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Recovery of aluminum from oxide particles in aluminum dross using AlF_3–NaF–$BaCl_2$ molten salt

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Abstract

To recover aluminum from aluminum dross, a floating separation of aluminum alloy from the oxides and subsequent electrolysis of the oxides was carried out in a molten salt bath of 33 mol% AlF_3, 51 mol% NaF and 16 mol% $BaCl_2$. With A356.0 casting alloy dross, 83% of the aluminum alloy was recovered by the floating separation. A further 4% of metallic aluminum was recovered by electrolysis in the molten salt containing the oxides separated from the dross. The optimum current for continuous operation is discussed considering a balance between the electrowinning and dissolution rates.

1. Introduction

Aluminum dross is generated during casting of aluminum or in remelting for recycling of aluminum. The dross contains aluminum oxide, aluminum alloys, and a small amount of the oxides of additive elements, and 0.2 million tons per year is generated by at the aluminum casting and melting in Japan [1, 2]. At present, the dross is collected mechanically from the surface of the liquid aluminum alloy during melting. Dross includes considerable amounts of aluminum alloy in addition to aluminum oxide, and it has been utilized as a deoxidation agent in steel making, as a refractory material, and as a cement material. Ohnishi et al. [3] reported that the aluminum in dross is used for reduction of nickel oxide by the Thermit reaction, but much larger volumes of dross are reclaimed in reclaimed land, and there will be limitations in the reclaimed land areas in the future. Therefore, the development of a new process in which dross is converted to useful materials is desirable. The authors have proposed such a process in which aluminum metal is reproduced from the dross using a molten salt [4]. The process consists of two steps. First, aluminum alloy is collected by separation from the dross in a molten salt by the differences in densities of aluminum alloys and oxides. In the second step, pure aluminum is extracted from the remaining oxide by electrolysis in a molten salt. A previous paper, reporting on the first step, showed that aluminum alloy was effectively separated from the oxide particles in a molten $BaCl_2$–NaCl–NaF salt mixture at a ratio of about 85 mass% of dross [4]. The metal oxide remaining in the molten salt contains a large amount of aluminum oxide, and in the second step of the electrolysis, the extraction rate of alumina should be balanced by the dissolution rate of the solid oxide of γ-Al_2O_3 into the molten salt to maintain continuous extraction. In the present paper, we change the composition of the molten salt from the $BaCl_2$–NaCl–NaF system to a AlF_3–NaF–$BaCl_2$ system, in order to proceed the floating separation between the aluminum alloy and oxides followed by electrowinning to metallic aluminum. The densities of both molten salts were controlled to be above that of metallic aluminum, here 1073 K. The electrolysis conditions are examined under which the dissolution rate of the oxide particles is balanced with the deposition rate of aluminum in the electrowinning.

2. Experimental

Chemical reagent γ-Al_2O_3 was used as the model oxide for the aluminum dross for the measurements of the dissolution rate of oxides into the molten salt. In addition, an aluminum dross which was produced in the casting process of ASTM A356.0 alloy (A356.0 dross) was employed, the composition of the ASTM A356.0 alloy is shown in Table 1.

A molten salt of 33 mol% AlF_3, 51 mol% NaF and 16 mol% $BaCl_2$ was used for the electrolysis of alumina

Table 1. Composition of the A356.0 alloy and floating aluminum alloy

Component	A356.0 alloy (w_A/mass%)	Floating aluminum alloy (w_F/mass%)
Al	90.7	93.2
Si	6.5–7.5	6.5
Mg	0.2–0.8	0.2
Other	<1.0	<0.1

to aluminum metal. To measure the dissolution of γ-Al_2O_3 into the molten salt, the salt of 250 g was melted at 1073 K in a high purity 42 mm diameter alumina ceramic tube, and 4 g of γ-Al_2O_3 as the model oxide was added. The oxide was mostly precipitated in the molten salt. After stirring the molten salt by a tungsten rod, a small part of the molten salt was sampled without the dispersed solid oxide every hour by a platinum sampler. The molten salt sample solidified into a pellet, and the aluminum concentration of the pellet was measured by X-ray fluorescence analysis (JEOL JCX-3220Z).

Figure 1 illustrates the equipment for the electrolytic extraction of metallic aluminum. Graphite rods, 16 mm in diameter were used as the test electrode and counter electrode, and pure aluminum rod was used as the reference electrode. The salt mixture, 700 g, was melted at 1073 K in the graphite crucible surrounded by a high purity alumina ceramic tube with 60 mm in inner diameter and 130 mm height. Alumina (γ-Al_2O_3), 20 g, was added to the molten salt. A polarization curve was measured under galvanostatic conditions in the 5–130 mA cm^{-2} current range.

Extraction of metallic aluminum from the A356.0 dross was also attempted with this process. The A356.0 aluminum dross, 120 g, was prepared as described in the previous paper [4]. The aluminum alloy was first separated as in the previous paper, then the oxide remaining in the molten salt was electrodeposited on metallic aluminum by the same procedure as above.

The aluminum alloys separated from the oxide or electrodeposited by electrolysis were analyzed with ICP atomic emission spectroscopy (Seiko instrument SPS-3000) after dissolution in 6 mol dm^{-3} HCl.

3. Results

3.1. *Separation of aluminum alloy from oxide in the molten salt*

As in the previous paper, A356.0 alloy dross was separated into aluminum alloy and oxides; 120 g of the

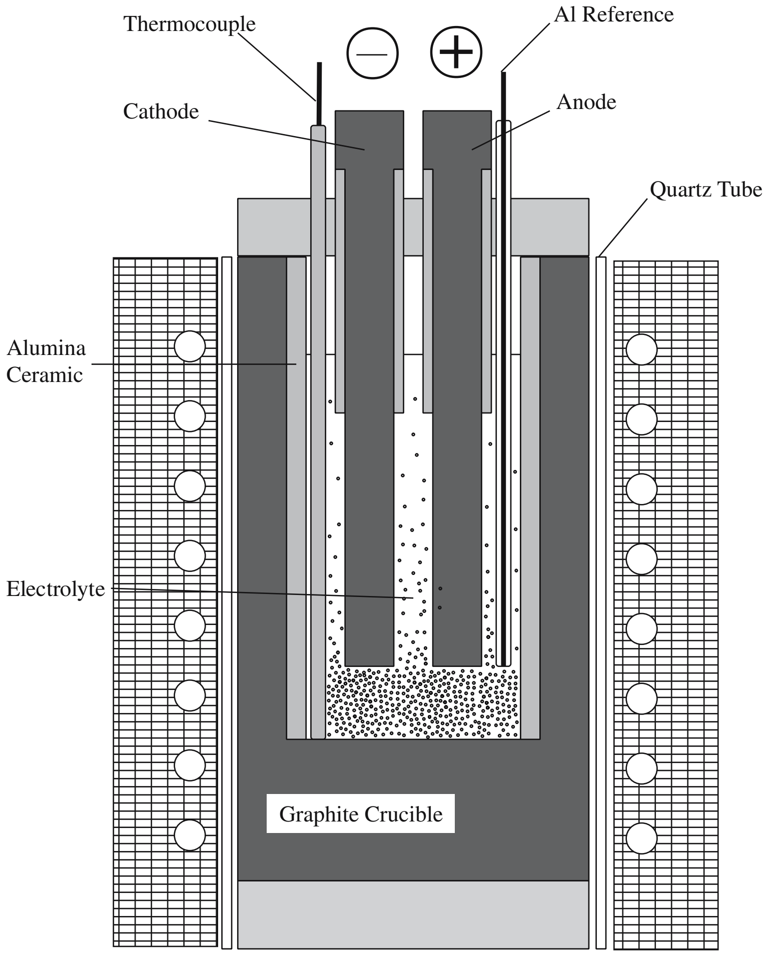

Fig. 1. Schematic illustration of the electrochemical cell.

A356.0 alloy dross was added to the molten salt, and stirred for 300 s. After 900 s of stagnation for 99.2 g of the aluminum alloy floated to the molten salt surface. The alloy floating on the molten salt was analyzed by ICP-AES, and as shown in Table 1, the composition of the aluminum alloy was very similar to that of the A356.0 alloy.

3.2. *Concentration changes of aluminum in the molten salt*

The initial concentration of aluminum ions in the molten salt was determined to be 10.8 mass%, which corresponds to the weight ratio of aluminum ions in the mixture of the AlF_3, NaF and $BaCl_2$ salts. The change in aluminum concentration in the molten salt with time after the addition of alumina (γ-Al_2O_3) is shown in Figure 2. The amount of aluminum dissolving from the alumina into the molten salt saturated in one hour following the addition of alumina. At saturation, the aluminum ions concentration in the molten salt increased by about 0.6 mass%.

3.3. *Concentration change of aluminum ions in the molten salt during electrolysis*

The concentration of aluminum began to decrease when cathodic deposition started at a constant current. The concentration change of aluminum ions in the molten salt during electrolysis is shown in Figure 3. The aluminum concentration increased by 0.6 mass% and was saturated in one hour as previously mentioned. When electrolysis was started at a constant current of 15 A, the aluminum ion concentration decreased to 10.3 mass% after three hours. This decrease shows that the rate of electrodeposition of aluminum from dissolved aluminum ions is higher than the dissolution rate from alumina (γ-Al_2O_3) particles into the molten salt in Figure 3. When the electrolysis was stopped, the aluminum concentration increased to almost the same level as before the electrolysis due to dissolution of alumina particles. The amount of metallic aluminum electrodeposited at 15 A for 3 h (162 kC) was 11.8 g, and the purity of the electrodeposited aluminum was determined as 99.9% by ICP atomic emission spectroscopy, and the calculated current efficiency was 78% for the applied electricity of 162 kC. This low current efficiency may be due to a side reaction between electrodeposited aluminum and CO_2 evolved by the electrolysis.

$$2Al + 3CO_2 \rightarrow Al_2O_3 + 3CO \qquad (1)$$

It may also be that a current of 15 A is not optimum for the continuous electrowinning of metallic aluminum for long periods of time. The electrowinning current may need to be decreased to achieve balance with the dissolution rate of the aluminum oxide.

3.4. *Polarization measurements*

The current–potential relation (polarization curve) was measured under galvanostatic conditions in the molten salt, and Figure 4 shows two polarization curves in the anodic region where carbon dioxide or chlorine evolution may occur. One is the polarization curve in the molten salt not containing alumina, and the other is the curve measured 3 h after the addition of alumina particles and where aluminum ions may be saturated. Before the addition of alumina (solid line), the open circuit potential of the aluminum electrode is 1.5 V (Al/Al^{3+}), and the anodic reaction is chlorine gas evolution

$$2Cl^- \rightarrow Cl_2 + 2e \qquad (2)$$

where the potential–current density curve is very steep. When alumina has been added and has dissolved in the molten salt (dotted line), carbon dioxide evolution occurs in addition to chlorine gas evolution

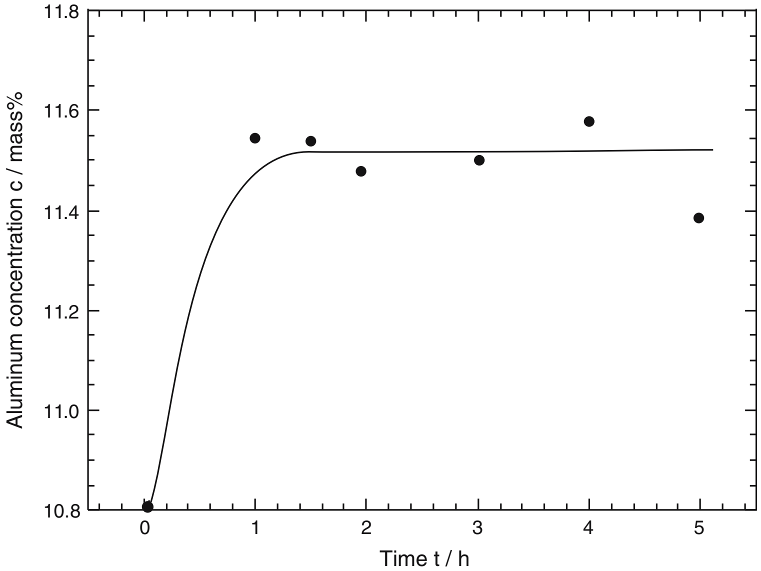

Fig. 2. Time change in the concentration of aluminum ions in the molten salt after addition of alumina.

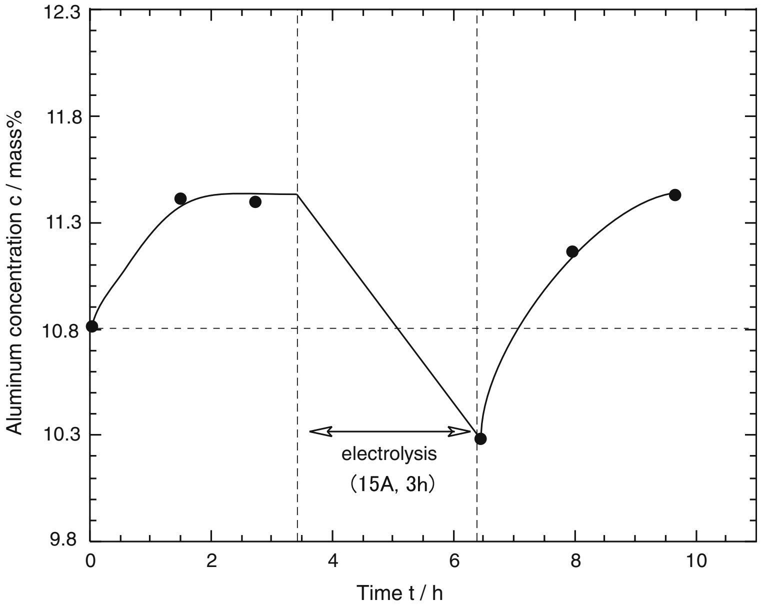

Fig. 3. Time change of concentration of aluminum in the molten salt before and after the electrolysis.

$$C + 2O^{2-} \rightarrow CO_2 + 4e \quad (3)$$

and the anodic overvoltage is smaller than before the alumina addition.

On the curve measured 3 h after the addition of alumina, the anodic reaction is different from that before alumina addition at a current density of about 0.02 A cm^{-2}. Above 0.02 A cm^{-2}, there is preferential chlorine gas evolution, when alumina has not been added because the concentration of oxide ions in the molten salt is low. When chlorine gas evolution is the main cathodic reaction, the composition of the molten salt is greatly changed during the electrolysis. At current density lower than 0.02 A cm^{-2}, the preferential reaction changes to carbon dioxide evolution. When we consider continuous extraction of metallic aluminum, the composition of the molten salt must be kept constant, and so a current density below 0.02 A cm^{-2} is desirable, here carbon dioxide evolution may be expected to occur preferentially.

As the extrapolation of the cathodic polarization curves was in agreement with the potential of 0 V (Al/Al^{3+}), the cathodic reaction may conceivably start with aluminum deposition.

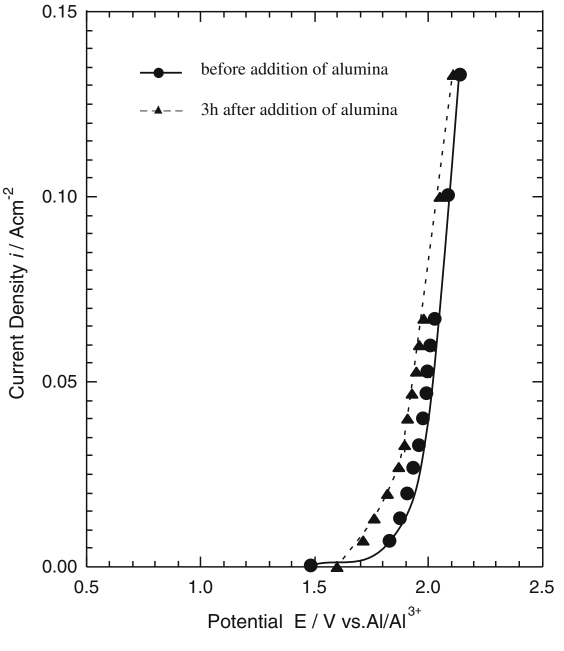

Fig. 4. Anodic polarization curves measured during the experiment in Figure 3 at 0 h (before addition of alumina), and at 3 h (after addition of alumina).

3.5. *Electrowinning of aluminum from A356.0 alloy dross*

Electrowinning of alumina in the molten salt containing the oxides separated from the A356.0 alloy dross in Section 3.1 was attempted by constant current operation. The change in the aluminum concentration in the molten salt during constant current electrowinning at 1.5 A (i.e., 0.02 A cm^{-2}) for 12 h is shown in Figure 5. The aluminum concentration in the molten salt remains constant, but decreases in the final stages of electrolysis. However, the concentration until 8 h in Figure 5 is possibly an overestimate, because the added A356.0 dross particles are very fine and dispersed in the molten salt. When sampling the molten salt for the analysis of the amount of aluminum ions dissolved, some of the very fine particles are possibly collected with the molten salt. At 10 h or longer operation after the addition of the dross, the molten salt changed to become clear and the dispersed dross particles coagulated to settle at the bottom. Although the analysis of the concentration of aluminum ions include some uncertainties, the

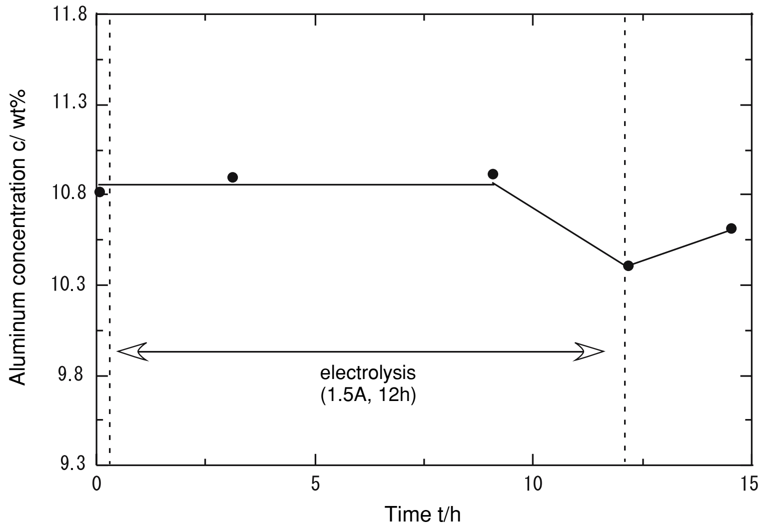

Fig. 5. Time change of concentration of aluminum ions in molten salt containing aluminum dross during electrolysis.

experiments show that the concentration of aluminum ions can be kept constant during electrolysis at a constant current of 1.5 A. After switching off the current, the concentration recovered in 2 h under stagnant conditions. The weight of the collected aluminum was 4.8 g, corresponding to a current efficiency of 79% for 65 kC of electricity consumed.

The purity of the electrodeposited aluminum is listed Table 2. The 98.8% pure electrodeposited aluminum contained 1.1 mass% Si and 0.07 mass% Fe. The Mg content was below the limit of detection.

4. Discussion

4.1. *Ionic species in the molten salt*

In the 33% AlF_3–51% NaF–16% $BaCl_2$ molten salt, aluminum may form complex ions with fluoride [4]. The reactions between AlF_3 and Al_2O_3 in the molten salt have been considered to be the following [5–10].

$$AlF_3 + 3NaF \leftrightarrows AlF_6^{3-} + 3Na^+ \tag{4}$$

$$AlF_6^{3-} \leftrightarrows AlF_4^- + 2F^- \tag{5}$$

$$4AlF_6^{3-} + Al_2O_3 \rightleftarrows 3Al_2OF_8^{4-} \tag{6}$$

Table 2. Comparison of current efficiency and purity of deposit aluminum using raw material of γ-Al_2O_3 and dross from the A356.0 alloy

	Weight of deposit Al (w_{Al}/g)	Electricity (Q/C)	Current efficiency (η/%)	Purity of deposit Al (%)
γ-Al_2O_3 (3 h)	11.7	45	78	99.9
A356.0 (12 h)	4.8	18	79	98.8

$$4AlF_4^- + Al_2O_3 + 8F^- \rightleftarrows 3Al_2OF_8^{4-} \tag{7}$$

Since aluminum ions are considered to form the $Al_2OF_8^{4-}$complex ions in the molten salt, aluminum deposition may preferentially start from the $Al_2OF_8^{4-}$ion.

$$Al_2OF_8^{4-} + 6e^- \rightarrow 2Al + O^{2-} + 8F^- \tag{8}$$

The Al_2O_3 in fluoride molten salt may produce oxygen ion, as in [11]

$$Al_2O_3 \rightleftarrows Al_2O^{4+} + 2O^{2-} \tag{9}$$

$$Al_2O_3 \rightleftarrows 2AlO^+ + O^{2-} \tag{10}$$

On a graphite anode, O^{2-} is oxidized to carbon dioxide as shown by equation (3).

When no alumina particles are added, the electrodeposition of aluminum ions as metallic aluminum takes place according to the following reactions,

$$AlF_6^{3-} + 3e \rightarrow Al + 6F^- \tag{11}$$

or

$$AlF_4^- + 3e \rightarrow Al + 4F^- \tag{12}$$

and the anodic reaction may be the chlorine gas evolution in Equation 2, and this would cause changes in composition of the molten salt.

4.2. *Recovery of metallic aluminum from the dross*

With oxide particles of the A356.0 dross, metallic aluminum can be recovered from the molten salt at the 1073 K. In the present cell containing 700 g of the molten salt, 4.8 g of metallic 98.8% pure aluminum was recovered by 65 kC (1.5 A current for 12 h) of electricity from 20.8 g of oxide particles in the dross. When the electrolysis is continued for longer times, the recovery of metallic aluminum would increases further. The current efficiency for electrowinning was 79%, and the remaining 21% was probably consumed by side reactions between metallic aluminum and carbon dioxide, as described in Equation 1. To enhance of the current efficiency, improvement to the cell structure, electrode configuration etc., will be necessary.

For electrowinning by continuous processing, the electrowinning rate, i.e., the electrolytic current must be balanced by dissolution of the aluminum oxide particles in the dross into the molten salt. Although the current that achieves the balance depends on the cell size and the amount of oxide particles, a current of 1.5 A was the optimum for continuous electrowinning in the present cell configuration. When the electrowinning was performed at a current of 1.5 A, the concentration of aluminum ions in the cell was almost constant, as shown by Figure 5. In Table 2, the current efficiency and the purity of metallic aluminum recovered from the alumina (γ-Al_2O_3) and oxide particles sampled from the A356.0 dross are shown. The metallic aluminum electrodeposited from the A356.0 dross included trace amounts of silicon, magnesium and iron.

When the electrowinning process from the oxide particles in the dross is combined with floating separation of the aluminum alloy in the molten salt, 87% of the aluminum in the A356.0 dross is recovered. In the floating separation, liquid A356.0 aluminum alloy was collected in the molten salt of AlF_3–NaF–$BaCl_2$ with an efficiency of 83% by utilizing the differences in densities of the aluminum alloy and the oxide particles. From the remaining oxide, it would further be possible to extract metallic aluminum of 4% by electrolysis in the same molten salt. With continuous prolonged electrowinning, metallic aluminum and aluminum alloy will be recovered with an efficiency above 90%.

Considering the overall energy needs of the process, the excess heat of the casting process can be used for the preparation of the molten salt and the aluminum alloy recovered by the process here can be used for the casting process. The processes described will lead to decreasing energy inputs.

5. Conclusions

(1) Metallic aluminum was produced from oxide particles from aluminum casting dross by electrolysis in a molten salt of AlF_3–NaF–$BaCl_2$ at 1073 K. By electrolysis at 1.5 A for 12 h, 4.8 g of metallic aluminum was produced from 20.8 g of oxide particles in the dross.

(2) Continuous operation is possible, when the electrolysis current is balanced with the dissolution rate of the oxide particles into the molten salt.

(3) With this system, recover of metallic aluminum from dross can be carried out at low energy cost, when the process is combined with floatation separation of aluminum alloy from the oxide particles in the molten salt.

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