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ELECTROCHEMICAL DETERMINATION OF CURRENT EFFICIENCY IN ALUMINIUM ELECTROLYSIS①

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ABSTRACT Current chronopotentiometry has been useed to measure current efficiency (CE) of aluminium electrolysis in fused pure cryolite, industrial electrolyte and low melting point electrolyte. The effect of temperature, alumina content and other factors on CE has been investigated. The results obtained have been discussed by Lillebuen model.

Key words: aluminium electrolysis current efficiency current chronopotentiometry

1 INTRODUCTION

CE is assessed by comparing the weight of aluminium produced at cathode with the theoretical weight deduced from Faraday's Law. For modern aluminium industry improvement of CE as a techno-economical parameter is very important. In laboratory study CE is one of the main bases for appraising the electrolytic parameters and electrolyte properties, and it is determined by the weight of metal obtained, analysing composition of anode gases, or the recently electrochemical method[1,2].

It is known that the aluminium dissolution loss is a main factor of decreasing CE[3,4]. In this paper we measured the dissolution rate of deposited aluminium and CE by current chronopotentiometry.

2 FUNDAMENTALS OF CE DETERMINATION

In the electrochemical system with three electrodes, when a cathodic current was applied to the working electrode for the deposition of certain amount of aluminium, a typical potential versus time ($E \sim t$) as Fig. 1 was obtained[5]. During the cathodic polarization, the potential of the working electrode was seen to rise fairly sharp. After time t_{red} the current switched to zero; a potential decay (t_d) corresponding to deposited pure aluminium was found from the $E \sim t$ curve. Due to the dissolution of metal into melt and alloying of aluminium with electrode substrate, pure aluminium at electrode depleted after t_d and the potential began to shift positively and slowly.

In the Hall-Heroult cells, pure aluminium was deposited at the cathode and dissolved

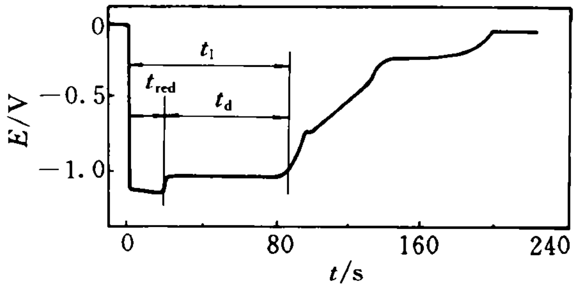

Fig. 1 Time dependence of electrode potential in industrial electrolyte

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partly into the molten electrolyte bath. So in our experiments we were interested in observing the dissolution loss of pure metal on the working electrode.

3 MASS BALANCE OF ALUMINIUM

Mass balance of aluminium gives:

$$Q_{red} = Q_a + Q_l \tag{1}$$

where Q denotes the amount of aluminium deposited on unit area of electrode in A · s/cm^2; the foot notes red, a and l represent "deposition", "alloying" and "loss" respectively.

It was found that aluminium dissolved at the same rate in cathodic polarization as in unpolarization conditions[5]. The rate of metal dissolution is:

$$r = \frac{Q_l}{t_l} = \frac{Q_l}{t_{red} + t_d} \tag{2}$$

and

$$Q_{red} = I \cdot t_{red}/S = t_{red} \cdot i \tag{3}$$

$$Q_a = 2nFC_0(D_m/\pi)^{1/2} \cdot t_l^{1/2} \tag{4}$$

where I is current intensity in A; S is working electrode area in cm^2; C_0 is concentration of diffusive aluminium atoms on working electrode surface in mol/cm^3; D_m is diffusion coefficient of aluminium atoms into electrode substrate to form alloy in cm^2/s, the value of D_m at various temperatures has been given in literature[5].

From the definition of CE, η can be given by:

$$\eta = \frac{Q_{red} - Q'_l}{Q_{red}} \tag{5}$$

where Q'_l is the amount of aluminium dissolved in time t_{red} and it is given by the following expression:

$$Q'_l = r \cdot t_{red} \tag{6}$$

Hence $\eta = 1 - r/i$ (7)

where i is current density in A/cm^2. CE may be calculated from equation (7).

4 EXPERIMENTAL

In the experiments, electrolytes were prepared from handpicked natural cryolite, and chemical reagents AlF_3, CaF_2, LiF, Al_2O_3, MgF_2 were used. The 80 g electrolyte was pre-mixed according to required composition to ensure homogeneity. The mixture was then put into a graphite crucible (high grade) which served as the counter electrode. The working electrode and reference electrode were tungsten wires (W) of 1.5 mm diameter which were contained in alumina sleeves. More details were given in literature[5].

5 RESULTS

(1) For cryolite melt (at 1 025 ℃)

Fig. 2 shows a plot of Q_l versus t_l measured in different polarization times and current densities by current chronopotentiometry. CE at different current densities was obtained from equation (7) and presented as curve 1 in Fig. 3. It indicates that in pure cryolite melt CE is only 75% at current density of 1.0 A/cm^2.

(2) For industrial electrolyte (at 960 ℃)

The electrolyte was taken from industrial cell of aluminium plant; its composition was: cryolite molar ratio of $NaF/AlF_3 = 2.84$, 5.5 wt.-% CaF_2, 3 wt.-% MgF_2, 6.5 wt.-% Al_2O_3 and about 2 wt.-% LiF. At value $r_l = 0.098$ A/cm^2, a plot of CE vs current densities is presented as curve 2 in Fig. 3. The characteristics of the plot were the same as that determined by some other methods[6].

(3) For low-melting point electrolyte (at

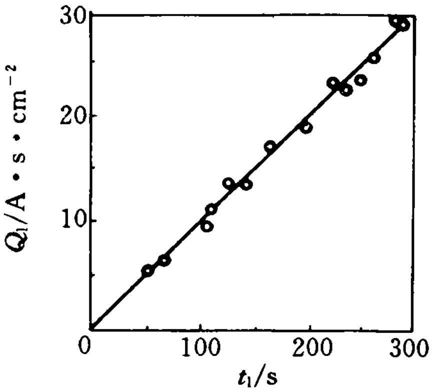

Fig. 2 Time dependence of aluminium dissolution loss in natural cryolite melts (T = 1 025 ℃)

850 ℃)

We also investigated the low melting point electrolyte which was composed of Na_3AlF_6(natural), 28 wt.-% AlF_3, 3 wt.-% CaF_2, 3 wt.-% LiF, 5 wt.-% Al_2O_3. When $r = 0.042\,3$ A/cm^2, curve 3 in Fig. 3 was obtained. All the three curves in Fig. 3 show that CE increases with current density.

(4) The effect of temperature on CE

The effect of temperature on CE has been studied in the electrolyte melt of the following composition: cryolite molar ratio of NaF/AlF_3 = 2. 75, 4 wt.-% CaF_2, 4 wt.-% MgF_2, 3 wt.-% LiF and 5 wt.-% Al_2O_3. CE at different temperatures is given in Fig. 4. It indicates that rising temperature leads to decreasing CE.

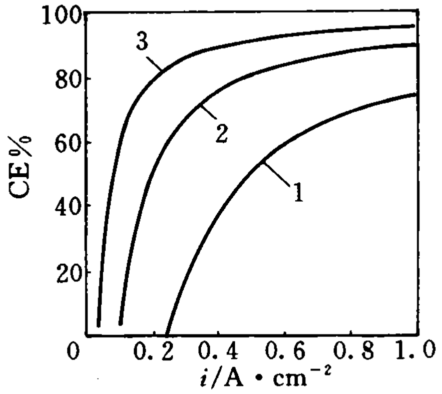

Fig. 3 The relationship between CE and current density

1—pure cryolite; 2—industrial electrolyte; 3—low melting point electrolyte

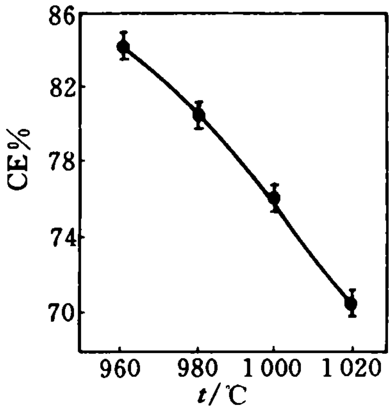

Fig. 4 The relationship between CE and temperature at current density 0. 600 A/cm^2

(5) The effect of alumina concentration on CE

In the same electrolyte as above, but with varying alumina contents, variation of CE with the alumina concentration is given in Fig. 5. It shows that current efficiency increases with increasing alumina concentration.

(6) Effect of dissolved aluminium on CE

After introducing 5. 0 g aluminium into the above electrolyte melt and holding the same temperature for three hours, we began to measure CE. The results were presented in Fig. 6. It indicates that the existence of dissolved aluminium can decrease the dissolution loss of cathodic product and increase the CE.

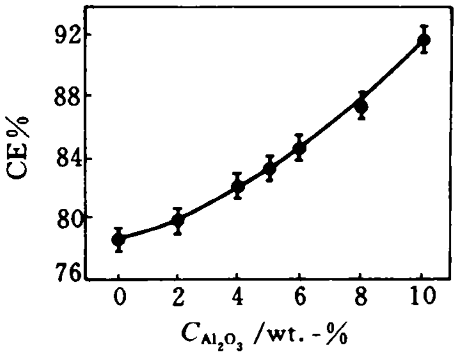

Fig. 5 The relationship between CE and aluminium concentration at current density 0. 600 A/cm^2

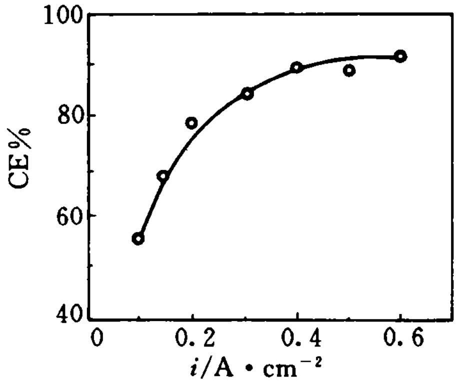

Fig. 6 The relationship between CE and current density in the presence of dissolved aluminium

6 DISCUSSION

According to the Lillebuen model[7], the rate of aluminium loss is controlled by mass transport of dissolved metal through a film at metal/melt interface and it can be expressed as follows:

$$r = nFD(C^0 - C)/\delta = K(C^0 - C) \quad (8)$$

where D is diffusion coefficient of dissolved metal in melt; C^0 is saturated concentration of metal in melt; C is metal concentration in bulk melt; δ is thickness of metal/melt interface layer; K is mass transport coefficient.

K , the transport coefficient at the interface layer, can be expressed by following equation:

$$K = kD^{0.67}\mu^{-0.5}v^{0.83}h_e^{-0.17}\rho^{1.5} \quad (9)$$

where k is constant; μ is viscosity of melt; v is velocity of melt referred to liquid aluminium at cathode; h_e is inter-electrode distance; ρ is density of melt.

Insertion of experimental results into equation (8) and (9) shows that the effect of bath temperature and composition on CE may be caused by changing the physico-chemical properties of melt and aluminium solubility. The effect of temperature, fluoride additives and alumina content on the items in equation (8), (9) and CE is presented in Table 1.

Equation (8) demonstrates that($C^0 - C$) is the driving force in the interface layer, so increasing C can decrease the aluminium loss. In the absence of aluminium C is equal to zero, because the amount of deposited aluminium on electrode surface is negligible as compared with the bulk of the melt. From Fig. 3 and Fig. 6 it is clear that on the condition of existing dissolved aluminium($C \neq 0$) CE increases more remarkably.

Table 1 Some influences on items in equation (8), (9) and CE

Influence factors	ρ	μ	C^0	D	CE
Temperature	↓	↓	↑	↑	↓
Alumina content	↓	↑	↓		↑
AlF_3	↓	↓	↓		↑
CaF_2	↑	↑	↓		↑
MgF_2	↑	↑	↓		↑
LiF	↓	↓	↓		↑

Notes: ↑ means increase, ↓ decrease.

CE was determined by double potentiostatic method in literature [1] and current reversal chronopotentiometry with a delay time in literature [2]. The results of the measurement are questionable since the interaction between the deposited aluminium and electrode substrate was not considered.

7 CONCLUSION

Current chronopotentiometry has been used firstly for the determination of CE of aluminium deposition from cryolite based melts. The measurement results indicate that at the same current density CE increases from pure cryolite, industrial electrolyte to low melting point electrolyte, and the existence of dissolved aluminium can increase the CE remarkably. Increasing current density in proper range is an effective way to increase CE.

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