

## ALUMINIUM ELECTROLYSIS AT

800~900°C —A NEW APPROACH TO ENERGY SAVINGS<sup>①</sup>

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## ABSTRACT

The freezing points of cryolite-alumina melts with the addition of  $\text{AlF}_3$ ,  $\text{CaF}_2$ ,  $\text{MgF}_2$  and  $\text{LiF}$  were measured. It was found that there was a wide range of lower freezing points below 800°C. Various physico-chemical and electro-chemical properties at 30°C above the corresponding freezing points were measured. Current efficiencies in a laboratory bench scale 100A cell were high (85~90% at 800~900°C), was low. It is assumed that aluminium electrolysis may be carried out at 800~900°C with lower energy consumption.

**Key words:** aluminum electrolysis lower temperature energy consumption

## 1 INTRODUCTION

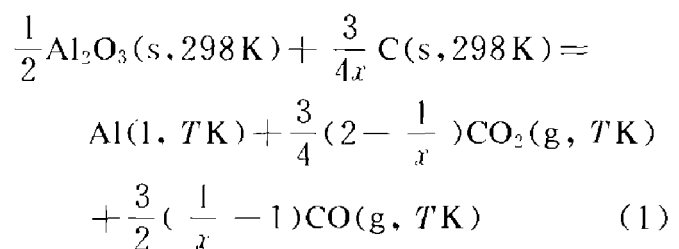
At the present the electrolysis of cryolite-alumina molten salts is the only process for the commercial aluminium production. The temperature of electrolysis is usually at 950~970°C. The cathodic product is liquid aluminium. The energy consumption is about 15 000 kWh/t Al (Soderberg cells) or 13 500 kWh/t Al (prebaked cells). For producing liquid aluminium an electrolysis temperature of 100~150°C higher than the melting point of aluminium is reasonable. The energy consumption in the present aluminium industry is rather high because the electrolytes used are very high in melting points. Therefore it is required to find and use electrolytes with lower melting points.

## 2 ENERGY CONSUMPTION

Theoretical energy consumption in aluminium electrolysis is composed of two part-

s; (a) the energy required for heating alumina and carbon; (b) the energy required for decomposing alumina.

The reaction is as follows<sup>[1]</sup>:



where  $x$  — current efficiency.

The energy for the above reaction is

$$H_{\text{total}} = 4.18[95625 + 13.240T + 8.85 \times 10^{-4}T^2 + 2.895 \times 10^5T^{-1} + x^{-1}(30694 + 2.2725T - 7.5 \times 10^{-1}T^2 - 1.365 \times 10^5T^{-1})] \quad (\text{J/mol Al}) \quad (2)$$

when  $x = 100\%$ ,

$$H_{\text{total}} = 5.4375 + 6.677 \times 10^{-1}T + 3.4867 \times 10^{-8}T^2 + 6.5859T^{-1} \quad (\text{kWh/kg Al}) \quad (3)$$

when  $x = 90\%$ ,

① Supported by the National Natural Science Foundation of China; manuscript received April 3, 1993

$$H_{total} = 5.8398 + 6.786 \times 10^{-4}T + 3.4509 \times 10^{-8}T^2 + 5.9329T^{-1}$$

(kWh/kg Al) (4)

The dependence of energy consumption on temperature is shown in Table 1.

From the above relationships, it can be seen clearly that the theoretical energy consumption decreases with increasing current efficiency and with decreasing temperature. At 1273K the theoretical energy consumption would be 6.348 kWh/kg Al at current efficiency 100%. It decreases as temperature decreases. The energy gradient is

$$\frac{d\Delta H_T^0}{dT} = -7.45 \times 10^{-4}$$

kWh/kg·Al·K (at 100%CE)

The relationship between theoretical decomposition voltage of alumina and temperature is

$$E_T = 1.8788 - 5.55 \times 10^{-4}T + \frac{RT}{6F} \ln a_{Al_2O_3}$$

The dependence of decomposition voltage of alumina with temperature is shown as Table 2 (under saturation conditions); At 1273 K,  $E_T = 1.1723V$ . Hence it follows that the decomposition voltage of alumina increases as temperature decreases. The voltage gradient is

$$\frac{dE_T}{dT} = +5.55 \times 10^{-4} V/K$$

As the free energy is included in the total energy, an increase in decomposition voltage

with decreasing temperature is no longer considered in the overall energy consumption.

### 3 EXPERIMENTAL RESULTS

#### 3.1 Freezing Point of Electrolytes

It was found that in the following system NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub>-MgF<sub>2</sub>-LiF there are electrolytes with wide range of low freezing point. Some of them are even lower than 700 C freezing points. This fact shows that there is a possibility of carrying out electrolysis at 800~900 C. This confirms the experimental results of Sleppy and Cochran<sup>[3]</sup>. Fig. 1 shows one section of this system.

#### 3.2 Metal Dissolution Loss in Electrolyte

30 g of electrolyte were melted in a graphite crucible with dia. 30 mm. After melting the temperature was raised to 30 C above the melting point and kept constant. Then one piece of electrolytically refined aluminium, about  $2.5 \pm 0.1g$ , was added to the molten electrolyte. After 45min, the crucible with its content was taken out from the furnace and cooled down. The weight of the metallic globule was weighed and the weight loss of aluminium was calculated.

The results of two parallel sets of experiments were plotted in Fig. 2(a). It is clearly seen that the metal dissolution loss in molten

**Table 1 The dependence of energy consumption(kWh/Kg Al) on temperature( T )**

T /K	1073	1098	1123	1148	1173	1198	1223	1248	1273
x = 100%	6.199	6.219	6.237	6.255	6.274	6.292	6.310	6.329	6.348
x = 90%	6.358	6.376	6.395	6.414	6.433	6.452	6.471	6.490	6.509

**Table 2 The dependence of decomposition voltage( E<sub>T</sub> ) on temperature( T )**

T /K	1073	1098	1123	1148	1173	1198	1223	1248	1273
E <sub>T</sub> /V	1.283	1.269	1.256	1.242	1.227	1.214	1.200	1.186	1.172

cryolite decreases as the temperature decreases, especially in the lower cryolite ratio (CR) region.

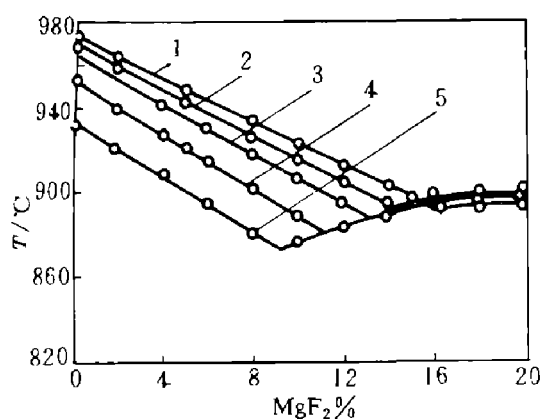


Fig. 1 Freezing point curves of cryolite-alumina melts with the addition of  $\text{CaF}_2$  (3wt.-%),  $\text{MgF}_2$  (4.2wt.-%) and  $\text{LiF}$  (2wt.-%)  
1—CR=3.0; 2—CR=2.7; 3—CR=2.5;  
4—CR=2.3; 5—CR=2.1

### 3.3 Electrical Conductivity

It was found that the electrical conductivity of the bath decreases with the cryolite ratio. See Fig. 2(b).

### 3.4 Bath Density

The bath density was measured at temperature 30 C above the freezing point of the electrolytes. As the density of the liquid aluminium increases with decreasing temperature, it is important to know the density difference between the liquid aluminium and bath when CR and temperature decrease.

The results of measurement were expressed in terms of the relative difference in density as follows:

$$\Delta d_r = \frac{d_1 - d_2}{d_1} \times 100\%$$

where  $\Delta d_r$  — relative difference in density,  $d_1$  — density of metal,  $d_2$  — density of bath.

The experimental results are plotted in Fig. 2(c) and(d). It was found that the rela-

tive density difference increases as CR and temperature decrease. Hence it is in favor of electrolysis at lower-temperatures.

### 3.5 Vaporization Loss of Electrolyte

30 g of electrolyte were melted in a platinum crucible, which was suspended by a platinum wire to a thermal balance. After melting the temperature was kept at 30 C above the the melting point of the electrolyte and the loss of the electrolyte within one hour was determined. The results of experiments were plotted in Fig. 2(e). It was found that the vaporization loss of electrolyte increases as the CR decreases from 3.0 to 2.0. However, in the CR range of 2.0 to 1.0, the vaporization loss of electrolyte decreases rapidly, this is obviously due to a significant decrease in temperature.

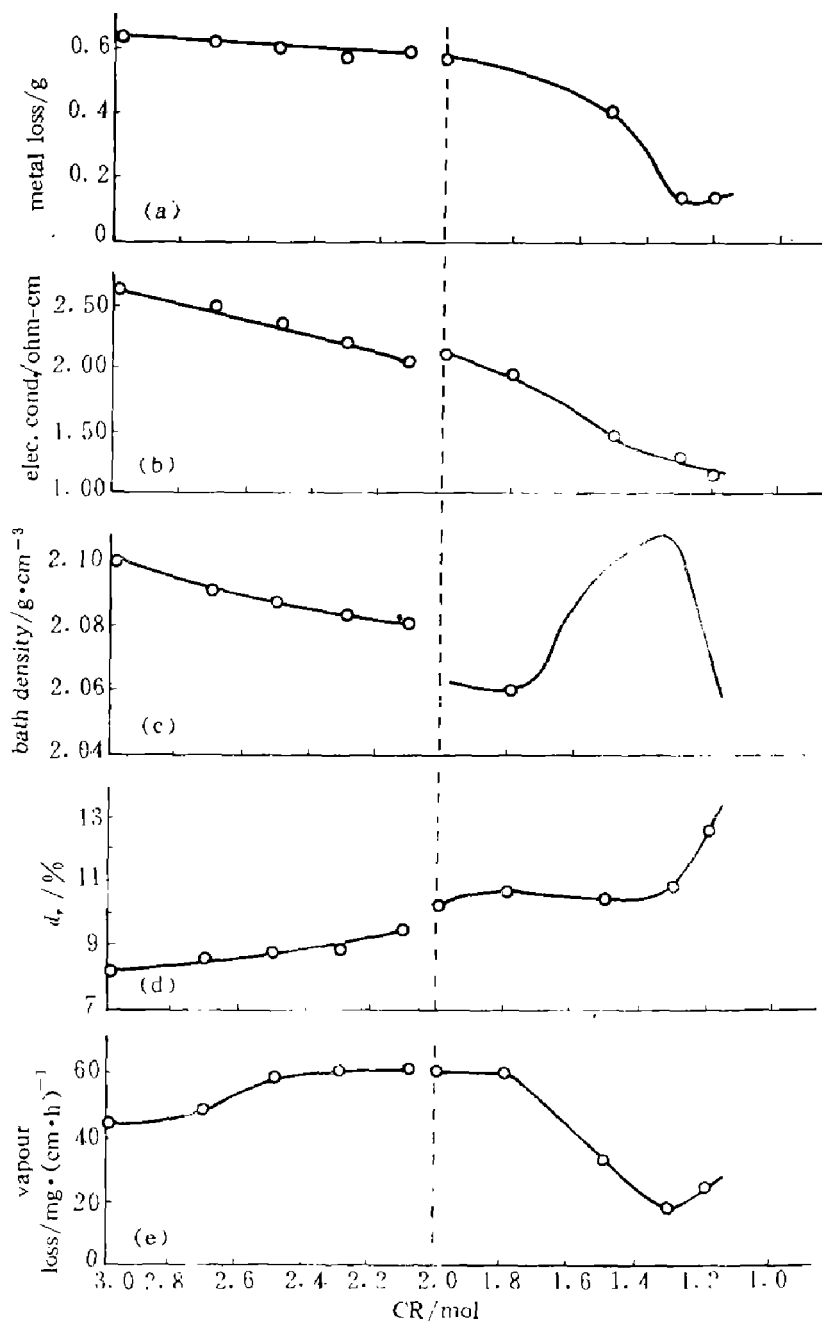
### 3.6 Dissolution Rate of Alumina in Cryolite

We calcined  $\text{Al}(\text{OH})_3$  at various temperatures in order to obtain different kinds of alumina (refer to the crystallization structure and specific surface area). As the electrolysis temperature decreases, the dissolution rate of alumina in molten cryolite decreases, too. In the experiments 200mg of alumina sample at various temperatures was used. The dried sample was packed in a basketwork made of  $\phi 0.5$ mm platinum wire. 50 g of cryolite with various CR were melted in a platinum crucible. After melting, the alumina sample together with the basketwork was put into the cryolite melts and sunk down to the bottom of the crucible. A Platinum wire stirrer ran at a speed of 100r/min. The distance of the lower surface of the stirrer to the sample is about 2cm. A strong beam of light from an iodine-tungsten lamp (1kW) was shined on the surface of the melt and the whole procedure of the dissolution of alumi-

na in cryolite was detected (Fig. 3). The time required for the dissolution of alumina was recorded. A longer time for the dissolution means a slower dissolution rate (see Table 3). It shows that a decrease in calcination temperature should be beneficial to the dissolution of alumina.

### 3.7 Anodic Overvoltage

The anodic overvoltage on the graphite anode was measured at various cryolite ratios and temperatures in the range of anodic current density  $0.01 \sim 1.0 \text{ A/cm}^2$ . The Tafel constants for each set of measurements are as



**Fig. 2 Physico-chemical properties of electrolyte at various cryolite ratios**  
 Left side; with 3.0wt.-%  $\text{CaF}_2$  + 4.2wt.-%  $\text{Al}_2\text{O}_3$   
 Right side; with 2.0wt.-%  $\text{CaF}_2$  + 3.0wt.-%  $\text{Al}_2\text{O}_3$ ;  
 Temperature; 30 C above the corresponding freezing point

Table 3 Dissolution rate of alumina in molten cryolite

Calcination temp/°C	700	800	900	1000	1180
Specific surface/m <sup>2</sup> ·g <sup>-1</sup>	125.1	108.9	86.6	40.7	0.3
Crystal structure	$\chi$	$\chi$	$\chi$	$k$	$\alpha$
<b>Dissolution rate</b>					
CR=1.7, 890 C	1' 20"	2' 05"	3' 50"	4' 30"	6' 05"
CR=2.0, 950 C	1' 15"	1' 28"	2' 18"	2' 30"	3' 35"
CR=2.3, 960 C	58"	1' 05"	1' 10"	2' 10"	2' 15"
CR=2.7, 980 C	58"	1' 08"	1' 28"	1' 45"	2' 15"

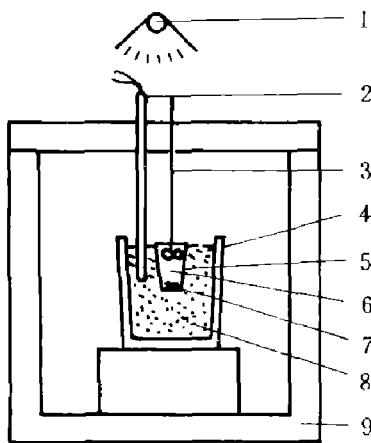


Fig. 3 Apparatus for measuring the rate of dissolution of alumina in molten cryolite

1—lamp; 2—thermocouple; 3—stirrer;  
4—corundum crucible; 5—Pt crucible; 6—  
molten cryolite; 7—alumina; 8—alumina;  
9—furnace

0.54V at the same current density. It means that the increase in anodic overvoltage is about 0.08V for a decrease of temperature 100 C.

### 3.8 Cathodic Overvoltage

The cathodic overvoltage on liquid aluminium was measured at various CR and temperatures, the range of cathodic current density is 0.2 ~ 2.0 A/cm<sup>2</sup>. It was found that the cathodic overvoltage increases as the CR and the temperature decrease. See Fig. 1. For CR = 1.7 and 880 C, the cathodic overvoltage is about 0.08V at a cathodic current density of 0.5 A/cm<sup>2</sup>. While for CR = 2.7 and 960 C, the cathodic overvoltage is about 0.06V at the same current density. It means that the increase in cathodic overvoltage is about 0.02V for a decrease of temperature 100 C.

### 3.9 Cryolite Crust on Cathode

Sleppy *et al*<sup>[2]</sup>, Thonstad *et al*<sup>[3]</sup>, Herstad *et al*<sup>[4]</sup> discussed the problem of cryolite crust on cathode. During the aluminium electrolysis, the Al<sup>3+</sup> ions discharge on the cathode, while the Na<sup>+</sup> ions discharge to a much less extent on it. Therefore, in the cathodic

follows:

CR=1.2, 780 C,  $a = 0.768V$ ,  $b = 0.263V$   
 CR=1.5, 860 C,  $a = 0.742V$ ,  $b = 0.258V$   
 CR=1.7, 880 C,  $a = 0.714V$ ,  $b = 0.274V$   
 CR=2.0, 900 C,  $a = 0.662V$ ,  $b = 0.218V$   
 CR=2.3, 950 C,  $a = 0.616V$ ,  $b = 0.200V$   
 CR=2.7, 960 C,  $a = 0.577V$ ,  $b = 0.195V$

It follows that the anodic overvoltage increases as the cryolite ratio and temperature decrease. For CR = 1.7 and 880 C, the anodic overvoltage is 0.62V at anodic current density of 0.7 A/cm<sup>2</sup>. While for CR = 2.7 and 960 C, the anodic overvoltage is

region the concentration of NaF will be greatly increased. This will cause cryolite to be deposited on the cathode when the temperature is not sufficiently high to maintain its molten state. In this experiment, a layer of cryolite crust was also detected on the cathode when the cathodic current density was higher and the electrolysis temperature was much lower. Under these conditions the cathodic overvoltage was higher. The crust formed between the graphite cathode and the aluminium globules, it also formed between the aluminium globules. The composition of the crust was examined with X-ray diffraction to be  $\text{Na}_3\text{AlF}_6$ ,  $\text{Na}_5\text{Al}_3\text{F}_{11}$  and  $\alpha\text{-Al}_2\text{O}_3$ . The cathode crust formation, however, may be lessened when the temperature of electrolysis is raised and the convection condition is kept well in the cell.

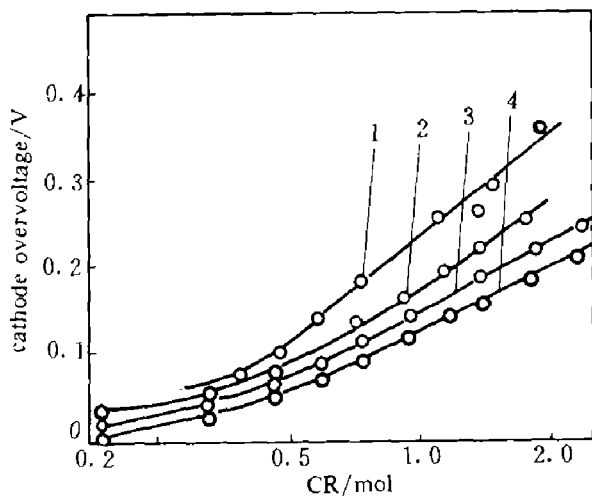


Fig. 4 Tafel plot for cathodic overvoltage  
 1—CR=1.0,880 C ; 2—CR=2.0,930 C ;  
 3—CR=2.3,950 C ; 4—CR=2.7,960 C

3.10 Anode Effect

The wettability of carbon anode by molten electrolyte and the critical current density (ccd) for initiation of anode effect was measured at various cryolite ratios. It was found that the  $\theta$  angle decreases and ccd increases as the CR decreases, when the temperature was kept constant. See Fig. 5.

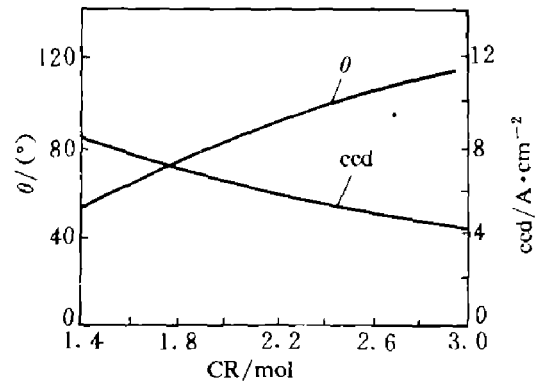


Fig. 5 Wetting angle and critical current density at various cryolite ratios(1000 C)

3.11 Carbon Consumption

According to the reaction  $\text{Al}_2\text{O}_3(\text{s}) + 1.5\text{C}(\text{s}) = 1\text{Al}(\text{l}) + 1.5\text{CO}_2(\text{g})$  the theoretical carbon consumption is 0.112g/Ah. Pearson *et al* found that for graphite anode the carbon consumption is about 101% ~ 105% of the theoretical value.

In this paper 100 g of electrolyte with various cryolite ratios were melted in a graphite crucible ( $d65\text{ mm}/48\text{ mm} \times 70\text{ mm}$ ). The inside of the crucible was lined with a corundum crucible ( $d46\text{ mm}/40\text{ mm} \times 70\text{ mm}$ ). In the bottom of the corundum crucible there is a hole ( $d30\text{ mm}$ ), in which 10 g of aluminium was melted. A graphite anode was immersed into the molten electrolyte. The duration of electrolysis for each run was 60min. The results of experiments were plotted in Fig. 6.

Two sets of experiments were carried out at anodic current density of  $0.56\text{ A}/\text{cm}^2$  and  $0.92\text{ A}/\text{cm}^2$ , separately. There is a minimum point on each anode consumption curve, its position is somewhere around  $\text{CR} = 1.5 \sim 1.6$ . However, the anodic consumption and surface condition after electrolysis are rather different. In the former case, the current density is smaller, the anode consumption is higher and the anode surface af-

ter electrolysis was rather rough. This means that the discharge of  $O^{2-}$  ions on the anode is selective, more on the active parts of anode. This will cause more carbon particles to be dropped down from the anode. In the latter case, the current density was higher, the anode consumption became less and the anode surface after electrolysis was more smooth. The lowest value of the anode consumption is about 0.114 g/Ah at CR = 1.7 and 870 C. This value is only 0.002 g/Ah above the theoretical one, i. e., at 102%.

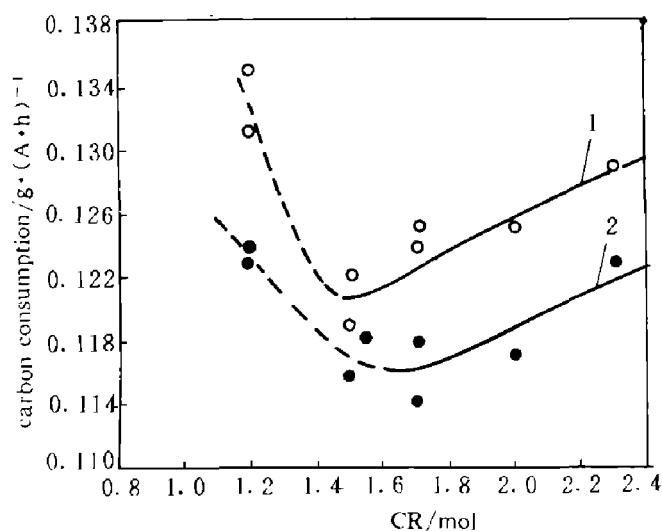


Fig. 6 Carbon consumption at various cryolite ratios

1—0.56 A/cm<sup>2</sup>; 2—0.92 A/cm<sup>2</sup>

### 3.12 Current Efficiency

Electrolysis was carried out in a 100 A cell, which is schematically shown in Fig. 7. A graphite crucible ( $d$  130 mm/120 mm  $\times$  220 mm) was placed in a stainless steel crucible ( $d$  160 mm/150 mm  $\times$  220 mm). About 2 500 g of cryolite-alumina mixture were melted in the graphite crucible. The cell was heated in a resistance furnace, the temperature was controlled to within  $\pm 1$  C. The graphite crucible also served as the anode. A graphite electrode ( $d$  45 mm) or a  $TiB_2$  electrode ( $d$  40 mm) served as a cathode. A sintered alumina crucible ( $d$  60 mm/

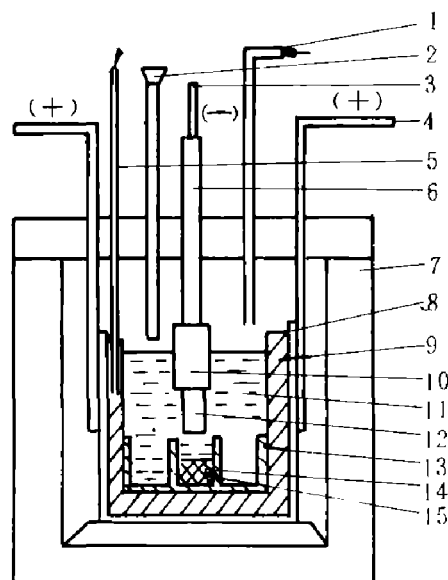


Fig. 7 Electrolysis cell (100)

1—Ar supply; 2—alumina supply; 3—cathode lead; 4—anode lead; 5—thermocouple; 6—corundum tube; 7—furnace; 8—stainless steel cup; 9—graphite crucible; 10—corundum tube; 11—cryolite-alumina melts; 12—graphite cathode; 13—corundum crucible; 14—corundum crucible; 15—aluminium liquid

50 mm  $\times$  70 mm) was placed under the cathode as a reservoir for the liquid aluminium produced. It dissolved slowly in the electrolyte when the cryolite ratio of the electrolyte and the temperature were lower, so it can be used for 7~8 times. The composition of the electrolyte used was with various cryolite ratios, ranging from 1.2~2.3. The alumina content in the bath was about 3~4%, which was analyzed before and after the electrolysis. Some additives were used, such as  $CaF_2$ ,  $MgF_2$ , or  $LiF$ . The electrolysis temperature was kept at 50~60 C above the melting point of the corresponding electrolyte. The current intensity for each run was about 100 A, the electrical quantity passed was recorded with a coulometer. The duration of electrolysis for each run was 2 h. The current efficiencies were in the range of 85~90%. It was high enough for laboratory bench scale cells. The high current effi-

ciency may be due to a low metal solubility in molten cryolite at lower temperatures (Fig. 8).

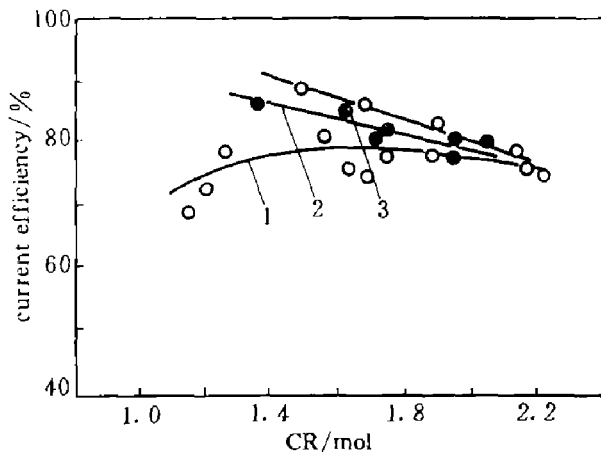


Fig. 8 Current efficiency at various cryolite ratios  
1—MgF<sub>2</sub>, 3%; 2—MgF<sub>2</sub>, 4.5%; 3—MgF<sub>2</sub>, 6%

#### 4 DISCUSSIONS

(1) The alumina dissolution rate in the electrolyte also decreased at lower cryolite ratios and lower temperatures. This defect may be overcome by using aluminas calcined at lower temperatures.

(2) The anodic and cathodic overvoltage are about 0.1 V higher than of that when normal electrolytes were used, about 0.1 V. This defect may be overcome by decreasing the current density of both electrodes, and improving the bath convection conditions.

(3) The electrical conductivity of the melts was low at lower cryolite ratios and

lower temperatures. Therefore, for the sake of carrying out electrolysis at lower temperatures (800 ~ 900 °C) it is better to modify the construction of electrolysis cells, i. e., using inert cathode. Inert cathode + lower temperature electrolysis may be a direction in the development of aluminium production. The energy consumption in this case may be less than 12000 kWh/t Al.

#### 5 CONCLUSION

From energy calculations and laboratory experiments it reveals that the electrolysis of cryolite-aluminium melts at lower temperatures (say, 800 ~ 900 °C) is possible. The current efficiency is high and the carbon consumption is low, and finally the energy consumption may markedly decrease. The lower temperature electrolysis may be an interesting subject in the future development of aluminium production.

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