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The electrolysis of Al_2S_3 in $AlCl_3$-$MgCl_2$-NaCl-KCl melts

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The electrolysis of Al_2S_3 has been investigated in $AlCl_3$–$MgCl_2$–NaCl–KCl melts. Experimental results obtained at 1023 K show that dissolved Al_2S_3 can be electrolysed to give aluminium and elemental sulphur. It has been found that the limiting current density for the electrolysis of Al_2S_3 in these melts is that at the anode and it increases with increasing Al_2S_3 concentration. It appears that within the current density range 0.2 to 1.2 A cm^{-2}, the cathodic current efficiency of the electrolysis of 5 wt% Al_2S_3 does not vary significantly with the current density. Within that current density range, current efficiencies of about 75 to 85% are obtained.

1. Introduction

The Hall-Héroult process for the production of aluminium by the electrolytic reduction of alumina dissolved in molten cryolite has remained essentially unchanged since its inception and is still the only process in commercial use. One of the most important disadvantages of the process is its relatively low energy efficiency. The energy cost for the production of aluminium is about 36% of the metal price [1], compared with 5.3% for copper, about 8% for zinc and lead, and 16% for steel. With the continuing shortage of energy, both currently as well as in future projections, the aluminium industry will clearly be at a disadvantage.

Extensive efforts have been made by the aluminium industry to reduce its energy consumption by improving the Hall–Héroult cell. In 1979, the Aluminium Association reported a 10.33% reduction in the amount of energy needed to make one kilogram of aluminium compared to the base year of 1972 [2]. The aluminium industry and other organizations are also actively engaged in research and development work focused on developing new technologies which could achieve higher energy efficiency. To date, only the Alcoa Smelting Process (ASP) in which aluminium is produced by the electrolysis of aluminium chloride in a molten chloride electrolyte shows promising energy and economic advantages over the Hall–Héroult process. A 15 000 ton/year pilot plant has been in operation in Texas since 1976 [3].

A recent survey conducted by Arthur D. Little, Inc. [4] for Argonne National Laboratory (ANL) has critically evaluated potential alternative processes for the production of aluminium. One of the major conclusions of the survey is that the only alternative technology at present which can compete in electrical energy consumption with the Hall–Héroult process is the ASP. However, for long-term research and development, aluminium sulphide and probably aluminium nitride electrolysis may offer potential advantages. Preliminary thermodynamic assessment [5] has indicated that the aluminium sulphide electrolysis could be a low energy alternative for the production of aluminium. The projected energy consumption for the process (7.0 kWh kg^{-1} Al) compares favourably with that of the conventional Hall–Héroult process (14.1 kWh kg^{-1} Al) and even with the figures indicated for the ASP (9.9 kWh kg^{-1} Al). To assess the feasibility of the proposed process, an experimental programme to study the electrolysis of Al_2S_3 in molten salts has been carried out at ANL.

The electrolysis of molten baths containing Al_2S_3 is not a new idea. The proposed use of a solution of aluminium sulphide in a fused salt electrolyte for the extraction of aluminium goes back to the late 19th century. In 1892, Bucherer [6] took out a patent for the electrolysis of sodium

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aluminium sulphide ($Na_6Al_2S_6$) in an electrolyte of alkali or alkaline earth fluorides or chlorides. Aluminium Industrie A.-G. [7] recommended aluminium sulphide instead of sodium aluminium sulphide. In the 1930s, German and Russian scientists initiated a revival of research into the aluminium sulphide electrolysis [8–11]. Those investigators carried out the electrolysis of Al_2S_3 in a mixture of cryolite with NaCl, and the maximum current efficiency obtained was reported to be about 55%. In 1976, the Light Metal Smelters Association of Japan undertook basic studies on the production of aluminium electrolytically from aluminium sulphide [12]. Their effort was later discontinued, it is believed, due to some problems encountered during their electrolysis work.

The electrolysis of Al_2S_3 has been investigated in $MgCl_2$–NaCl–KCl eutectic (50–30–20 mol%) at 1023 K by the present authors [13]. The results show that Al_2S_3 dissolved in the eutectic can be electrolysed to produce molten aluminium at the cathode and sulphur at the anode. Although reasonable current efficiency can be obtained, the electrolysis has to be conducted below a limiting cathodic current density to prevent the co-deposition of magnesium. This limiting current density is found to be rather low ($\sim 300\,\text{mA cm}^{-2}$) and may be too low to be of practical value. Efforts have thus shifted towards using a melt containing $AlCl_3$; such a melt increases the solubility of Al_2S_3 [14] and consequently permits higher current densities. In the present paper, the results of the electrolysis of Al_2S_3 in $MgCl_2$–NaCl–KCl eutectic containing $AlCl_3$ are reported.

2. Experimental procedure

The cell and the procedure used in the present studies has been described in detail elsewhere [13]. Essentially, the cell consists of an alumina crucible containing the molten salt electrolyte. Two rectangular graphite plates are employed as the cathode and the anode. Molten aluminium produced at the cathode is collected in a boron nitride (or graphite) collector placed directly under the electrode. A hood made of molybdenum is placed over the anode to condense sulphur gas. Purified $MgCl_2$–NaCl–KCl eutectic and $AlCl_3$ were obtained from Anderson Physics Laboratories, Champaign, Illinois. Aluminium sulphide (Cerac-Pure, 99.9% purity) was used without further purification. The experiments were carried out inside a VAC helium atmosphere glovebox already described [13].

3. Results and discussion

The electrolysis of Al_2S_3 was carried out in a $MgCl_2$–NaCl–KCl eutectic melt at 1023 K and the results have been reported previously [13]. The eutectic was chosen as the electrolyte for two reasons: (a) thermodynamic considerations [14] indicated that $MgCl_2$ might help solubilize Al_2S_3 by the reaction,

$$MgCl_{2(\text{soln})} + Al_2S_{3(\text{s})} = 2AlSCl_{(\text{soln})} + MgS_{(\text{s})},$$

and (b) $MgCl_2$ was expected to increase aluminium deposition efficiency as shown in aluminium chloride electrolysis [15]. Results of electrolysis experiments conducted at 1023 K using the eutectic as the solvent show that dissolved Al_2S_3 can be electrolysed to give molten aluminium and elemental sulphur. The current efficiency of the constant current electrolysis increases with increased current density and reaches a value of about 80% at a current density of about $200\,\text{mA cm}^{-2}$ in the eutectic containing 2 wt% Al_2S_3. It has been found that for each Al_2S_3 concentration, the electrolysis has to be conducted below a limiting cathodic current density. At the saturation solubility of Al_2S_3 in the molten salt (1.34 wt% S), the limiting cathodic current density is about $300\,\text{mA cm}^{-2}$. Also, for a batch operation, the limiting current density will decrease as the Al_2S_3 content of the melt is depleted during electrolysis. The low limiting cathodic current density limits the aluminium production rate to a low level; this level may be too low to be of practical value. Present aluminium processes employ a much higher current density. The current density ranges from 0.7 to $1.2\,\text{A cm}^{-2}$ in the Hall-Héroult cell [16] and from 0.8 to $2.3\,\text{A cm}^{-2}$ in the ASP cell [17].

From the voltage/current curves for the electrolysis of Al_2S_3 in the eutectic [13], it appears that the low aluminium ion (or aluminium ion containing species) concentration is the primary cause of the cathodic current density limitation. There are two possible ways to modify the process in order to be able to operate the electrolytic cell

Table 1. Solubility of Al_2S_3 in $AlCl_3$–$MgCl_2$–NaCl–KCl melts at 1023 K

Wt % $AlCl_3$ in $MgCl_2$–NaCl–KCl eutectic	*Solubility of Al_2S_3 as wt % S*
0	1.34
2	4.44
5	4.94
10	6.26
15	6.51

at higher current densities (a third way is to enhance the mass-transfer rate by mechanical means; however, this is difficult to implement in practice, thus, is rarely used in molten salt electrolysis). The two methods are (a) use of an electrolyte containing common aluminium ions, or (b) use of an electrolyte having higher Al_2S_3 solubility. It has been found that $AlCl_3$ can be used in both methods to mitigate this low current density problem. The presence of $AlCl_3$ in the melt not only provides common aluminium ions but also enhances the solubility of Al_2S_3 by the reaction [14],

$$AlCl_{3(soln)} + Al_2S_{3(s)} = 3\,AlSCl_{(soln)}.$$

The solubility of Al_2S_3 in terms of wt % sulphur in $AlCl_3$ containing melts is detailed in Table 1 [14].

It can be seen from Table 1 that $AlCl_3$ increases the solubility of Al_2S_3 in the molten salt mixture. Thus, cells for the electrolysis of Al_2S_3 in $AlCl_3$–$MgCl_2$–NaCl–KCl melts may be operated at higher current densities as shown later in this paper. It has also been found that the presence of $AlCl_3$ in the eutectic has no effect on the anodic oxidation of sulphide ions (or sulphide ion containing species). Figure 1 shows typical voltammograms of Al_2S_3 in $MgCl_2$–NaCl–KCl eutectic with and without $AlCl_3$. As seen from the figure, with the addition of 1 wt % $AlCl_3$, no peak current is observed for the deposition of aluminium, which is expected because a significant amount of $AlCl_3$ is present. Mechanistic tests [18] applied to the voltammogram in Fig. 1b confirm that the oxidation of sulphide ions occurs in a two-step mechanism as in the case of $MgCl_2$–NaCl–KCl eutectic, i.e., the oxidation involves the two-electron discharge of sulphide ions, followed by the dimerization of sulphur atoms, which is very fast and very much displaced towards S_2 [19].

The electrolysis of Al_2S_3 was carried out in $MgCl_2$–NaCl–KCl eutectic containing 10 wt % $AlCl_3$ at 1023 K. Significant volatilization of $AlCl_3$

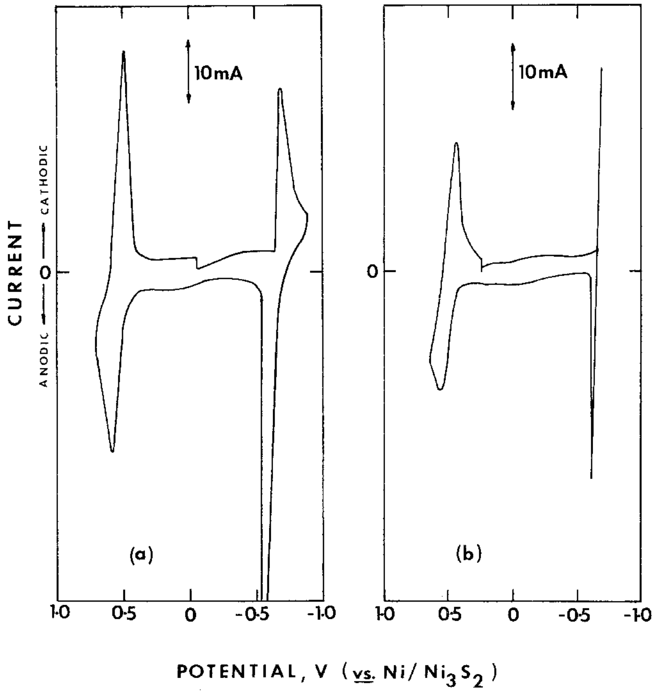

Fig. 1. Voltammograms of Al_2S_3 in melts at 1023 K (a) $MgCl_2$–NaCl–KCl eutectic electrolyte. Al_2S_3 concentration, 5.40×10^{-6} mol cm^{-3}. Sweep rate, 100 mV s^{-1}. Electrode area, 2.10 cm^2. (b) $MgCl_2$–NaCl–KCl eutectic + 1 wt% $AlCl_3$. Al_2S_3 concentration, 4.18×10^{-6} mol cm^{-3}. Sweep rate, 50 mV s^{-1}. Electrode area, 2.32 cm^2.

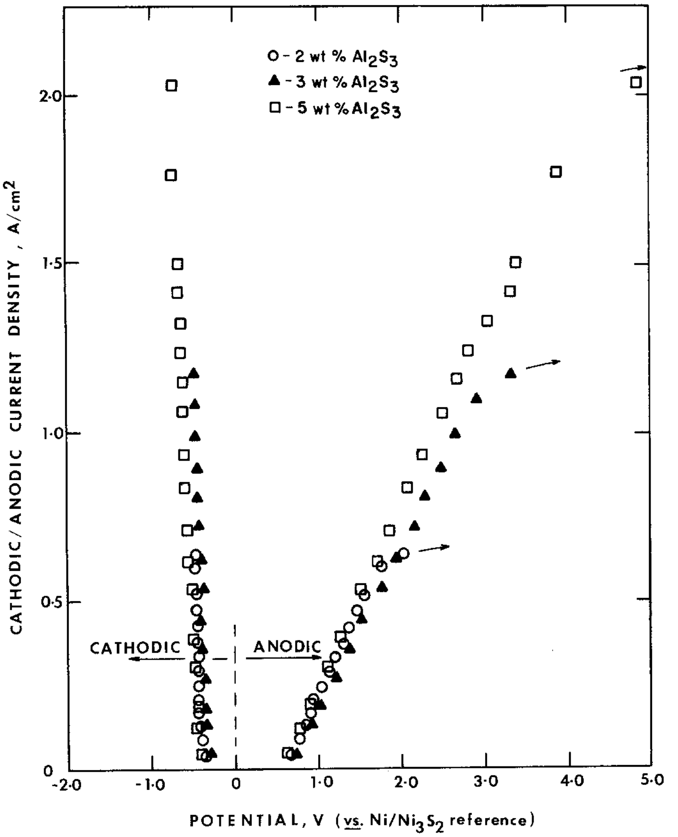

Fig. 2. Plots of current density versus cathodic and anodic voltages (uncorrected for ohmic drop) for the electrolysis of Al_2S_3 in $MgCl_2$–NaCl–KCl eutectic containing 10 wt% $AlCl_3$. $T = 1023$ K. Electrode spacing = 3 cm; o: 2 wt% Al_2S_3; ▲: 3 wt% Al_2S_3; □: 5 wt% Al_2S_3.

was observed during the experiments; however, enough $AlCl_3$ remained in the molten salt to dissolve up to 5 wt% Al_2S_3. Figure 2 shows the plots of the cathodic and anodic components of the steady-state cell voltage (uncorrected for ohmic drop) versus the anode/cathode current density at three Al_2S_3 concentrations (2, 3 and 5 wt% Al_2S_3). As seen from Fig. 2, the anodic voltage increases much more rapidly than the cathodic voltage as the current density increases. A limiting anodic current density is observed for each Al_2S_3 concentration. Above the limiting anodic current density, the evolution of either S_2Cl_2 or Cl_2 occurs and the cell voltage rises very rapidly due to the rapid rise of the anode voltage (as indicated by arrows in Fig. 2). Extrapolations of cell voltage components to zero current density in Fig. 2 give a decomposition voltage of about 1 V for Al_2S_3 at 1023 K, in good agreement with the value estimated from Ferrante's thermodynamic data [20] and the value obtained from the curves for the molten eutectic without the presence of $AlCl_3$ [13].

Comparison of the voltage/current curves for the electrolysis of Al_2S_3 in $MgCl_2$–NaCl–KCl eutectic electrolyte and in the eutectic containing 10 wt% $AlCl_3$ (such a comparison is shown in Fig. 3 for 2 wt% Al_2S_3) shows that at the same Al_2S_3 concentration, the current density for the electrolysis is anodically limited in the eutectic with $AlCl_3$, whereas it is cathodically limited in the eutectic without $AlCl_3$. The anodic limiting current density in the eutectic containing 10 wt% $AlCl_3$ is about 3 to 3.5 times the cathodic limiting current density in the eutectic without $AlCl_3$. If the diffusion layer theory is applied, at the same concentration, the limiting current density is proportional to nD/δ where n is the number of electrons involved in the electrochemical reaction, D is the diffusion coefficient and δ is the thickness of the diffusion layer. Thus, the higher anodic limiting current density can be partly explained by the higher diffusion coefficient for sulphide ions (2.73×10^{-5} cm^2 s^{-1} for sulphide ions compared with 1.03×10^{-5} cm^2 s^{-1} for aluminium ions [19]). The shape of the voltage/current curve in

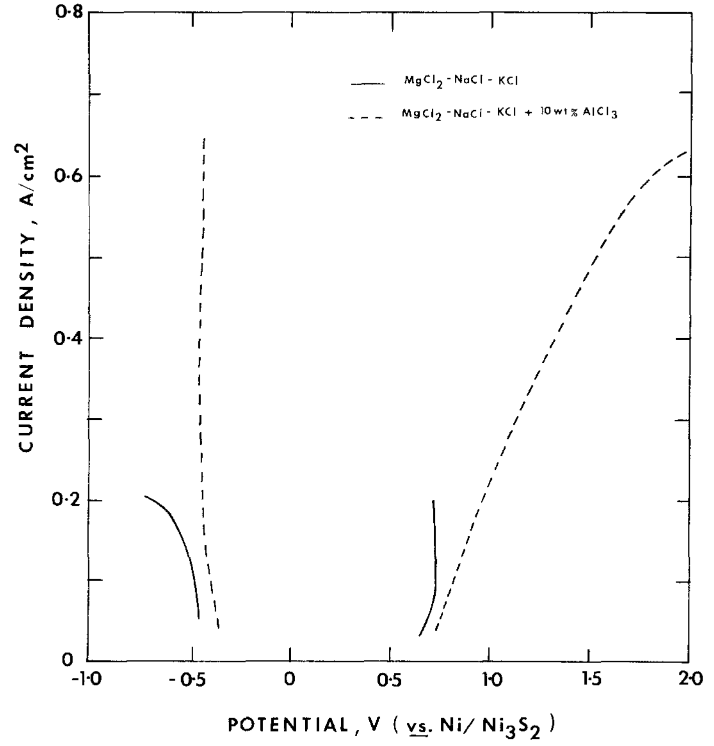

Fig. 3. Comparison of current density/voltage curves for the electrolysis of Al_2S_3 (2 wt%) in $MgCl_2$–NaCl–KCl eutectic and in the eutectic containing 10 wt% $AlCl_3$.

the eutectic containing $AlCl_3$ is somewhat different from that in the eutectic without $AlCl_3$. Further work is required to obtain more information to explain this difference.

The electrolysis of Al_2S_3 to produce aluminium for cathodic efficiency determinations was carried out in $MgCl_2$–NaCl–KCl eutectic containing 10 wt% $AlCl_3$ with an Al_2S_3 concentration of 5 wt%. Sulphur was detected by X-ray analysis as an anode product. Aluminium deposits were collected as granules of varying sizes. The current efficiencies were determined at different current densities. Within the current density range 0.2 to 1.2 A cm^{-2}, current efficiencies of about 75 to 85% were obtained. It appears that within this current density range, the cathodic current efficiency for the electrolysis of Al_2S_3 does not vary significantly with current density. It should be noted that below 0.2 A cm^{-2}, the efficiency of the electrolysis was found to increase with increased current density using the eutectic as the electrolyte. Not enough information is available at present to provide an explanation for this. However, the results obtained indicate the possibility of producing aluminium by the electrolysis of Al_2S_3 in an $AlCl_3$ containing melt with acceptable current density and current efficiency.

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