— Technical Paper —

Improvement of Chlorine Electrode in Al-Cl₂ Cell in NaCl-KCl Melt by Rotation

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Received November 30, 1998; Accepted February 9, 1999

To decrease the reaction polarization of the cathodic reaction of $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ in Al-Cl₂ electrochemical cell in NaCl-KCl melt at 1023 K, we developed a cell system with a vertically rotating electrode composed of sliced graphite disks which are partially immersed in the melt. The apparent reaction resistance of the cathodic reaction was evaluated from transient potential and current changes of the cell. The reaction resistance decreases with an increase of the number of the graphite disks. The resistance is a function of the rotation rate of the electrode and exhibits the minimum value around a rotation rate of 20 rpm. The dependence on the rotation rate may be explained from Cl₂ concentration in a thin melt layer formed on the graphite electrode during exposure to Cl₂ gas phase. The rotation may introduce a continuous supply of the thin melt layer with a high concentration of Cl₂ to a reaction place at a meniscus part on the graphite electrode. However, if the rotation rate is too high, the exposure time of the thin melt layer to Cl₂ gas is not enough to establish an equilibrium concentration of Cl₂ in the layer.

Key Words: Al-Cl₂ Cell, Molten Salt, Rotating Electrode, Chlorine Electrode

1 Introduction

We have proposed a cycle system for aluminum in which aluminum scrap is electrochemically recovered to pure aluminum.¹⁻³⁾ The system is schematically shown in Fig. 1. In the proposal the process for the recovery consists of three stages; (1) chlorination of aluminum scrap in a molten salt to form aluminum chloride, (2) purification of aluminum chloride by sublimation, (3) electrowinning of pure aluminum from aluminum chloride. In the system chlorine gas, Cl₂, evolved in the stage (3) is used in the stage (1). For chlorination in the stage (1) we operate an electrochemical cell (Al-Cl₂ cell) in molten salt of NaCl-KCl with the following reactions.

The electric power from the cell is available as a supplement for operating the process of electrowinning of aluminum in the stage (3). In order to establish this system for the cyclic use of aluminum with relatively low cost, the performance of the electrochemical cell of Al-Cl₂ should be mostly improved.

Since reaction rate of the cell is reported to be

limited by the cathodic reaction (2) of Cl₂ to Cl⁻,¹⁾ large enhancement of the reaction rate is necessary to improve the cell performance. It was shown by Konda *et al.*¹⁾ and Knutz *et al.*⁴⁾ that the reduction rate of Cl₂ to Cl⁻ is controlled by diffusion of Cl₂ in the melt and that the reduction takes place mainly at the meniscus formed on the wall of graphite electrode

Fig. 1 Flow chart of an electrochemical cycle system for reproduction of pure aluminum from scrap aluminum.

above a contact line of the gas / melt interface. At the meniscus, a thin melt layer is formed on the wall of graphite electrode and an easy diffusion path of Cl_2 from gas phase to the electrode is created. In the upper part of meniscus far from the gas / melt interface, however, the diffusion of the reduction product, Cl^- , to the bulk of melt is very limited and the large ohmic resistance of the thin melt layer at the meniscus interferes the current flow. Accordingly reaction current is concentrated at the meniscus in the neighbor of the contact line of the gas / melt interface on the graphite electrode. Konda *et al.* further measured output power under a constant load of the cell in which the level of melt surface was moved up or down:¹⁾ When the level is raised, the output power increases; however, when it is reduced, the power decreases. This behavior may be explained as the illustration of Fig. 2. Movement of the melt surface level introduces a new thin layer at the gas / melt interface on the wall of graphite electrode. During the upward movement the new thin layer contains Cl_2 at a high concentration which was in equilibrium with Cl_2 pressure at gas phase.⁵⁾ However, during the downward movement it contains Cl_2 at a relatively low concentration, because the concentration at the thin layer was in equilibrium with that of Cl_2 at the bulk of melt. The difference in the output power between the upward and downward movement is thus considered to reflect difference in concentration of Cl_2 at the thin layers formed in the neighbor of gas / melt interface. From the results of Konda *et al.*¹⁾ it is seen that the upward movement of melt surface

Fig. 2 Schematic diagram of Cl_2 reduction during upward (top) and downward (bottom) movements of the melt.

level relative to the electrode wall is mostly effective for obtaining high output power. Since the continuous rise of surface level of melt is not easy for ordinary cells, a relative movement of melt surface level to electrode should be artificially brought about by other techniques.

In this paper we adopt a vertically rotating carbon electrode for Cl_2 reduction for obtaining the relative movement of melt surface level. The renewal thin layer formed on the wall at the rotating electrode contains Cl_2 at a high concentration in equilibrium with Cl_2 pressure during exposure to gas phase and thus the new cell system exhibits a high efficiency. We report here the improvement of cell current-overvoltage relation by using the rotating graphite electrode for the cathodic reaction of Cl_2 to Cl^- .

2 Experimental

Schematic diagram of experimental apparatus with the rotating graphite electrode as a cathode is shown in Fig. 3. The electrolytic cell is made of quartz tube and cell bottom end is closed with fused salt of electrolytic melt. The size of the cell is about 115 mm diameter and 280 mm length. The cell is placed in an electric furnace which has a window for observation of inside of the cell during experiment. A small pocket is installed in the quartz tube to receive the melt flowing out through the rotating electrode. The melt stored in the pocket overflows to the cell during

Fig. 3 Schematic diagram of Al-Cl_2 cell with a rotating electrode composed of sliced graphite desks. The disks are partially immersed in NaCl-KCl melt.

the prolonged experiment. The rotating electrode is inclined at 10 degree. One side of the rotating axis is set on the small pocket and the other side is connected to motor for rotation. The electrode is rotated in a range from 4 to 70 rpm. The rotating graphite electrode consists of sliced graphite disks (Tokai Carbon Co. Ltd., EE-250), the number of which are 11 (electrode A) and 14 (electrode B). The diameter of the disk is about 60 mm. The geometric lengths of the contact line of gas/melt interface on the graphite disk electrodes were, 0.68 and 0.84 m for A and B, respectively, which were calculated from the size and the number of the disks. Chlorine gas, Cl_2 , is introduced from quartz cover into the cell. The level of the electrolytic melt is controlled by changing gas volume of Ar introduced from a gas inlet in Fig. 3. Aluminum is placed on graphite crucible and used as an anode.

The electrolytic melt used was an equimolar mixture of NaCl-KCl containing 2 mol % AlCl_3 at a temperature of 1023 K (750 °C). We measured transient changes of the cell voltage and current between the anode and cathode during switch-on and -off of a constant-load circuit. The transient changes were recorded by a digital logger, Hioki 8851.

3 Results and Discussion

The potential drop under constant load operation from an open circuit voltage of the cell consists of three polarizations; the first is a reaction overvoltage at the anode for reaction (1), the second a reaction overvoltage at the cathode for reaction (2), and the third an ohmic overvoltage in the melt. As previously reported¹⁾ the reaction overvoltage for the anode is so small that we can neglect the contribution to the potential drop. Two remaining overvoltages can be divided by a measurement of potential transient responding to the switch-on or -off of the shunt circuit with a constant load. The ohmic overvoltage was calculated from an instantaneous change after the switch-off of the circuit and the cathodic reaction overvoltage from a graduate change afterward. Figure 4 shows the overvoltage of the cathodic reaction thus obtained as a function of current for the electrode (A). The current range to 4 A in Fig. 4 corresponds to a range of $8 \times 10^{-3} \text{ A cm}^{-2}$ with assuming a total surface area of the disk electrodes. If the reaction place is assumed to be only meniscus parts at the gas/melt interface, as previously described, the current at 4 A may correspond to $59 \times 10^{-3} \text{ A}$ per unit meniscus length in cm. As seen in Fig. 4 the rotation of electrode induces smaller overvoltage than that without rotation; for example, the overvoltage at 20 rpm rotation is as small as the

Fig. 4 Overvoltage for the reaction of Cl_2 to Cl^- on the rotating electrode as a function of cell current.

two-third at 0 rpm. This decrease of the overvoltage is due to continuous supply of Cl_2 by rotation as discussed later.

If we assume that the reaction resistance does not depend on current, for the sake of convenience, we can calculate an average reaction resistance for the cathodic reaction from the current-overvoltage relation as a function of the rotation rate.

The dependence of the apparent reaction resistance on rotation rate is shown in Fig. 5. The reaction resistance under rotation state becomes smaller than that of under stagnant state (*ie.* 0 rpm). The reaction resistance of electrode B exhibits a smaller value than that of electrode A. This result is explained from different length of the gas/melt interface on the graphite disk electrodes. The result on the influence of the length on the reaction resistance is in agreement with those of Konda *et al.*¹⁾ and Kitamura *et al.*^{6,7)}

The reaction resistance for the cathodic reaction

Fig. 5 Dependence of the apparent reaction resistance on rotation rate for the rotating electrodes consisting of 11 graphite disks (electrode A) and 14 disks (electrode B).

around 20 rpm exhibits the minimum value in the both electrodes as seen in Fig. 5. This rotation corresponds to a linear velocity about 63 mm s^{-1} at the most outside of the disk electrodes. When the rotation rate increases at the higher than 20 rpm, the reaction resistance increases again. The dependence of the resistance on rotation rate can be explained from exposure time to Cl_2 gas phase of the thin melt layer formed on the rotating graphite disks of electrode. A schematic illustration of the rotating disk is shown in Fig. 6(a) where about a quarter of the disk is immersed in melt and the other three quarters are exposed in gas phase. When the disk electrode is rotated, a thin layer of the melt may covers the disk electrode in gas phase. Cl_2 in gas phase can dissolve into the thin melt layer, so that concentration of Cl_2 in the thin melt layer may increase with exposure time to gas phase as shown in Fig. 6(b). The reaction rate

Fig. 6 (a) Schematic illustration of a rotating disk electrode of graphite partially immersed in the melt. (b) Changes of concentration of Cl_2 and thickness of the thin melt layer formed on an exposure part of the rotating graphite disk electrode as a function of exposure time to Cl_2 gas phase.

of Cl_2 to Cl^- is proportional to the concentration of Cl_2 , $C(\text{Cl}_2)$, in the thin melt layer, the thickness, d , of the thin melt layer, and the length, l , of the gas / melt interface with a width, w , in contact with the disk electrodes.

$$r = kC(\text{Cl}_2)dlw \quad (3)$$

The thickness of the thin melt layer is probably functions of exposure time of gas phase and of linear velocity of the disk, both of which are determined by the rotation rate and viscosity of the melt. We believe from consideration of the viscosity value of the melt that the decrease of thickness takes place only in the initial stage of exposure time and that the thickness is almost constant after the prolonged exposure time, as shown in Fig. 6(b). Since the length of the gas / melt interface on the disk electrodes is geometrically determined, the reaction rate is greatly influenced by Cl_2 concentration, $C(\text{Cl}_2)$ in the thin melt layer. When the thin melt layer reaches the gas / melt interface, the reaction of $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ can start. As long as the thin melt layer containing Cl_2 on the disk electrode is in gas phase, however, the reaction of Cl_2 to Cl^- in the thin melt layer does not take place at a significant rate because of the large ohmic and large diffusion resistances, as previously mentioned. When the rotation rate increases, for example, at more than 20 rpm in Fig. 5, the reaction resistance increases again. The increase may be explained from a not enough exposure time of the thin melt layer to Cl_2 gas. The increase of the resistance is thus due to a relatively low Cl_2 concentration in the thin melt layer, $C(\text{Cl}_2)$. To establish an equilibrium concentration of Cl_2 in the thin melt layer an enough long time period for exposure to Cl_2 gas may be necessary. For a rotation rate of 20 rpm, the exposure time is estimated to be about 2 s from the cell geometry. The minimum exposure time period for obtaining the equilibrium concentration may be about 2 s (ie. the rotation rate at about 20 rpm). If the exposure time period is shorter than 2 s, ie., the rotation rate higher than 20 rpm, the Cl_2 concentration of the thin melt layer does not reach the equilibrium value.

4 Conclusions

To decrease the reaction overvoltage of the cathodic reaction of $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ in Al-Cl_2 cell in NaCl-KCl melt at 1023 K, we developed a cell system with a vertically rotating electrode composed of sliced graphite disks which are partially immersed in the melt.

(1) The reaction resistance for the cathodic reaction decreases with an increase of the number of the

graphite disks.

(2) The reaction resistance decreases with the rotation rate of the electrode and exhibits the minimum value around a rate of 20 rpm. The further increase of the rotation rate brings about an increase of the reaction resistance.

(3) The dependence on the rotation rate may be explained from Cl_2 concentration in the thin melt layer formed on graphite electrode during exposure to Cl_2 gas phase: rotation may introduce a continuous supply of the thin melt layer with a high concentration of Cl_2 to a reaction place at the meniscus part on the graphite electrode. However, if the rotation rate is too high the exposure time of the thin melt layer to Cl_2 gas is not enough to establish an equilibrium concentration in the layer.

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