LOW TEMPERATURE ALUMINUM ELECTROLYSIS IN NaF-AlF_3-BaF_2-CaF_2 BATH SYSTEM①

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ABSTRACT Multiple regression equations on liquidus temperature, electrical conductivity and bath density of NaF-AlF_3-BaF_2-CaF_2 system were obtained from experiments designed using orthogonal regression method. In 100 A experimental cell with low melting point electrolyte at 750 ℃, current efficiency (CE) was 90.57 % and specific energy consumption was 12.27 kWh per kg Al. Because of the fact that aluminum metal obtained float on the surface of molten electrolyte, this electrolysis method was named as low temperature aluminum floating electrolysis. The results showed that the new low temperature aluminum electrolysis process in NaF-AlF_3-BaF_2-CaF_2 bath system was practical and promising.

Key words low temperature aluminum electrolysis NaF-AlF_3-BaF_2-CaF_2 bath system aluminum floating

1 INTRODUCTION

Since the Hall-Héroult process was invented one hundred years ago, it has been the only aluminum production method in the world[1]. The process has many weak points, such as low unit productivity, low energy utilization (less than 50 %), high electrolytic temperature (usually at 950 ℃), a great deal of carbon quality material consumption, serious environmental pollution and so on. It is well known that the melting point of aluminum is 660 ℃, therefore, aluminum electrolysis at 700 ~ 800 ℃ range should be practicable. Low temperature aluminum electrolysis (LTAE) is generally accepted to be the development tendency of aluminum production technology due to its potential of increased current efficiency (CE), reduced energy consumption, increased cell life, easier adoption of inert materials for electrodes and cell lining and environmental protection[2]. So the subject of LTAE has been paid great attention[3-12]. However, any breakthrough in researches on LTAE has not yet been made up to date because there exist a number of problems like cathodic crust when using low melting point electrolyte from cryolite system.

In this paper, a new electrolytic aluminum production process with NaF-AlF_3-BaF_2-CaF_2 system as electrolyte different from the Hall-Héroult process was presented, named as low temperature aluminum floating electrolysis because of the fact that aluminum metal obtained float on the surface of molten electrolyte.

2 EXPERIMENTAL

2.1 Raw materials

In the experiments, γ-Al_2O_3 analyzed by XRD as raw material was prepared by roasting high-grade $Al(OH)_3$ at 600 ℃ for 10 h, the electrolytes were compounded with dehydrated ana-

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lytical grade chemicals NaF, AlF_3, BaF_2 and CaF_2.

2.2 Experimental method

To select the low melting point electrolyte from NaF-AlF_3-BaF_2-CaF_2 system, the physicochemical properties of the bath system was systematically studied based on the experiments designed using three-factor quadratic orthogonal regressive method. Gradual cooling curve method, Wheatstone bridge method and hydrostatic weighing method were adopted to measure the liquidus temperature (t), the electrical conductivity (κ) and the density (ρ) of the molten electrolyte respectively.

Electrolysis was carried out in a 100 A electrolysis cell, which is schematically shown in Fig.1. The electrodes made from the graphite material with a density of 1.7 g/cm^3 were arranged parallelly in cathode-anode-cathode form and the two cathodes were in multiple with the anode respectively. The anode-cathode distance was 20 mm. About 3 500 g electrolyte was employed for each run. The electrical quantity passed was recorded with HA-1 type coulometer, the CE was calculated from the amount of aluminum metal produced and determined by weighing after the experiments.

Fig.1 Schematic diagram of 100 A electrolysis cell

1 —Graphite anode; 2 —Corundum housing; 3 —Graphite cathode; 4 —Corundum separate plate; 5 —Aluminum liquid; 6 — Molten electrolyte; 7 —Corundum crucible

3 PHYSICOCHEMICAL PROPERTIES OF NaF-AlF_3-BaF_2-CaF_2 BATH SYSTEM

3.1 Orthogonal experiment conditions and results

The three-factor quadratic orthogonal regressive element level coding, orthogonal experiment conditions and results are listed in Table 1 and 2 respectively.

Table 1 Element level coding

Element	Cryolite ratio	$w(BaF_2)$ / %	$w(CaF_2)$ / %
Coding sign	R	B	C
Base level(0)	1.2	20	15
Changing distance(Δ)	0.658	4.115	4.115
Upper level(+)	1.858	24.115	19.115
Low level(-)	0.542	15.885	10.885
Upper asterisk arm(+ γ)	2.0	25	20
Low asterisk arm(- γ)	0.4	15	10

Table 2 Orthogonal experiment condition and results

No.	R	B	C	t/ ℃	κ /($\Omega^{-1}\cdot cm^{-1}$)	ρ /($g\cdot cm^{-3}$)
1	-1	-1	-1	698.7	1.2829	2.6938
2	-1	-1	+1	669.7	0.9471	2.8408
3	-1	+1	-1	649.9	0.8951	3.2720
4	-1	+1	+1	630.4	0.6403	3.3940
5	+1	-1	-1	884.4	1.7827	2.4597
6	+1	-1	+1	869.0	1.4359	2.5714
7	+1	+1	-1	779.7	1.3749	3.1834
8	+1	+1	+1	724.0	1.0491	3.3999
9	$-\gamma$	0	0	620.4	0.8577	3.0535
10	$+\gamma$	0	0	872.0	1.4643	2.7368
11	0	$-\gamma$	0	705.6	1.3960	2.8294
12	0	$+\gamma$	0	657.9	0.9260	3.4935
13	0	0	$-\gamma$	690.9	1.2042	3.0802
14	0	0	$+\gamma$	644.6	0.9448	3.2895
15	0	0	0	660.9	1.1610	3.1880

κ and ρ were measured at a 30 ℃ superheat.

3.2 Regression equations and remarkable quality test

Based on the measured results, the following equations were obtained by multiple regression analysis and the electrical conductivity (κ) and the density (ρ) of the molten electrolyte were modified with temperature coefficient ranging at 700 ~ 800 ℃.

$$t = 1093.8 + 32.69R - 31.59B - 7.687C - 7.46RB - 1.043RC - 0.227BC + 135.173R^2 + 0.879B^2 + 0.319C^2 \quad (1)$$

$$\kappa = 1.2726 + 6.1932R + 0.0357B - 0.0164C - 0.0046RB + 0.0038RC + 0.0008BC + 0.00852R^2 - 0.0022B^2 - 0.0013C^2 + 0.0034\Delta t \quad (2)$$

$$\rho = 1.2859 + 0.5088R + 0.0772B - 0.0023C + 0.0194RB + 0.0027RC + 0.0006BC - 0.4467R^2 - 0.0008B^2 - 0.0002C^2 - 0.003\Delta t \quad (3)$$

where t is the liqudus temperature in ℃, κ is the electrical conductivity in $\Omega^{-1}\cdot cm^{-1}$, ρ is the bath density in $g\cdot cm^{-3}$, Δt is the difference between bath temperature and bath superheat of 30 ℃ in ℃, R is the cryolite ratio, B is the BaF_2 content in % and C is the CaF_2 content in %.

The test values of F and t showed the regression Eqns.(1), (2) and (3) were remarkable at $\alpha = 0.001$ level, accurate and reliable at the studied ranges, which indicated that the equations could describe the changing effects of the plysicochemical properties with electrolytic constituent in the studied area.

4 LOW TEMPERATURE ALUMINUM ELECTROLYSIS

Based on the regression equations, after comprehensive considering the electrolytic physicochemical properties, low point bath from $NaF-AlF_3-BaF_2-CaF_2$ system was selected as aluminum electrolyte. The technological conditions of aluminum electrolysis in 100 A electrolysis cell are as follows.

The electrolytic composition: cryolite ratio is 1 and the concentrations of BaF_2, CaF_2 and Al_2O_3 are 20 %, 15 % and 5 % respectively; the electrolysis temperature: 750 ℃; the anode-cathode distance: 2 cm; cathodic density: 0.75 $A\cdot cm^{-2}$; duration of electrolysis: 4 h.

Under these conditions, the purity of aluminum produced was 99.95 %, the average indices of economy and technology with 5 runs were that the electrolysis cell voltage was 3.73 V, CE was 90.57 % and the specific D.C. energy consumption was 12.27 kWh per kg Al.

In the electrolysis experiments, the liquidus temperature of electrolyte used was 639.6 ℃, when the bath temperature was 750 ℃, the electrical conductivity was 1.326 $\Omega^{-1}\cdot cm^{-1}$ and the bath density was 2.9498 $g\cdot cm^{-3}$.

It is different from the traditional Hall-Héroult process that during the electrolysis, the aluminum liquid floated on the surface of the molten electrolyte because the density of the molten aluminum produced is lower than that of the molten electrolyte. Therefore, the new aluminum electrolysis process is known as the aluminum floating electrolysis process(AFEP). As seen in Fig.1, define the area between the anode and cathodes as the working area(WA), the area between the cathodes and the electrolysis sidewall as the gathering aluminum area (GAA). The aluminum electrolysis experiment is described as follow: when an electrical current passed the WA, CO_2 gas bubbles liberated from the anode and aluminum drops were produced on the cathodes, then CO_2 gas bubbles carried the molten electrolyte with aluminum liquid moving upwards. In the WA, the upper electrolyte flow was saturated by CO_2 gas, hence, the electrolyte density was lower than that of the electrolyte in the GAA. The bath density difference between the WA and the GAA, known as bubble pumping effect(BPE), made the electrolyte flow in the WA enter the GAA through an opening on the cathodes. In the GAA, aluminum droplets floated on the electrolyte surface and the electrolyte flow sank into the WA, thus forming a circulation. It can be seen that the BPE is the motive force for the electrolyte flow circulation. The electrolysis experiments showed that the electrolysis cell structure was reasonable.

The AFEP compared with the Hall-Héroult process has the advantages as follows: lower operating temperature, 750 ℃; higher CE and lower D.C. energy consumption; no detrimental but beneficial alumina sediment in preventing anode effects from occurring, because of alumina sediment having nothing to do with the cathodes so as not to affect the electrolysis process and melting in contact with the molten electrolyte directly, thus it could keep alumina concentration in the cell balance and production process stabilization; great rise of productivity in the future cell designed like magnesium electrolysis cell being multiple chamber; easier adoption of inert materials for electrodes and lining and useful to environmental protection.

5 CONCLUSIONS

(1) Multiple regression equation on physicochemical properties, including liquidus temperature, electrical conductivity and bath density of $NaF-AlF_3-BaF_2-CaF_2$ system were obtained from experiments designed using orthogonal regression method. The equations were then verified by F and t test. The results showed that the regression equations were remarkable at $\alpha = 0.001$ level, accurate and reliable in the studied ranges.

(2) Multiple regression equations can be used for cryolite ratios from 0.4 to 2.0, BaF_2 concentration from 15 % to 25 %, CaF_2 concentration from 10 % to 20 % and the equations (2), (3) at a bath temperature of 30 ℃ superheat.

(3) Aluminum has been successfully produced in a 100 A laboratory-scale cell with $NaF-AlF_3-BaF_2-CaF_2$ system at 750 ℃. Aluminum liquid has been obtained floating on the molten electrolyte surface, and the new aluminum production process is known as low temperature aluminum floating electrolysis.

(4) The bubble pumping effect is the motive force maintaining electrolyte circulation in the aluminum floating electrolysis cell. According to this principle, a future industrial electrolysis cell can be designed. The electrolysis experiments showed that the structure on the aluminum floating electrolysis cell was reasonable.

(5) In 100 A experimental cell with the low melting point electrolyte of which cryolite ratio was 1, the BaF_2 and CaF_2 content were 20 % and 15 % respectively at 750 ℃, the current efficiency reached 90.57 %, the specific D.C. energy consumption was 12.27 kWh per kg Al. The experiment result showed the new low temperature aluminum floating electrolysis process was practical and promising.

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