A DESIGN PRINCIPLE OF BIPOLAR ELECTRODES
FOR ELECTROWINNING CELL FROM CHLORIDE MELTS

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ABSTRACT

A design principle of bipolar electrodes for liquid metal electrowinning cell was discussed theoretically. By taking into consideration of volume balance and homogeneous circulation of the chloride melt, general equations were deduced for determination of each sectional area of the bipolar electrodes. The values of design parameters were checked experimentally by operating the laboratory-scale cells constructed with the proposed design principle in which following variables were supposed to be known; the number of the inter-spacing reaction zones and a total sectional area of the cell, an average surface area and thickness of the bipolar electrodes, a distance between electrodes, specific conductivity of the chloride melts and decomposition voltage of aluminum chloride in the melt at various concentrations at operational temperatures.

INTRODUCTION

Experimental studies on the electrowinning of liquid aluminum from the chloride melts containing aluminum chloride in the bipolar electrode cells have been carried out for many years in our laboratory to develop a novel process for electric energy saving (1)–(3). This electrowinning process is the same in principle as that opened by Aluminum Company of America in 1973.

As well known, in the ALCOA bipolar electrode cell, all electrodes having a horizontal surface are stacked and also both products from the anode and the cathode move counter-currently in the cell. On the other hand, in the bipolar electrode cell developed in our laboratory the surfaces of the electrodes have a slope to the horizontal plane and so the anodic and the cathodic products can be separately moved in the cell.

In this paper, the prerequisite was firstly discussed for homogeneous circulation of the melts through the center holes, the inter-spacing reaction zones, and the periphery clearances in the bipolar electrode cell. The general equations were derived for determination of the
sectional areas of the bipolar electrodes stated above. According to these equations, nine kinds of bipolar electrode cells were constructed and the values of design parameters were checked by the laboratory-scale tests.

THEORETICAL

Prerequisites for homogeneous circulation of melts

At first, let us consider a circulating path of the chloride melt in the bipolar electrode cell under steady state conditions during electrowinning of liquid aluminum.

The chloride melt, replenished with aluminum chloride in the upper part of the cell, is flowing down through the center hole of the electrodes and enter into each of the inter-spacing reaction zones wherein aluminum chloride decomposes to liquid aluminum at the cathode and chlorine gas at the anode surface. The residual melt and the chlorine gas evolved will move toward the cell wall and then rise up as bubbles through the periphery clearance between the electrodes and the cell wall. Finally, the chlorine gas as bubbles transfer from the melt into gas phase at the upper part of the cell.

Driving force for such circulation of the melt is owing to the gas lift effect in the periphery clearance. Accordingly, in order to supply a fresh melt containing aluminum chloride into each of the inter-spacing reaction zones between the electrodes without any delay in all bipolar electrodes, it is necessary for the melt to move at a constant velocity by means of a gas bubble lift force irrespective of levels of the melt. For the prerequisite of a constant volume ratio of the melt and the gas, bubbles have to be maintained at any level of the melt within the periphery clearances. As shown in Fig.1, this condition can be satisfied by making decreases of both sectional areas of center holes and periphery clearances in integer series. However, it is not so easy to determine practically these values because each of the electrode surfaces, which gives directly the gas volume from the anode, has to be determined from difference between the sectional area of the cell and the area summation of the center hole and the periphery clearance. The latter area is also dependent upon the gas volume. Therefore, it seems that an universal design principle for construction of the bipolar electrode cell is essential and will be discussed in the next paragraph.

Design rules of bipolar electrodes

The volume of chlorine gas evolved from anode surface is proportional to the effective current \( I_E \) through the bipolar electrode. This gas volume seems to be almost independent of the bipolar electrodes because the effective current is expressed to be nearly the same as those for all of the electrodes. Since the value of \( I_E \) can not be measured directly,
the value of an applied current $I_T$ was used tentatively instead of the $I_B$ value.

Taking the gas volume evolved from the anode surface into consideration, the following relationship should be obtained at the lowest bipolar electrode.

$$S_g^O \times i_g = \bar{S}_E \times i_T$$ (1)

In this equation $S_g^O$ is a sectional area occupied by the gas bubbles in the periphery clearance at the lowest bipolar electrode. $i_g$ is a current density which is defined as the current through the bipolar electrode divided by the cross sectional area of the gas bubbles, which can move upward smoothly in the periphery clearance. $\bar{S}_E$ is an average surface area of the electrodes, and $i_T$ is an applied current density.

The value of $\bar{S}_E$ in equation (1), which can be finally obtained after decision of all parameters, might be assumed to equal that at the middle level of the bipolar electrodes, namely, the $n/2$ bipolar electrode, because the bipolar electrodes have a similar shape to each other and vary their sizes systematically.

At the $n/2$ bipolar electrode at the middle level, a total sectional area of the cell vessel $S_T$ is given by the following relationship,

$$S_T = \frac{S_e^O}{2} + (n/2) \cdot (S_c^O + S_p^O + S_g^O)$$ (2)

where $S_c^O$ and $S_p^O$ are sectional areas for the center hole and for the melt in the periphery clearance, respectively, at the lowest bipolar electrode as defined for $S_g^O$.

In order to represent these areas of $S_c^O$ and $S_p^O$ as a function of $S_g^O$ two additional parameters were newly introduced, namely,

$$V_g = \frac{S_p^O}{S_g^O}$$ (3)

and

$$V_m = \frac{S_c^O}{S_p^O}$$ (4)

In these equations $V_g$ denotes the sectional area ratio of the melt to the gas bubbles in the periphery clearance and $V_m$ the sectional area ratio of the melt in the center hole to that of the periphery clearance. Substitution of the equations (3) and (4) into the equation (2) yields a following relationship.

$$S_T = \frac{S_e^O}{2} + (n/2) \cdot (V_g \cdot V_m + V_g + 1) \cdot S_g^O$$

736
\[
S_g^E = \frac{S_T}{2} + (n/2)\left( V_g \cdot V_m + V_g + 1 \right) x \frac{S_E^F}{2} \left( \frac{i_T}{i_g} \right) (5)
\]

Providing the values of \( n, i_T, i_g, V_g \) and \( V_m \), the values of \( S_g^E \) can be determined for the cell with a total sectional area of \( S_T \) as follows:

\[
S_g^E = S_T / \left[ 1 + (n/2) \cdot \left( V_g \cdot V_m + V_g + 1 \right) x (i_T / i_g) \right] (6)
\]

\[
S_g = S_g^E \cdot \left( i_T / i_g \right) (7)
\]

By using the equation (7), sectional areas for the electrode surface \( S_g \), the center hole \( S_c \), and the periphery clearance \( (S_g + S_p) \) can be determined by following equations and schematically shown in Fig.2.

\[
S_g^m = S_T - m \cdot ( V_g \cdot V_m + V_g + 1 ) S_g^O (8)
\]

\[
S_c^m = m \cdot V_g \cdot V_m S_g^O (9)
\]

\[
(S_p^m + S_g^m) = m \cdot ( V_g + 1 ) S_g^O (10)
\]

In these equations \( m \) is a positive integer and denotes the number of bipolar electrodes stacked, that is, the electrode with number \( m=1 \) is the lowest bipolar electrode, which is opposite to an end-cathode connected with a DC supplier, whereas the electrode of number \( m=n \) is an end anode. The aluminum particles are falling down through the center hole and nitrogen gas as a carrier gas is introduced along with aluminum chloride vapor. In the above consideration these effects of volume of aluminum particles and carrier gas were ignored for the volume and lifting velocity of the melt. Furthermore, it was assumed that the gas bubbles were completely separated from the melt into the gas phase at the top level of the melt.

**EXPERIMENTAL**

**Electrode**

The bipolar electrodes, both end-anode and end-cathode and terminals were cut from a graphite rod to possess fifty four kinds of the electrode shapes specified according to the design rule stated in the preceding section. The parameters adopted for the cell design are as follows:
Total sectional area of the quartz cell vessel, $S_T$, is 100.3 cm$^2$; number of the inter-spacing reaction zones, $n$, is five. The applied current density, $i_T$, is 1.0 A/cm$^2$ and the value of $i$ is supposed to be 75 A/cm$^2$.

Two parameters of $V$ and $V_m$ are variable, i.e., 2, 3, and 5 for $V$ as well as 0.4, 0.7, and 1.0 for $V_m$, respectively.

As one of the examples, the horizontal sections of each electrode designed for $V=3$ and $V_m=0.4$ are given in Fig. 3. In the cell design, a diameter for the smallest center hole was determined to allow aluminum particles drop from the cathode surface without any interference, and also the largest bipolar electrode limited its diameter within the allowable difference between thermal expansion coefficients of the cell wall and electrode materials. The electrolytic cell consisted of a transparent quartz tube, 113 mm in diameter and 1 m in length, and is heated externally by a nichrome wire wound furnace with an electric power capacity of 4 kw. To look at the inside of the cell during electrolysis a long rectangular window was scooped through the furnace bricks. Further, this furnace is possible to be divided into four blocks and surrounded by the separable walls for heat-insulation. The structure of the cell and the furnace are represented schematically in the center region of Fig. 4.

Melt preparation and supply of aluminum chloride

The mixture of magnesium chloride and sodium chloride in the proportion of 25 and 75 mol% was used as a solvent melt with a melting point of 660°C. The solvent melt was firstly melted in additional furnace and then poured into the cell at about 700°C. The bottom of the quartz tube cell was self-sealed by freezing of the melt and sodium chloride granules at relatively low temperatures. The total amount of the solvent melt is about 4.5 Kg in each run.

From the results obtained in our previous studies, it was found that the concentration of aluminum chloride in the melt has to be kept as low as possible during electrolysis at 750°C in order to establish high current efficiency and low bath voltage. In this investigation an automatic supplier of aluminum chloride was developed after several modifications. This new equipment consisted of a large glass container for aluminum chloride and a vibrational rotary feeder. As shown in Fig. 4, solid particles of aluminum chloride first fall down through the rotary feeder into the melt composed of sodium chloride and aluminum chloride mixtures. The aluminum chloride is able to vaporize and is purified at the same time since the impurities accompanied by the aluminum chloride remain in the melt in the boiler. Aluminum chloride vapor can be transferred by nitrogen gas stream into the melt in the electrolytic cell. The amount of aluminum chloride supplied in this way can be precisely determined by monitoring the weight of whole system of aluminum chloride supplier; also the supply rates were controlled easily by using the rotary feeder with various revolution rates.
Exhaust of chlorine gas

As shown in Fig. 4, chlorine gas evolved during electrolysis will move toward the 10% sodium hydroxide solution through the exhaust systems by pumping with an aspirator under nitrogen gas stream used for supply of aluminum chloride into the cell. Aluminum chloride from the cell and other volatile matters were collected in glass condenser and plastic separator connected to the exhaust system.

Electrolytic procedures

Prior to the start of electrolytic experiment, pre-electrolysis was carried out for 30 minutes in order to remove the impurities contained in the solvent melt. Then aluminum chloride was supplied into the melt, according to the procedures described. After the concentration of aluminum chloride in the melt reached an appropriate level, aluminum electrolysis was commenced and continued for five hours.

During the electrolytic experiment, bath voltage was recorded every 3 minutes, and the relationships between applied currents and bath voltages were measured every 30 minutes. At the same time, a small amount of the chloride melt was sampled for chemical analysis of aluminum chloride, and also the sodium hydroxide solution was exchanged to determine the total amounts of chlorine gas evolved during electrolysis in the 30 minute intervals. After a run, the melt was exhausted from the bottom of the cell by melting down the self-sealed salt.

RESULTS

Several examples of the relationship between the applied current and bath voltage are given in Fig. 5 for different design parameters. From the results shown in the figures, it was clearly observed that every bipolar electrode can be operated in a so-called multi-cell when the bath voltages are larger than about 10 V.

In the intermediate range of the applied current the bath voltage is directly proportional to the applied current whereas with increase in the applied current the deviation of the bath voltage from the linear relationships was demonstrated, shifting toward higher values. It seems that this deviation is due to the gas bubbles that can not rise smoothly through periphery clearance due to its great volume.

DISCUSSION

The linear relationship between the applied current density and the bath voltage could be determined theoretically according the calculative procedures (3,4), providing physico-chemical properties of the chloride
melt. As shown in Fig.5, the calculated bath voltages for various applied current densities obey the linear relationship between them. The linear relationships calculated for nine kinds of the bipolar electrode cells were compared with the experimental results obtained for fifty four cases. From these comparisons it was found that the calculated relationships were in fairly good agreement with the experimental ones for the cases of relatively small values of \( V_g \) and \( V_m \).

Meanwhile, with increases in these values of \( V_g \) and \( V_m \), the calculated results tended to deviate from the experimentally determined ones as demonstrated in Fig.5 for the case of \( V_g = 5 \) and \( V_m =0.4 \). It can be considered to arise from the heterogeneous distribution of the by-pass current through the periphery clearance.

As shown in Fig.5, in the large values of the applied current the deviation of the bath voltage was observed from the linear relationship between them. The upper current density, at which the deviation was initially observed, was denoted as the \( i^{UP} \) in the present investigation.

Figure 6 shows the dependencies of \( V_m \) on the upper current density obtained for various values of \( V_m \). The effective current, \( I_g \), which corresponds to the rate of gas evolution at the lowest bipolar electrode, was calculated with the modified equivalent circuit (3) at the upper applied current \( i^{UP} \). The value of \( I_g \) was firstly divided by the area of the periphery clearance at the lowest bipolar electrode and further divided by the value of \( i^{UP} \). In order to reexamine the value of \( I_g \), which was 75 A/cm\(^2\) at \( i^{UP} =1.0 \) A/cm\(^2\), the current densities for smooth gas lift obtained above, \( i_0 \), were calculated for various values of \( V_m \). It was found that the values of \( i_0 \) varied from 50 to 60 A/cm\(^2\) with increase of \( V_m \) irrespective of the values of \( V_g \). Therefore, the value of 60 A/cm\(^2\) should be used for the design of the bipolar electrode cell.

**CONCLUSION**

In the present study the design principle was first considered for the bipolar electrode cell. In the experimental study the bipolar electrode cells with five units were constructed with the proposed design principle and then operated for electrowinning of liquid aluminum from the chloride melts at 750 °C.

It was demonstrated for the moderate values of \( V_g \) and \( V_m \) that the calculated and observed relationships between the bath voltage and the applied current density are fairly in good agreement. However, with increases in both the values of \( V_g \) and \( V_m \), the calculated relationships tend to deviate gradually from the observed ones. This means that the by-pass resistance, \( R_g \), in the equivalent circuit (3) might be changed because of the heterogeneous distribution of by-pass current in the periphery clearance of the bipolar electrode cell.
It is worthwhile to note from the point of view for saving energy that the applied current should exist within the linear relationships between the bath voltage and the applied current, and the cell design parameters such as $V_g$, $V_m$, $i_0$ and $i_T$ should be selected as low as possible to avoid decrease in the cell efficiency of the bipolar electrode cell and increase in the bath voltage.

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Figure 1  Circulating Path of Melt and Gas in the Bipolar Electrode Cell.

Figure 2 Constitution of Total Sectional Area in the Bipolar Electrode Cell.

Figure 3 An Example of Horizontal Sections of the Bipolar Electrode Design.

Figure 4 Schematic Diagram of Experimental Apparatus.
Figure 5 Relationship between Bath Voltage and Applied Current Density for the Design Cell.

Figure 6 Relationship between Upper Current Density and Ratio of Melt to Gas.