Electrolytic preparation of Al-Ca master alloy on liquid Al cathode[①]

YANG Bao-gang(杨宝刚) , QIU Zhu-xian(邱竹贤) , GAO Bing-liang(高炳亮)

School of Materials and Metallurgy,
Northeastern University, Shenyang 110006, P. R. China

Abstract : As a newly developing superplastic aluminum alloy, Al-Ca alloy has been widely used in industry, however the technology for preparing Al-Ca master alloy and its influencing factors need to be further studied. Therefore the Al-Ca master alloy was prepared by using liquid aluminum cathode and a mixture of 80 %CaCl$_2$-18 %KCl-2 %CaF$_2$ as the molten salt electrolysis in a laboratory electrolyte cell; the effects of electrolysis temperature, cathodic current density and electrolytic duration on current efficiency and Ca content of Al-Ca alloy as well were studied. Through laboratory experiments, the parameters for smooth electrolytic reaction were proposed. The proper electrolysis technology is as follows: with the 80 %CaCl$_2$-18 %KCl-2 %CaF$_2$ electrolyte, the electrolytic temperature is 973 K and the cathodic current density is 0.8 A/cm^2, the electrolysis can go on smoothly and a calcium content of 17.5 %(mass fraction) can be obtained. With the increase of electrolysis duration, the calcium content in the alloy increases whereas the current efficiency decreases.

Key words : Al-Ca master alloy; electrolysis; current efficiency; calcium content　　　　　**Document code : A**

1　INTRODUCTION

As a newly developing super-plastic aluminum alloy, Al-Ca alloy has not only good plasticity, but also good mechanical property, good welding property and strong resistance of corrosion after being formed. Therefore, a lot of metallurgical scientists have devoted to the research of Al-Ca alloy[1~6]. In the literature[3,4], Qiu provided some parameters for the preparation of Al-Ca master alloy.

For the preparation of the Al-Ca alloy, a mixing process was traditionally used in industry. Due to the high reactivity of Ca, the metal Ca was easily oxided and there was a big metal loss during the mixing process, so the operation process should be protected with inert gas. However, the mixing process was complicated and it cost much. Molten salt electrolytic preparation of Al-Ca alloy in one step can simplify the production technology, decrease the loss of calcium and lower the production cost. In addition, the Al-Ca master alloy produced by electrolysis has only few impurities and high quality.

As a supplement of the former literature[3,4], this present paper is devoted to the factors which affect the electrolysis target and some problems in the electrolytic process in order to determine a proper technology for the preparation of Al-Ca master alloy.

2　EXPERIMENTAL APPARATUS AND TECHNOLOGY

Fig.1 illustrates the electrolysis apparatus for the preparation of Al-Ca master alloy.

The electrolysis cell consists of a graphite cru-cible, which was lined with a corundum crucible. At the bottom of the corundum crucible there was a hole. Liquid aluminum was added to cover the hole and served as the cathode. The anode was made of a spectral purity graphite rod of diameter 20 mm. The graphite rod was protected by a corundum tube. The graphite crucible was placed in an outer iron crucible. The iron crucible was used for electric connection to the cathode. Chemical reagents used in experiments, such as CaCl$_2$, KCl, CaF$_2$ were dried at the temperature 673 K for 4 h before electrolysis.

The electrolysis condition and its variables see Table 1.

3　RESULTS AND DISCUSSION

3.1　Calculation of current efficiency

Current efficiency is the ratio of the actual metal quantity obtained and the theoretical metal quantity during electrolysis, it can be calculated on the weight difference of the metal before and after electrolysis, the equation is as follows:

$$\eta = \frac{\Delta m}{CIt} \times 100 \% \qquad (1)$$

But in the small electrolysis cell, due to the mechanical loss and chemical loss, the equation above leads to bigger mistake. However, the current efficiency in this paper adopts the following equation and it has high precision[7]. The calcium content in the alloy can be measured by the atomic fluorescence spectrometry.
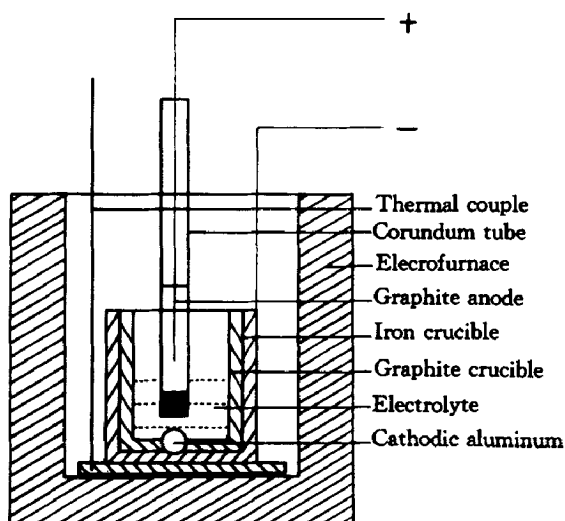
$$\eta = \frac{m_1 w(100 - w)}{CIt} \times 100 \% \qquad (2)$$

where　m_1 —mass of Al added before electrolysis, g; w — concentration of Ca in the alloy, %(mass

Table 1   Electrolysis condition and variables

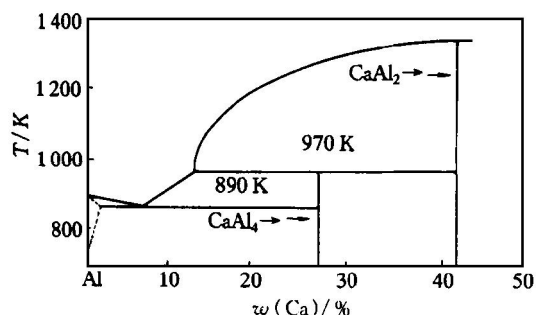| Composition of electrolyte/ %			Al cathode/ g	Electrode gap/ c m	Temperature/ K	Cathodic current density/ (A·c m⁻²)
CaCl₂	KCl	CaF₂				
80	18	2	15 .0 ±0 .1	3 .0 ~ 3 .5	943 ~ 1 033	0 .6 ~ 2 .0

Fig .1   Apparatus of electrolysis cell

fraction) ; C—electrochemical equivalent of Ca , 0 .747 71 g/ A·h ; I—current , A ; t—electrolysis time , h .

3 .2   Influence of cathodic current density

The electrode process for the preparation of Al- Ca alloy by liquid Al cathode can be supposed as follows[8] :

(1) calcium ions transfer to the surface of cathode by ionic migration ;

(2) calcium ions release electrons at the surface of aluminum cathode and reduce into calcium atoms ;

(3) calcium atoms diffuse on liquid aluminum surface and into liquid aluminum(some dissolve in the liquid , others form Al- Ca compounds(see Fig .2)) ;

(4) dissolved calcium and Al- Ca compound diffuse at a slow rate from the aluminum surface to the

inner part of liquid aluminum cathode .

So the step (4) is the controlling step of the whole electrode process and decides the rate of the whole process . In order to make calcium atoms diffusing into the inner part of the cathode and forming alloy , the metal calcium part produced at unit area and unit time (the producing rate , shows in the cathodic current density i_k) must match with the rate of calcium diffusing to the inner part and forming alloy(the alloy forming rate i_k alloy) , it may be expressed as follows :

$$i_k = i_{k, \text{alloy}} = - D_{\text{dif}} \frac{dc}{dx} \times q^{-1} \qquad (3)$$

where $i_{k, \text{alloy}}$—cathodic current density matching with the alloy forming rate , A/ c m² ; dc/ d x —concentration gradient of calcium atoms at the diffusion layer of the cathodic inner part , g/ c m⁴ ; D_{dif} —diffusion coefficient of calcium atoms in the liquid aluminum , c m²/ s ; q —electrochemical equivalent of Ca , g/ (A· s) .

From the alloy forming process , it shows that when $i_k \leqslant i_{k, \text{alloy}}$, the whole alloy forming process can go on effectively and smoothly .

It is obvious that the cathodic current density has an important influence on the calcium content and the current efficiency when the temperature is at 973 K , the electrolyte is 80 % CaCl₂-18 % KCl-2 % CaF₂ , the experimental results are shown in Fig .3 and Fig .4 .

As seen from Fig .3 , the current efficiency is very low at lower cathodic current density ; when the current density reaches 0 .8 A/ c m² , the current efficiency has a maximum value ; when the current density increase slowly after 0 .8 A/ c m² , the current

Fig .2   Aluminum- calcium binary phase diagram
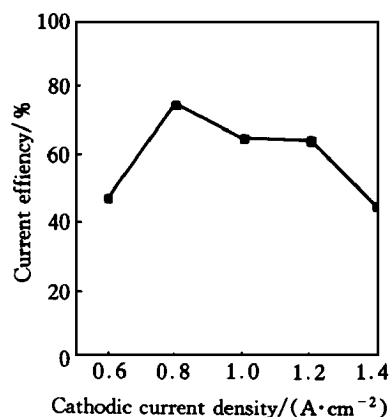
Fig .3   Influence of cathodic current density on current efficiency
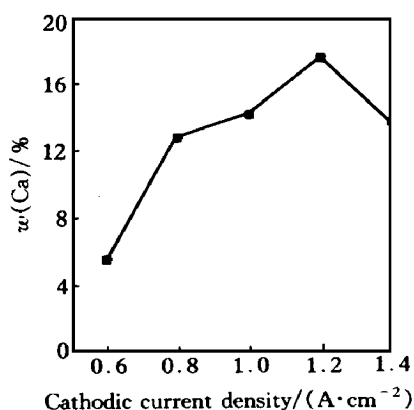
Fig .4　Influence of cathodic current density on calcium content in the Al‑Ca alloy

efficiency decreases a little , however , the current efficiency will decrease apparently at very high current density . Seen from Fig .4 , the calcium content in the alloy increase with the increasing of cathodic current density and it can reach as high as 17 .5 %(mass fraction) . The calcium content and current efficiency will decrease apparently when i_k reaches a certain degree . It is due to the fact that the alloy forming rate falls behind the the calcium producing rate , so as to make the remaining calcium dissolve in the electrolyte and react with oxide and so on , and leads to the decrease of current efficiency .

3 .3　Influence of electrolysis temperature

Temperature is one of the important factors which affect current efficiency . The cathodic current density in the experiment is 0 .8 A/cm^2 . The experiment results about electrolysis temperature are shown in Figs .5 and 6 .

As seen from Figs .5 and 6 , the highest current efficiency and the highest calcium content can be obtained in the temperature range of 953 ~ 993 K . When the temperature is below 953 K or above
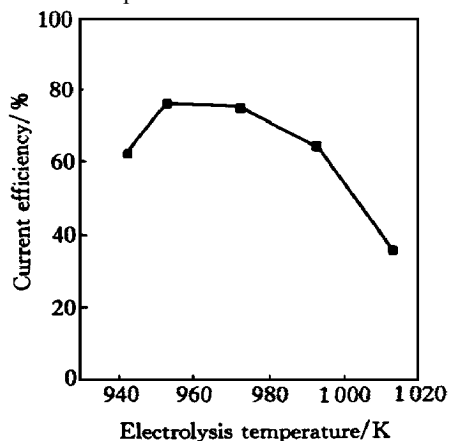

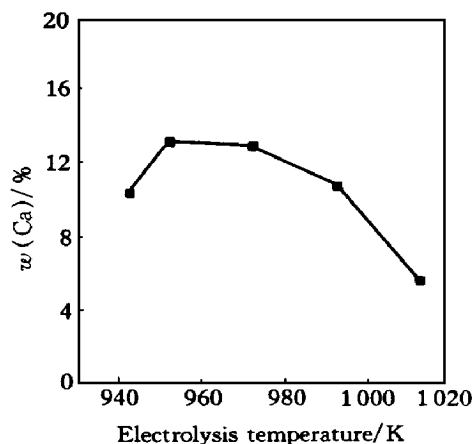**Fig .5**　Influence of temperature on current efficiency

Fig .6　Influence of temperature on calcium content in the Al‑Ca alloy

993 K , the current effiency and the concentration of calcium decrease a little . At lower temperature , calcium diffuses in the aluminum at lower rate and the alloy forming rate decrease , therefore the current efficiency decrease ; at higher temperature , the loss of calcium increases , calcium dissolves in the electrolyte or reacts with O$_2$, carbon and forms hard‑dissolved compounds before it forms alloy with the aluminum cathode , therefore , the concentration of calcium decreases especially rapidly at higher temperature . However , the proper temperature for the preparation of Al‑Ca alloy on liquid aluminum cathode is at 953 ~ 993 K .

3 .4　Influence of electrolysis duration

This experiment is carried out at 973 K and the cathodic current density is 0 .8 A/cm^2 . The experiment results are shown in Fig .7 and Fig .8 .

As seen from Figs .7 and 8 , an increase of electrolysis duration will cause the current efficiency decrease whereas the calcium content in the alloy increases . Because with the increase of electrolysis duration , the calcium product and the calcium content
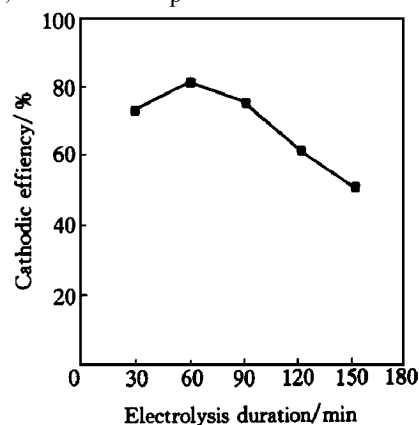

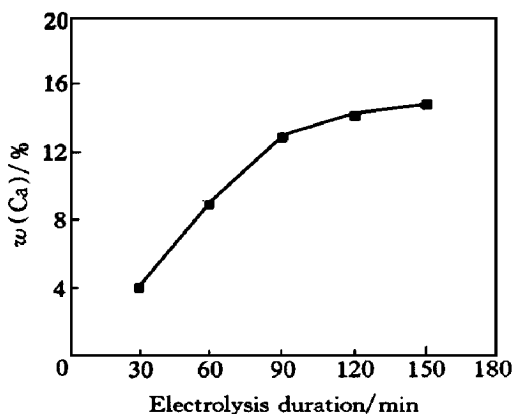**Fig .7**　Influence of electrolysis duration on current efficiency

Fig .8 Influence of electrolysis duration on calcium content in the Al- Ca alloy

in the alloy increase , the calcium diffuse rate in the liquid aluminum will rapidly decrease , the dissolution of Ca into the molten cell will also rapidly increase , therefore , the current efficiency decreases .

3 .5 "Inactive" during the alloy forming process

During the process of forming Al- Ca master alloy with liquid aluminum cathode , if the condition has not been controlled properly , it will lead to "inactive" and the alloy forming rate will decrease rapidly or even stop , the electrolysis will worsen , the electrolyte target such as current efficiency will decrease seriously .

Reasons which lead to "inactive" during alloy forming process are supposed as follows :

(1) The dehydration of the agent $CaCl_2$ may not have been complete . The presence of moisture leads to the electric discharge of hydrogen ion and the molten $CaCl_2$ being oxided , loss of current and current efficiency , deformation of electrode , and worsen also the electrolysis process .

(2) Hard- melting calcium carbonate and calcium oxide cover on the surface of aluminum cathode and cause the decrease of $i_{k, alloy}$.

(3) The actual cathodic current density $i_k \gg i_{k, alloy}$, metal calcium forms solid calcium- rich containing compound and covers the surface of cathode .

(4) The temperature of cathodic zone is too low to make the diffusion rate of calcium atoms in the aluminum decrease .

(5) With the continuous electrolysis , the calcium concentration gradient at the inner part of aluminum cathode will decrease and $i_{k, alloy}$ will decrease too . So when the actual cathodic current density i_k keeps constant , whereas the gap between i_k and $i_{k, alloy}$ will be larger and larger , so during the later period of electrolysis the "inactive" phenomenon will

appear easily .

However , in order to make the aluminum cathode keeps "active" during electrolysis , some steps must be adopted : Control suitable cathodic current density ; raise the temperature of cathodic zone properly ; control quantity of cathodic aluminum and make aluminum not too thick ; control impurities (such as water non- dissolved compounds , carbon content in the electrolyte) and so on . In this way it can keep the electrolysis process smooth .

4 CONCLUSIONS

1) During the preparation of Al- Ca master alloy by liquid aluminum cathode , cathodic current density , electrolysis temperature , electrolysis duration have much effect on current efficiency and calcium content . The proper electrolysis target can be obtained at 973 K , with the 80 % $CaCl_2$-18 % KCl- 2 % CaF_2 electrolyte and the cathodic current density 0 .8 A/cm^2 . A calcium content 1 7 .5 %(mass fraction) in the Al- Ca alloy can be obtained .

2) In order to make the alloy forming process go on smoothly , some steps must be done : control suitable cathodic current density , raise the temperature of cathodic zone properly , control quantity and thickness of cathodic aluminum , and control impurities content in the electrolyte .

REFERENCES

[1] Morre D M and Morris L R . Superplastic aluminum alloy products and method of preparation [P] . U S Patent 41 26448 , 1 978 .

[2] Morre D M and Morris L R . A new superplastic aluminum sheet alloy [J] . Mat Sci & Eng , 1 980 ,43 :85 ~ 92 .

[3] QIU Zhu- xian and SU Quan- qing . Preparation of Al- Ca master alloy by electrolysis of chloride- fluoride melts [J] . Chin J Met Sci Technol , 1 992 , 8 :98 ~ 101 .

[4] QIU Zhu- xian , SU chuan- jing , LI Qing- feng , et al . Aluminum- calcium master alloys prepared by molten salt electrolysis [J] . Aluminium , 1 996 , 72 : 85 ~ 89 .

[5] Perez- Prado M T , Cristina M C , Ruano O A , et al . Microstructural evolution of annealed Al- 5 % Ca- 5 % Zn sheet alloy [J] . J Mater Sci , 1 997 , 32(5) :1 313 ~ 1 318 .

[6] SHU Quan- qing , QIU Zhu- xian . Aluminum- calcium master alloys prepared in the fused salts [J] . Light Metals , (in Chinese) , 1 991 (4) : 23 ~ 28 .

[7] ZHANG Ming- jie , QIU Zhu- xian , HUO Song- ling . Preparation of Al- Li alloy in molten salts [J] . Rare Metals , (in Chinese) , 1 988 , (4) : 249 ~ 253 .

[8] YU Zhong- xing , LIANG Hu- qi , LU Qing- tao , et al . Electrolytic preparation of Al- Sr alloy by liquid Al cathode [J] . Shanghai Metals (non- ferrous metals) , (in Chinese) , 1 987(2) :2 ~ 6 .

(Edited by ZHU Zhong- guo)