New Molten Salt Electrolysis Using Plasma Arc Electrode

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Conventional smelting with a carbon reductant is not used to obtain metals with high affinity for oxygen. Molten salt electrolysis is often used for the extraction of such metals. Although no carbon dioxide emission is expected in principle, huge amounts of CO₂ are generated in actual molten salt electrolysis, where graphite electrodes are used as anodes. This is why the graphite is an indispensable material for high-temperature molten salt. For example, more than 1.2 tons of CO₂ are emitted per 1.0 ton production of aluminum in a conventional molten salt electrolysis. We are developing a CO₂-free process using arc electrodes. Alumina (Al₂O₃) mixed cryolite and AlF₃ are used as test materials. Electrolysis is conducted in a stainless steel chamber under an inert Ar atmosphere. The arc is generated as a gaseous anode using a water-cooled plasma torch in constant current mode. The production of aluminum was confirmed by the experiment.

Key Words : Molten salt, Electrolysis, Anode, Plasma arc, Aluminum, Aluminum Oxide

1. Introduction

It is not easy to obtain metals with high affinity for oxygen by conventional smelting processes using carbon reductant. Molten salt electrolysis methods are often used for smelting of such metals. Although in principle, no emission of carbon dioxide is expected in molten salt electrolysis, huge amounts of CO₂ are generated in actual processing, where graphite electrodes are used as anodes. This is why the graphite has been considered as an indispensable material for the processing of the molten salt at high temperature.

In a molten salt bath of metallic oxide, M_mO_n is dissociated as

Under an applied electric field, metallic ions and oxygen ions move

toward negative poles and positive ones, respectively. At cathodic electrodes

At anodic electrodes, which comprise carbon materials,

and

and/or

Thereby more than 1.2 tons of CO₂ are emitted in the production of

Figure 1 Schematic illustration of conventional molten salt electrolysis using graphite electrode.

Figure 2 Conceptual diagram of new molten salt electrolysis using reverse polarity DC arc electrode.

one ton of Aluminum using electrolysis processes.

Present work was intended to develop CO₂-free electrolysis, replacing solid anodes with gaseous anodes. Experiment was carried out using aluminum oxide. A conventional process with solid graphite anode and a process with a gaseous arc anode are depicted in Figure 1 and Figure 2, respectively.

Few studies have described such trials. Taylor and Wang investigated smelting of Cr₂O₃⁽¹⁾ by the similar CO₂-free process and Larson and Eager proposed Ti production processes⁽²⁾ by the method.

2. Experiment

2.1 Experimental Arrangement

The experimental apparatus consisted of the reactor assembly and reverse-polarity DC plasma torch assembly as shown in Figure 3. All experiments were performed in a water-cooled stainless steel chamber to maintain the inert atmosphere.

The mold was made of graphite in shape with a height of 120 mm, inner diameter of 100 mm and outer diameter of 120 mm. As shown in Figure 4, it was thermally insulated by ceramic fiber wool to minimize heat loss. A 6-mm-diameter copper rod was placed in the graphite mold to fire the arc.

The water-cooled plasma torch portrayed in Figure 5 comprises a tungsten rod electrode (anode) and a ceramic nozzle, which gives the arc definition and serves to direct the arc to an external cathode

Figure 3 Schematic illustration of the experimental apparatus.

Figure 4 Arrangement of the graphite mold and the plasma torch.

Table 1 Composition of the material used in experiments.

Substance	Chemical formula	Mass fraction
Cryolite	Na_3AlF_6	0.90
Aluminum fluoride	AlF_3	0.05
Alumina	Al_2O_3	0.05

(molten salt). The arc was operated in a DC transferred mode. Argon gas was introduced as the plasma gas into the torch at the mass flow rate of 0.45 g/s. The torch was mounted on the top of the stainless steel chamber.

The plasma torch and the graphite mold were electrically connected to the positive and negative poles of the DC power supply (SS-120P; Daiden), respectively.

2.2 Material

The starting material was a mixture of reagent grade α type- Al_2O_3 powder (certified purity, 99.0 mass %), reagent grade cryolite, Na_3AlF_6 , (certified purity, 90.0 mass %) and reagent grade of aluminum trifluoride, AlF_3 (certified purity, 98.0 mass %). The composition of material is shown in Table 1, which is similar to that used in conventional electrolysis process. The presences of Na_3AlF_6 and AlF_3 contribute to reduce the melting temperature of the material. The melting temperature of the mixed material is 1253 K⁽³⁾, which is much lower than that of pure alumina (2327 K). After weighing the three reagents, the mixture was sintered at 1000 K. The sintered material was crushed into small pieces.

2.3 Experimental Procedure

The pieces of the crushed sintered material were put into the mold. Then the mold was placed in the reaction chamber. The torch position was adjusted at 2 mm above the copper rod. Before the arc started, the air in the chamber was replaced with argon gas. Immediately thereafter the arc ignition, the torch position was shifted to 40 mm above the copper rod. To prevent the reactor assembly from heat shock, the arc was started at the current of 30 A and gradually increased to 80 A. The variations of the arc current and the arc voltage were recorded with time. So far as the initial material is in a solid state, it is not electrically conductive. In this situation, the arc was produced between the torch and the copper rod. The melting of the copper rod resulted in the melting of surrounding material because the melting temperature of the material (1253 K) is lower than that of copper (1357 K). When the layer of molten material (molten salt) was formed above the copper, the electrolysis of alumina started as shown in Figure 6. In the molten pool, aluminum ions (actually complex aluminum ions) moved toward the copper, at the surface of which the ions turned to aluminum atoms then they were reacted with copper melt into Cu-Al alloy. After the certain time of electrolysis operation, the arc was shut off and the material was cooled for 1 hour in the chamber.

Figure 5 Photograph of the plasma torch used in this study.

Then, metal product (Cu-Al alloy) was extracted from the slag.

The product metal was dissolved by the aqua-regia solution. The obtained solution was analyzed using inductively coupled plasma mass spectroscopy (iCAP 6500; Thermo Fisher Scientific Corp.). The amount of metallic aluminum produced by electrolysis was evaluated from measurements of Al concentration in the alloy product.

3. Results and Discussion

It was observed that the reverse polarity arc was stably terminated on the molten slag surface as shown in Figure 7. In other words, the arc was confirmed to serve as an anode for the molten slag. A typical variations of the arc current and the arc voltage with time is portrayed in Figure 8, where the drastic voltage increase was observed from 50 V to 120 V at 50 s. The increase of the voltage was attributed to the presence of molten slag above the copper. Namely, the electrolysis started at 50 s. The surface level of the molten slag fluctuated with time. The sudden decrease in the arc voltage at 130 s in Figure 8 might be resulted from the termination of the arc on the copper for the short time.

Figure 9 shows the metallic product obtained by the arc operation for 290 s. The increased mass from the original copper rod of 15.69 g to the final product of 16.64 g indicates that the amount of metal produced by the electrolysis was 0.95 g. Table 2 portrays results of chemical analysis for Al and Na using ICP mass spectroscopy. The amount of Al estimated from Table 2 was 0.98 g. Agreement between the weight measurement and chemical analysis was good.

The current efficiency of the arc-driven electrolysis can be

Figure 6 Schematic illustration of experimental procedure: (a) initial state without arc, (b) early state with arc which terminates on the copper rod and (c) steady state where the electrolysis occurs.

Figure 7 Photograph of reverse polarity arc observed through the viewing window.

Table 2 Chemical composition of the metallic product analyzed by ICP mass spectroscopy.

Al	Na
5.69 [mass %]	0.055 [mass %]

estimated from Figure 8. The following relation should be satisfied between the amount of Al (W) obtained during the electrolysis and total aluminum ions (Q) transferred through the molten salt.

$$W = \frac{M}{F} \cdot Q \quad (6)$$

In that equation, M is the aluminum molar mass, n_v is the aluminum ionic valency, and F is the Faraday constant. If the efficiency of current contributed to the electrolysis is expressed as η , then

$$Q = \frac{\eta}{n_v} \int I dt. \quad (7)$$

Therefore,

$$W = \eta \frac{M}{n_v \cdot F} \int I dt. \quad (8)$$

As shown in Figure 8, the electrolysis is assumed to start at 50 s after the arc ignition and end at 290 s. The total charge driven by the arc was predicted as 18150 Coulomb according to the integral

Figure 8 Variations of arc current and arc voltage with time.

Figure 9 Al-Cu alloy obtained by molten salt electrolysis using arc electrode.

of Eq. (7) from $t=50$ s to $t=290$ s. Using the experimental result of $W=0.95$ g, the current efficiency η was estimated as 0.56. It is known that the current efficiency was 0.85-0.95 in a conventional process. The reason why the efficiency was low in the present work has not yet been clear. Further study should be done.

4. Conclusions

Fundamental experiments of the arc driven electrolysis were carried out for alumina base molten slag. It was confirmed that the reverse polarity arc stably terminated on the surface of the molten slag. Aluminum was successfully obtained using plasma arc electrode. It means that consumable solid electrode of a graphite cathode can be replaced by a gaseous arc electrode. In conclusion, the possibility of CO₂-free process in molten salt electrolysis was confirmed. The current efficiency was estimated to be 0.59 in the

present experiment. The reason why the efficiency was low in the arc process has not yet been clear. Further study should be done.

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