *wt.*%Ce_2O_3 is used as an electrolyte to investigate, the relationship between the applied current and the back electromotive force is represented in the solid curve in Figure 1.

When Ce_2O_3 is added into the molten LiF-KCl-CeF_3 salt, the back electromotive force decreases by 0,25 V at the same applied current, which means that O^{2-} from Ce_2O_3 replaces Cl^- and continues to discharge on the graphite anode. Since the reducibility of O^{2-} is stronger than that of Cl^-, it is oxidized to O_2 and releases CO_2 on the graphite anode.

The effect of temperature on the back electromotive force

Figure 2 shows that the back electromotive force tends to decrease with increasing the temperature. Since the heat transfer process is more rapid as the temperature increases, the mobility of the molten salt system becomes better and the conductivity is stronger, and the back electromotive force is related to the conductivity of the molten salt. Therefore, the back electromotive force decreases with increasing temperature. The fitting regression between the electrolytic temperature and the back electromotive force agrees with the Arrhenius equation.

$$k=A\exp(-E/RT) \qquad (1)$$

Where A is pre exponential factor, E (J/mol) is conductance activation energy, R (J/mol·K) is gas constant, and T (K) is temperature.

It is known that the reciprocal of temperature and conductivity is exponential function according to equation (1). Due to the positive activation energy, the conductivity of molten salt increases with increasing the electrolytic temperature, further resulting in the decreased back electromotive force.

The effect of electrode distance on the back electromotive force

At 820 °C, pre-electrolysis is carried out for 10 min and the relationship between the electrode distance and back electromotive force is investigated at 3 A when all parameters are stable.

According to Figure 3, with increasing electrode distance at first, the back electromotive force rises rapidly. When the electrode distance reach 3 cm and more, the back electromotive force is stable at about 1,82 V. Because of the short electrode distance, metal cerium deposited at the cathode is easier to diffuse towards the graphite anode, and then it is oxidized. It provides the chance of the secondary reaction, which leads to make

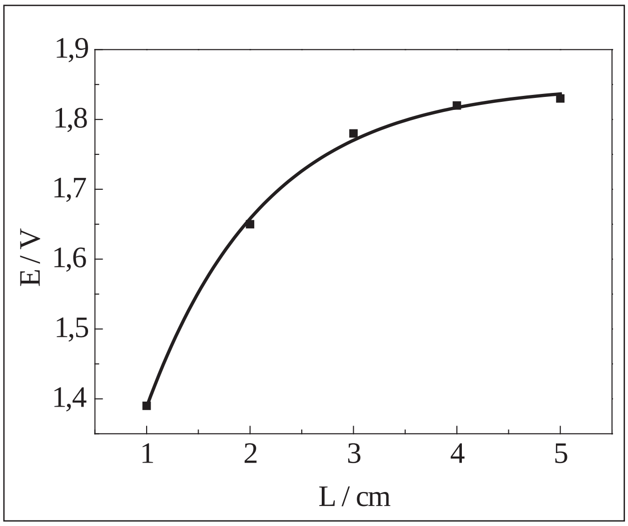

Figure 3 Relationship between electrode distance and back electromotive force

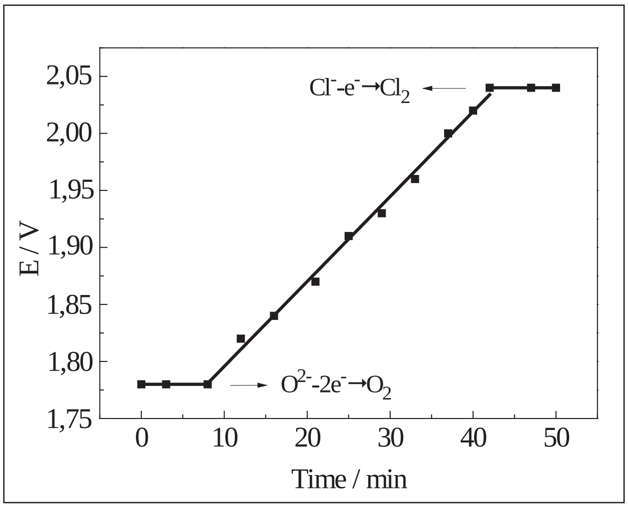

Figure 4 Relationship between electrolysis time and back electromotive force

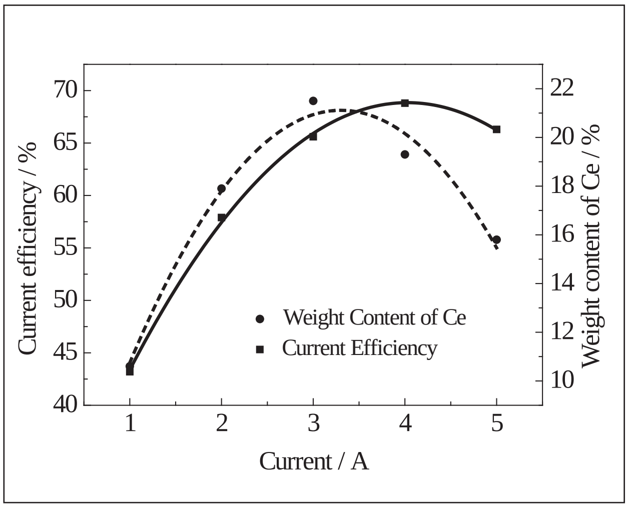

Figure 5 Effect of current intensity on current efficiency and content of Ce (cathodic area: 32 cm^2)

the back electromotive force smaller. While the electrode distance increases, due to products between two electrodes separated well, the back electromotive force is maintained at a larger value. In practical production, if the current efficiency is kept constant, the electrode distance can be decreased as much as possible to reduce the ohm-potential drop of the molten salt between two electrodes, which is an important region for saving electricity during the electrolysis process.

The effect of electrolysis time on the back electromotive force

As can be seen in Figure 4, there are two potential platforms in the curve, which correspond to O^{2-} and Cl^{-} discharge, respectively. It is observed that the potential drops to 1,78 V immediately after adding 2 *wt.*%Ce_2O_3 into the LiF-KCl-CeF_3 salt. This platform corresponds to the electrolysis process of Ce_2O_3 and then emits O_2. With the electrolysis time prolonged, the concentration of O^{2-} in molten salt is constantly consumed. When the concentration of O^{2-} is not enough to meet the demand of electrode discharge, Cl^{-} begins to discharge on the graphite anode, and the potential gradually increased to reach the platform of 2,04 V at the same time. Since the oxide has reacted completely at this platform, discharge ion corresponds to Cl^{-} which emits Cl_2. According to the periodic change of the back electromotive force with electrolysis time, the measured feeding period is 50 min.

The effect of current intensity on current efficiency and the content of Ce

Changing current intensity to prepare Al-Ce alloys via electrodeposition for the same time of 2 h at 820 °C, the relationships between current intensity and the current efficiency are shown in Figure 5.

The current efficiency of Ce in the initial stage increase with the increase of the current intensity as shown in Figure 5, which the current efficiency of Ce reaches the maximum value of 68,8 % at the current intensity of 4 A and then falls back. Because of the lower current intensity electrolysis, the deposition quantity of silicon is small and the precipitation rate is slow, and the concentration gradient is low, which leads to lower Al-Ce alloying rate, therefore the current efficiency in initial stage is not high. When the alloying speed of Ce element is consistent with the precipitation rate of Ce element, the current efficiency reaches the maximum value of 68,8 %. As the applied current increases to a certain current intensity, it is necessary to pay attention to the influence of the discharge amount of the anodic escaping gas on the electrolysis process, and the disturbance caused by the stirring action to the molten salt becomes stronger, which causes the deposited silicon to be turned out to the molten melt surface, so that the current efficiency of the electrolysis process is reduced.

Moreover, the content of precipitated cerium increases with the increase of current intensity at first. When the current intensity reaches 3 A, the precipitation of cerium reaches the maximum value of 21,5 %. When the current intensity exceeds 3 A, the content of cerium on the Al-based alloy begins to decrease. It is mainly due to the gradual increase of the current intensity, the ability of Ce(III) which deposits on the cathode and nucleates becomes stronger firstly and then weakens. When the current intensity is larger, the nucleation rate of Ce(III) is lower than the electrochemical deposition rate of Ce(III), which resulting in a part of Ce(III) deposited on liquid aluminum is too late to diffuse to form the alloy. Therefore, the content of cerium in the alloy decreases.

The X-ray diffraction analysis of Al-Ce alloy

In order to further study the crystal composition of the alloy sample, galvanostatic electrolysis was carried out in LiF-KCl-CeF_3-Ce_2O_3 molten melt for 2 h at 3 A and 820 °C, which the results are shown in Figure 6. At this electrolytic current, except for Al, five other Al-Ce

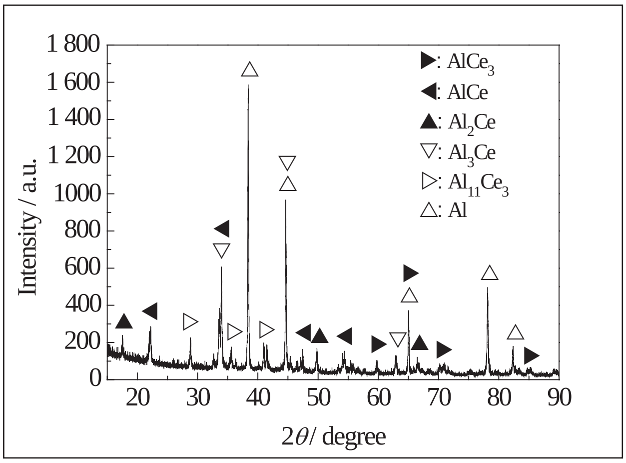

Figure 6 XRD pattern of Al-Ce alloy sample

alloys are observed as $Al_{11}Ce_3$, Al_3Ce, Al_2Ce, AlCe and $AlCe_3$. Once again it confirms that Ce(III) can be reduced through electrodeposition.

CONCLUSIONS

The process parameters, *e.g.* back electromotive force and current efficiency, was investigated on the liquid aluminum cathode in LiF-KCl-CeF_3 molten salt at 820 °C. The results show that the back electromotive force increases with the current increase. When the temperature raises, the back electromotive force decreases a little. With prolonging the electrolysis time, the back electromotive force increased gradually, and the feeding period determined is 50 min. At 820 °C, Al-Ce alloy with the cerium content of 21,5 % (mass fraction) was prepared by electrolyzing for 2 h at 3 A and the current efficiency can reach 65,6 %. Finally, the obtained deposit analyzed by X-ray diffraction are Al, $Al_{11}Ce_3$, Al_3Ce, Al_2Ce, AlCe and $AlCe_3$.

Acknowledgements

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