JOURNAL OF APPLIED ELECTROCHEMISTRY **28** (1998) 1265–1268

Content of sodium and lithium in aluminium during electrolysis of cryolite-based melts

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Received 9 March 1998; accepted in revised form 16 June 1998

The content of sodium and/or lithium in polarized and nonpolarized aluminium in contact with cryolite melts was determined in a laboratory cell. The cryolite-based melts contained 0 to 20 mass % excess AlF_3 and 0 to 2.5 mass % LiF. The cathodic current density ranged from 0 to 0.5 A cm^{-2}. The lithium content in aluminium increases linearly with increasing concentration lithium fluoride in the melt. It also increases with increasing cathodic current density and decreasing cryolite ratio. On the other hand the sodium content decreases with increasing concentration of LiF in the melt. This effect is more notable at higher current densities.

Keywords: *aluminium electrolysis*, *impurities*, *sodium*, *lithium*, *aluminium*

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1. Introduction

Aluminium is produced by the electrolysis of alumina dissolved in cryolite based melts. The primary cathodic reaction occurring at the surface of the molten aluminium cathode is the reduction of Al(III)-containing species. The next most-favoured cathodic reaction is the deposition of sodium which forms an alloy with aluminium. The difference between the deposition potential of aluminium and sodium under the conditions of electrowinning of aluminium is about 0.25 V. As a result the aluminium produced always contains sodium as an impurity in the concentration range of about 20–200 ppm. Besides cryolite (Na_3AlF_6) and alumina the electrolyte contains an excess of AlF_3 with respect to Na_3AlF_6 (usually up to 12 mass %), 2–5 mass % CaF_2, and, in some cases also an addition of LiF and/or MgF_2. As a result aluminium contains impurities like Ca, Li and Mg. Sodium is an undesirable impurity in aluminium. However, as has been shown by Tabereaux [1], a high sodium content in aluminium in industrial reduction cells correlates with a high current efficiency during electrolysis. It is known that the sodium concentration in the aluminium pad of modern prebaked cells having superior magnetic compensation and stable operating conditions is substantially higher compared with the content of sodium in older cells with Söderberg anodes. In this paper we present data on the content of sodium and lithium in equilibrium with cryolite based melts and during electrolysis in a laboratory cell.

Data on the content of sodium and/or lithium in molten aluminium which is in equilibrium with cryolite-based melts has been published by several authors [2–6]. However, almost no data on the content of sodium and/or lithium in cathodically polarized aluminium have been reported. The only exceptions are the data based on analysis of aluminium tapped from industrial cells [7] and data by Vetyukov and Borisoglebski [8]. The only data on the content of lithium and sodium in polarized aluminium were presented by the present authors [9].

2. Experimental details

For preparation of the samples the following chemicals were used. Cryolite of analytical grade (Merck), lithium fluoride of analytical grade (Lachema Brno), AlF_3 was sublimed (99.5%); the aluminium was of 99.999% purity.

A homogenized mixture of Na_3AlF_6–AlF_3–LiF–Al_2O_3 was weighed to 60 g into a graphite crucible together with 60 g of aluminium. A molybdenum plate at the bottom of the crucible served as current supply to the cathode. In most experiments a corundum lining was used and the melt was saturated with alumina. The scheme of the laboratory cell is depicted in Fig. 1. Dissolution of the corundum lining kept the concentration of alumina near saturation. This made it possible to carry out the electrolysis for several hours. The alumina content in saturated melts can be calculated according to the equation given by Solheim *et al.* [10]. It is important to note that the presence of alumina in the melt influences the equilibrium sodium content in aluminium only to a small extent [6].

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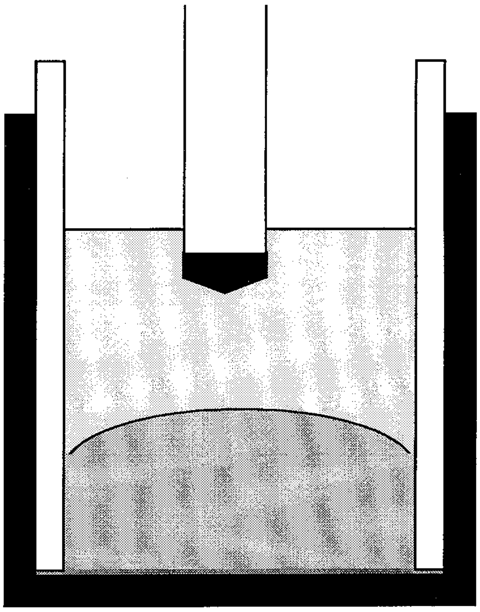

Fig. 1. Experimental graphite crucible. (Inner dia. 44 mm, height of aluminium 24 mm, interpolar dist. 5 mm).

The crucible was placed in a furnace preheated to a chosen temperature. After melting the sample was kept for another 30 min at that temperature. When equilibrium (or a steady state) was achieved, 0.8 g of metal was siphoned into quartz glass tube (inner diameter of 4 mm) equipped with a syringe. The sample was quenched in water mixed with ice. The cooled sample was cleaned mechanically, dissolved in HCl (diluted to 1:1) and analysed. The contents of sodium and lithium were determined by atomic absorption spectroscopy. The standard deviation of the lithium content of was 0.3 ppm. The standard deviation of sodium depended on concentration and was about 5% of the content of Na in aluminium.

The compositions of the investigated systems were as follows:

$$\mathrm{Na_3AlF_6} + 10\,\mathrm{mass\%\ xs\ AlF_3};$$

$$\mathrm{Na_3AlF_6} + 20\,\mathrm{mass\%\ xs\ AlF_3}$$

$$(\mathrm{Na_3AlF_6} + 10\,\mathrm{mass\%\ xs\ AlF_3}) + 0.5;1.0;1.5;2.0;2.5\,\mathrm{mass\%LiF}$$

$$(\mathrm{Na_3AlF_6} + 20\,\mathrm{mass\%\ xs\ AlF_3}) + 0.5;1.0;1.5;2.0;2.5\,\mathrm{mass\%LiF}$$

The measurements were carried out at a temperature of 1000 °C. The total current flowing through the cell was 0, 2 and 4 A, which corresponds approximately to the cathodic current densities of 0, 0.25 and 0.50 A cm^{-2}.

3. Results and discussion

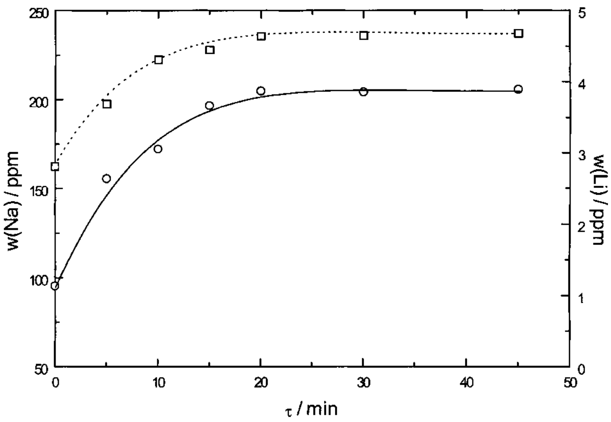

Fig. 2. Time dependence of the sodium and lithium contents in polarized aluminium. Key: (○) content of sodium (corresponds to the left-hand axis) and (□) content of lithium (corresponds to the right-hand axis).

Figure 2 shows an example of the time dependence of the concentration of sodium and lithium in polarized aluminium. It follows that, for the experimental arrangement used in this work, a time of 30 min was sufficient to obtain a steady concentration of sodium and lithium in aluminium. When aluminium was not polarized a time of 15 min was found to be sufficient for establishing equilibrium. The distribution of current in the laboratory cell used is rather uneven. A realistic estimation of current distribution in a laboratory cell was made using the procedure described by Zorić *et al.* [11] and current densities used in this paper are based on that work.

The content of sodium and lithium in polarized aluminium obtained for different cathodic current densities and two different concentrations of $\mathrm{AlF_3}$ in the melt are plotted as a function of the concentration of LiF in Figs 3–6. It follows that the content of lithium in aluminium in the investigated concentration range increases linearly with increasing concentration of LiF in the melt and with increasing current density. The data for zero current density correspond to the equilibrium values and are in good agreement with the data of Tabereaux and Peterson [4].

The rate of chemical and electrochemical reactions taking place at the aluminium/melt interface at the temperatures of electrolysis is high because of the very high exchange current density [14] and thus there is an equilibrium between the melt adjacent to the

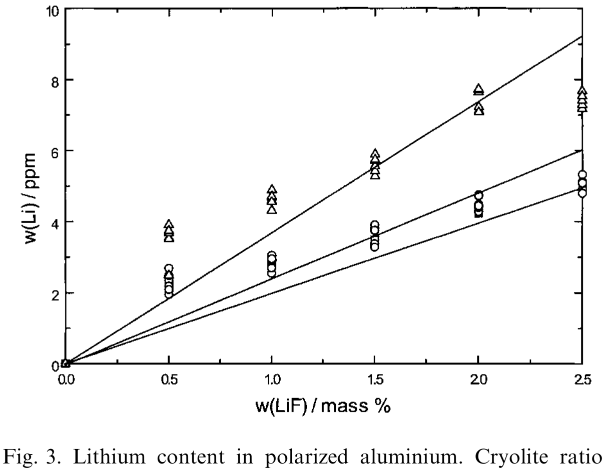

Fig. 3. Lithium content in polarized aluminium. Cryolite ratio, *CR*, of the melt was 2.35. Key for *j*: (□) 0, (○) 0.25 and (△) 0.5 A cm^{-2}.

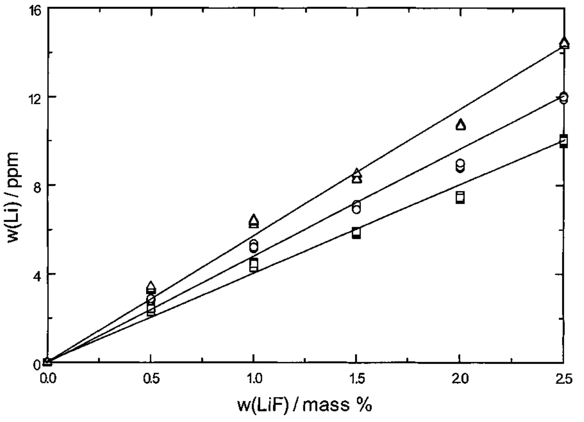

Fig. 4. Lithium content in polarized aluminium. Cryolite ratio, *CR*, of the melt was 1.85. Key for *j*: (□) 0, (○) 0.25 and (△) 0.5 A cm^{-2}.

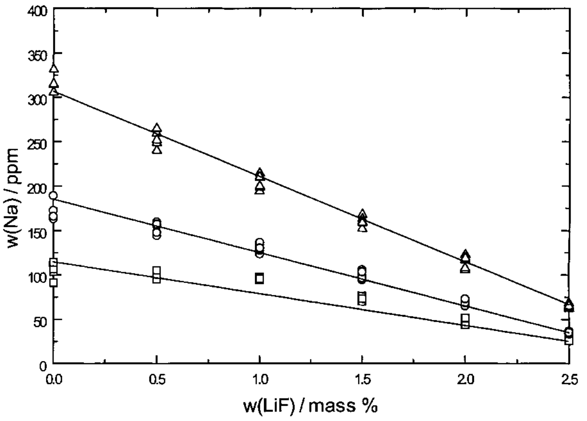

Fig. 5. Sodium content in polarized aluminium. Cryolite ratio, *CR*, of the melt was 2.35. Key for *j*: (□) 0, (○) 0.25 and (△) 0.5 A cm^{-2}.

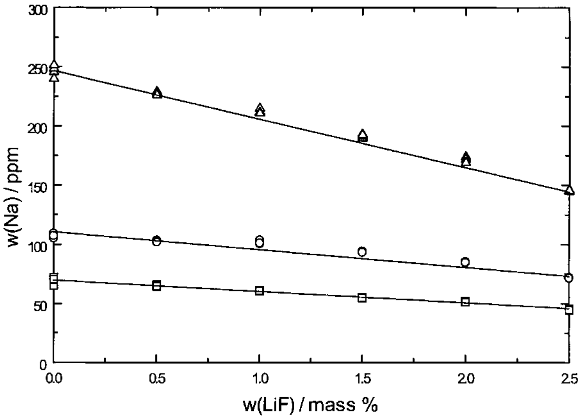

Fig. 6. Sodium content in polarized aluminium. The cryolite ratio, *CR*, of the melt was 1.85. Key for *j*: (□) 0, (○) 0.25 and (△) 0.5 A cm^{-2}.

cathode and the metal. Thus, the sodium and lithium contents in aluminium are related to the composition of the melt at the aluminium/melt interface by the reaction

$$\text{Li (in Al)} + \text{NaF} = \text{Na (in Al)} + \text{LiF}$$

The equilibrium content of sodium and lithium in aluminium can be described by the following reactions [6]:

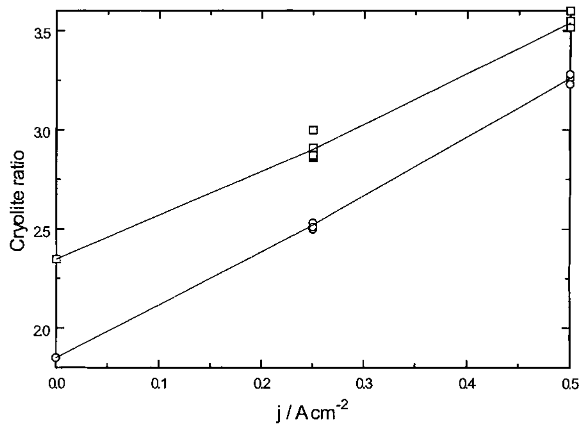

Fig. 7. Cryolite ratio, *CR*, of the melt at the phase boundary aluminium–melt. (□) *CR* = 2.35 (in the bulk); (○) *CR* = 1.85 (in the bulk).

$$4\,\text{NaF} + \text{Al} = 3\,\text{Na (in Al)} + \text{NaAlF}_4$$

$$3\,\text{LiF} + \text{NaF} + \text{Al} = 3\,\text{Li (in Al)} + \text{NaAlF}_4$$

The composition of the melt at the interface near the cathode can be estimated. From Fig. 7 it can be seen that the molar ratio $CR = n(\text{NaF})/n(\text{AlF}_3)$ increases at the metal/melt interface with increasing current density. This change in composition between the bulk of the electrolyte and the layer adjacent to the cathode causes the cathodic concentration overvoltage which can be determined experimentally [12].

The concentrations of sodium in aluminium are plotted as a function of the concentration of LiF in the melt in Figs 5 and 6. The concentration of sodium in aluminium increases with increasing current density. However, it decreases with increasing concentration of LiF in the melt. The higher the current density the larger is the effect of lithium fluoride on the sodium content in aluminium. This can be explained by the contribution of lithium cations to the transport of electrical charge in the cell. The changes in composition at the electrode surface influence the cathodic overvoltage.

In a way similar to that used by Sterten [13] it can be assumed that the cathodic overvoltage (as the sum of the transference numbers *t* (NaF) and *t* (LiF) is assumed equal to unity) is given by:

$$\eta_C = -\frac{RT}{F}\ln\left(\frac{c(\text{Na},j)}{c(\text{Na},j=0)}\right)^{t(\text{NaF})} \times \left(\frac{c(\text{Li},j)}{c(\text{Li},j=0)}\right)^{t(\text{LiF})}$$

Concentrations instead of activities are used because of the validity of Henry's law for low contents of lithium and/or sodium in aluminium.

Experimental verification of this relationship is in progress.

Acknowledgements

This work was supported by courtesy of the Slovak Grant Agency (grant 95/5195/204).

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