



Alkali and earth alkaline metal contents in the aluminium cathode in aluminium electrolysis

P. FELLNER¹, V. DANIELIK¹ and J. THONSTAD²

¹Department of Inorganic Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovakia

²Department of Materials Science and Electrochemistry, Norwegian University of Science and Technology, N-7491 Trondheim, Norway

Received 13 March 2000; accepted in revised form 9 May 2000

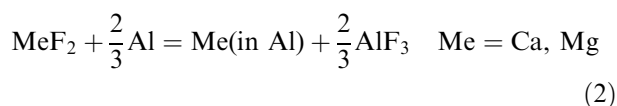
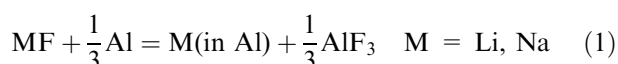
Key words: alkali metals, aluminium electrolysis, earth alkaline metals, impurities

Abstract

The contents of sodium, lithium, calcium and magnesium in aluminium in contact with NaF–AlF₃-based melts in laboratory and in industrial aluminium cells were investigated in the temperature range 950–1030 °C. The experimental data were compared with a thermodynamic model. It was found that the addition of alumina or CaF₂ to the NaF–AlF₃ melts has only a minor effect on the equilibrium content of sodium in aluminium. Cathodic polarization enhances the content of sodium in aluminium. However, polarization has a smaller effect on the concentrations of lithium, calcium and magnesium in aluminium in industrial cells.

1. Introduction

Sodium and calcium are always present as undesired impurities in aluminium produced by the so-called Hall–Heroult process [1]. When lithium fluoride and magnesium fluoride are added to the cryolite-alumina-based electrolyte, the metal will also contain lithium and magnesium as impurities due to exchange equilibria of the type



The contents of alkali and earth alkali metals in aluminium in equilibrium with cryolite melts have been investigated by several authors [2–14]. Tingle et al. [2] studied time, concentration and temperature dependence of the contents of sodium in aluminium in equilibrium with NaF–AlF₃ melts. Dewing and van der Kouwe [3, 4] derived a regression equation describing the contents of sodium and magnesium in aluminium in equilibrium with cryolite-based melts. Peterson and Tabereaux [5] published a regression equation describing the contents of sodium, calcium and magnesium in aluminium in equilibrium with cryolite-based melts at 970 °C. Experimental data on the content of lithium in polarized aluminium obtained in a laboratory

cell were published by Fellner and Danielik [6] and by Danielik et al. [7].

The electrolyte used for the electrowinning of aluminium always contains alumina and calcium fluoride. In this paper we present results of laboratory investigations of the effect of these components on the equilibrium contents of sodium and calcium in aluminium. We also present data on the contents of lithium, calcium and magnesium in aluminium sampled from industrial cells. These data are compared with equilibrium concentrations of impurities calculated on the basis of a thermodynamic model.

2. Experimental

To prepare the samples analytical grade chemicals were used (Lachema Brno), AlF₃ was sublimed from commercial grade AlF₃; the aluminium was of 99.999% purity. A homogenized mixture of Na₃AlF₆ + AlF₃ + Al₂O₃ + CaF₂ or MgF₂ (90 g) was weighed into a sintered alumina crucible together with 60 g of aluminium, and the melt was saturated with alumina. When the melt was not saturated with alumina, thin-walled pyrolytic boron nitride (BN) crucibles (Ø = 26 mm, h = 40 mm) were used. The alumina content in saturated melts can be calculated according to the equation given by Solheim et al. [15]. 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 was achieved, 0.8 g

of metal was siphoned from the alumina crucible into a quartz glass tube (inner diameter 4 mm) equipped with an attached syringe. The sample was quenched in water mixed with ice.

When BN crucibles were used, they were removed from the furnace and quenched in a stream of argon. The cooled metal sample was cleaned mechanically, dissolved in HCl (diluted to 1:1) and analyzed. The contents of sodium and calcium were determined by atomic absorption and ICP spectroscopy, respectively. The standard deviation of the determination of calcium was 0.3 ppm. In the case of sodium the standard deviation depended on the concentration and equaled ca. 5% of the content of Na in aluminium. This deviation significantly exceeds the analytical error and is probably affected by evaporation of sodium from the molten aluminium during solidification.

Molten aluminium sampled from Söderberg 70 kA cells (ZSNP, Ziar and Hronom, Slovakia) was cooled in cast-iron crucibles. This method of sampling is not suitable for the determination of sodium, but it yields reliable data for lithium and magnesium. The contents of the impurities Li, Ca and Mg in industrial samples were analyzed using the methods mentioned above.

3. Results and discussion

The experimental laboratory data showing the influence of alumina and/or calcium fluoride on the contents of sodium in aluminium in equilibrium with the molten system NaF–AlF₃ are presented in Figs. 1 and 2. It can be seen that these additions have only a minor effect on the content of sodium in aluminium. The lines in the figures will be discussed below. The influence of the composition of the melt on the content

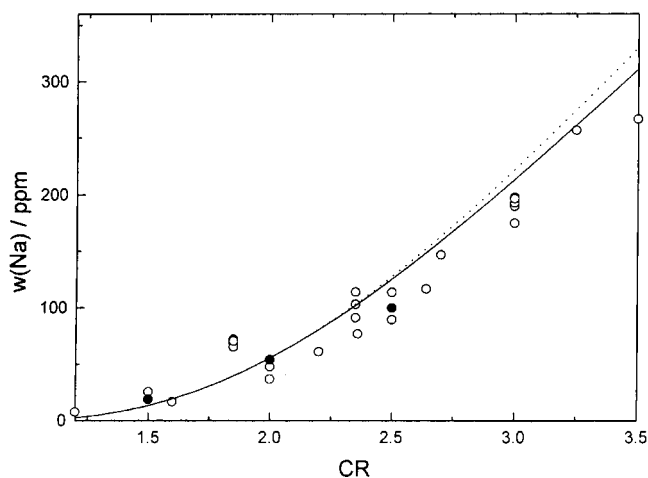


Fig. 1. Plot of the equilibrium content of sodium versus CR. The effect of the addition of alumina to the melt NaF–AlF₃ is shown. (●) data for melts without alumina (this work); (○) data for melts saturated with alumina (this work and literature data [2, 13]); (dotted line) model calculation for the melt NaF–AlF₃; (full line) model calculation for the melt NaF–AlF₃ saturated with alumina.

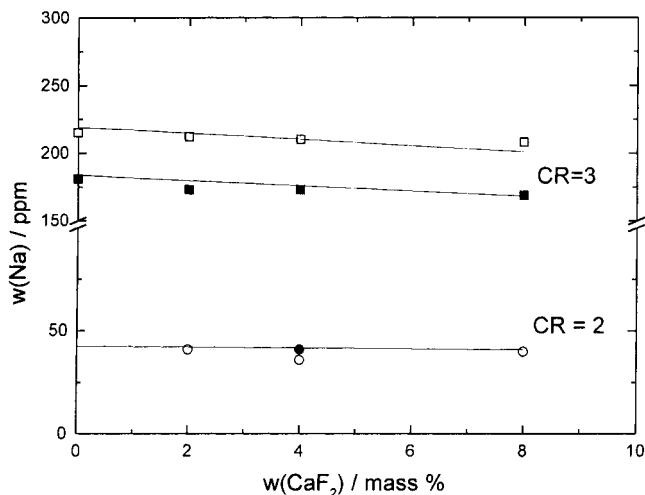


Fig. 2. Influence of CaF₂ on the content of sodium in aluminium. (□) data at 1030 °C, the melt (CR = 3) was saturated with alumina; (■) data at 970 °C, the melt (CR = 3) was saturated with alumina; (○) data at 970 °C, the melt (CR = 2) was saturated with alumina; (●) data at 970 °C, the melt (CR = 2) contained no alumina; (full line) calculated according to the thermodynamic model.

of calcium in aluminium is shown in Fig. 3. It can be seen that the content of calcium in aluminium depends both on the concentration of calcium fluoride in the melt and on CR (CR denotes the molar ratio of NaF and AlF₃). The dependence of the concentration of magnesium in aluminium on melt composition is shown in Fig. 4.

Qualitatively, the influence of the additions of CaF₂ or MgF₂ on the thermodynamic properties of the electrolyte can be described in terms of the acid–base concept of cryolite-based melts [5, 16]. In this paper,

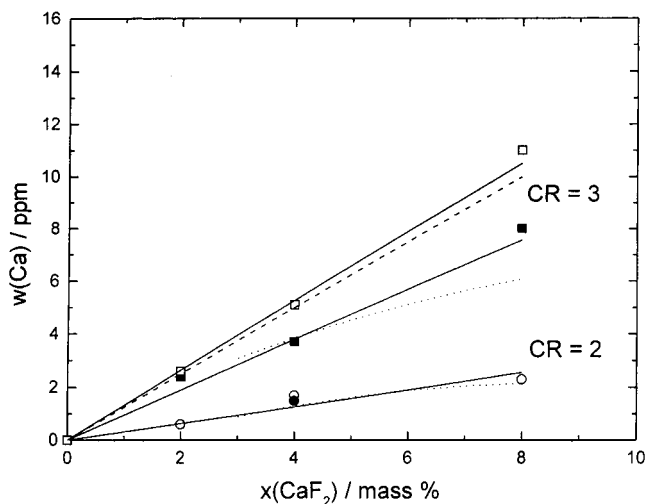


Fig. 3. The content of calcium in aluminium as a function of the content of CaF₂ in the melt for CR = 2 and CR = 3. (□) data at 1030 °C, the melt (CR = 3) was saturated with alumina; (■) data at 970 °C, the melt (CR = 3) was saturated with alumina; (○) data at 970 °C, the melt (CR = 2) was saturated with alumina; (●) data at 970 °C, the melt (CR = 2) contained no alumina; (full line) calculated according to the thermodynamic model; (dashed line) Thonstad et al. [10] (1020 °C); (dotted line) from equation of Peterson and Tabereaux [5] (970 °C).

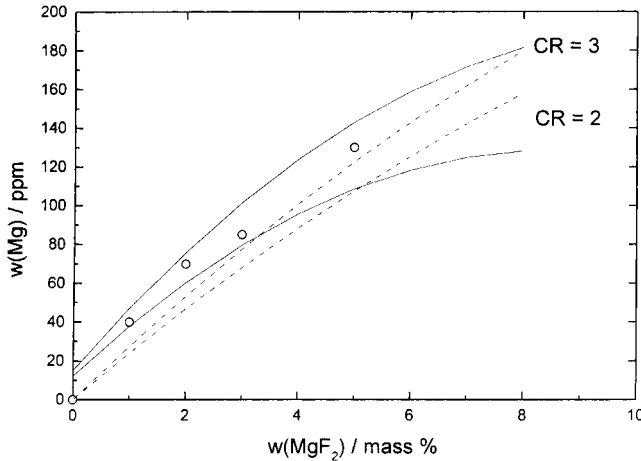
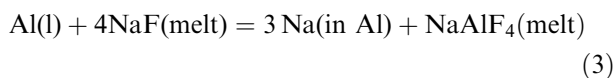


Fig. 4. Dependence of the content of magnesium in aluminium on the content of MgF_2 in the melt and of CR. (O) data at CR = 3 and at 970 °C, the melt was saturated with alumina; (full line) from equation of Peterson and Tabereaux [5]; (dashed line) from equation of Dewing and Kouwe [3, 4].

the experimental data on the contents of sodium and calcium in aluminium are compared with calculations based on a thermodynamic model. The model is based on the following assumptions and approximations:

1. In the first step the composition co-ordinates of the system $\text{NaF}-\text{AlF}_3$ are transformed to the system $\text{NaF}-\text{NaAlF}_4$. This transformation does not reflect the real ionic composition of the melt, but at low and high concentrations of AlF_3 in the melt this approximation is close to the physical reality.

2. The content of sodium in aluminium, which is in equilibrium with the melt, can be described by the reaction scheme



The equilibrium constant of the reaction was calculated from the thermodynamic data published in the JANAF tables [17]. The standard Gibbs energy of formation of $\text{NaAlF}_4(\text{l})$ was taken from a paper by Sterten et al. [18]. At the temperature of 1000 °C, the value of the equilibrium constant was found to be $K = 3.25 \times 10^{-4}$. The activity coefficients of sodium (and of the other impurities) in aluminium were reviewed by Sigworth and Engh [19]. The Henrian activity coefficient of sodium in aluminium at 1000 °C related to mole fractions equals 175.

3. The excess Gibbs energy of the system $\text{NaF}-\text{NaAlF}_4$ is expressed by the equation

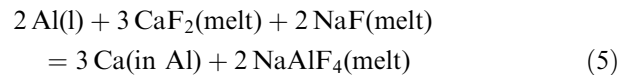
$$\begin{aligned} \Delta G^E / (\text{J mol}^{-1}) &= x(\text{NaF})x(\text{NaAlF}_4) \left\{ a_0 + a_1x(\text{NaAlF}_4) \right. \\ &\quad \left. + a_2[x(\text{NaAlF}_4)]^2 + a_3[x(\text{NaAlF}_4)]^3 \right\} \quad (4) \end{aligned}$$

where

$$\begin{aligned} a_0 &= -(95\,614 \pm 3435) + (43.97 \pm 0.72) T/\text{K}; \\ a_1 &= -(249\,306 \pm 24\,954) + (202.31 \pm 3.15) T/\text{K}; \\ a_2 &= (659\,134 \pm 56\,370) - (502.06 \pm 6.69) T/\text{K}; \\ a_3 &= -(457\,426 \pm 39\,638) + (347.90 \pm 5.01) T/\text{K}. \end{aligned}$$

4. The parameters of the above equation and the equilibrium constant K were determined by a non-linear regression analysis (the criterion of the least squares, confidence level 99%) using the available experimental data for the content of sodium in aluminium [2, 5, 8, 9, 13], the vapour pressure of NaAlF_4 [20] and the solid-liquid equilibrium of NaF with the melt [21]. For the enthalpy of mixing of the system $\text{NaF}-\text{NaAlF}_4$ the data by Holm [22] and by Hong and Kleppa [23] were used.

5. The concentration of calcium in aluminium was calculated from the equilibrium of the following reaction, using the same sources of thermodynamic data [17, 18] as mentioned above:



At 1000 °C the equilibrium constant equals $K = 5.67 \times 10^{-22}$. The activity coefficient of calcium in aluminium at 1000 °C related to mole fractions is 8.6×10^{-3} [19]. The activity coefficient of CaF_2 in the melt was assumed to be constant in the concentration range under study. Its value 1.7 (related to mole fractions) was estimated from the equilibrium solidus-liquidus data [24].

6. Magnesium fluoride forms complexes in fluoride melts [25, 26]. The best agreement with the experimental data was obtained under the assumption that MgF_2 forms MgF_4^{2-} complexes.

Good agreement of the experimental and calculated data suggests that the model describes the thermodynamic behaviour of the system well. It should be mentioned that the parameters of the thermodynamic model presented above are more precise than those published previously [8].

The contents of lithium and magnesium in aluminium sampled from industrial cells are plotted in Fig. 5 as a function of the concentrations of LiF and MgF_2 in the bath. The CR of the bath was 2.8 and the temperature was 960–970 °C. The equilibrium laboratory data for the concentration of impurities are shown as straight lines in the figure. It follows that, within the limits of error, the contents of lithium and magnesium in aluminium sampled from industrial cells were close to the equilibrium values. The laboratory investigation has shown that the content of lithium increases with cathodic polarization [6, 7]. This effect, however, is marked only at high current densities.

The behaviour of calcium in aluminium electrolysis was studied by Thonstad et al. [10]. In the cited work, laboratory data were obtained for the melt Na_3AlF_6-

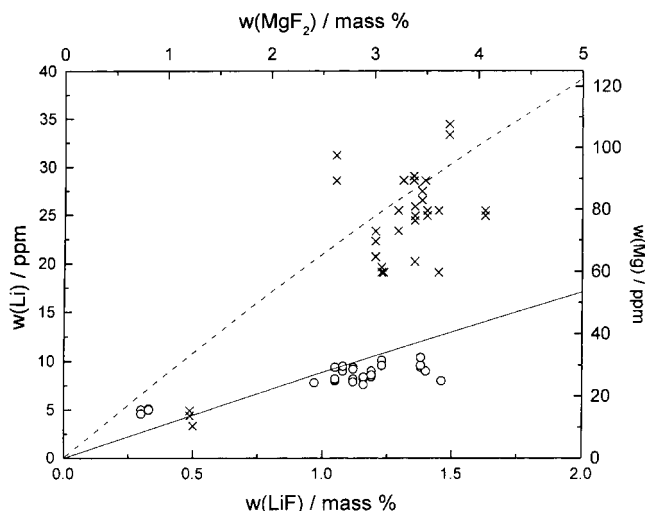


Fig. 5. Contents of lithium and magnesium in aluminium sampled from industrial Söderberg cells as a function of the contents of LiF and MgF₂ in the melt. (O) content of lithium; (X) content of magnesium; (full line) equilibrium values of lithium [7], (dashed line) equilibrium values of magnesium [3, 4].

CaF₂ at 1020 °C. These data are in fair agreement with the present study. Thonstad et al. [10] determined also the content of calcium in aluminium sampled from industrial cells having cryolite ratio in the range 2.6–2.9. Some new cells used neutral or slightly basic bath (CR = 3–3.2). They found that in industrial cells the content of calcium in aluminium varied linearly with the concentration of CaF₂ in the bath. At 6 mass percentage of CaF₂ the content of calcium in aluminium was between 6–10 ppm. The mean value was 7.5 ppm. This value is in reasonable agreement with the equilibrium value of calcium in aluminium when we take into account that the CR at the aluminium cathode increases up to the value of 3.5 [7]. The data published by Prasad et al. [11] are too high for the content of calcium and too low for sodium in comparison with other literature data [2–10, 12–14].

It can be concluded that polarization of the aluminium cathode at the current densities used in industry, i.e. 0.5–0.6 A cm⁻², does not influence significantly the concentrations of lithium and alkaline earth metals in aluminium. The concentration of these impurities can be estimated on the basis of equilibrium values calculated from thermodynamic data.

Acknowledgements

One of the authors (Dr. V. Danielik) wishes to express his gratitude to Dr. A. Solheim for supervising his work

during his visit at the Institute of Electrochemistry, NTNU, Trondheim. The stay made it possible to measure the equilibrium content of sodium in aluminium in boron nitride crucibles without the presence of alumina in the melt. This work was supported by courtesy of the Slovak Grant Agency (VEGA 1/6250/99).

References

1. K. Grjotheim, C. Krohn, M. Malinovský, K. Matiašovský and J. Thonstad, 'Aluminium Electrolysis', 2nd edn (Aluminium-Verlag, Düsseldorf, 1982).
2. W.H. Tingle, J. Petit and W.B. Frank, *Aluminium* **57** (1981) 286.
3. E.W. Dewing and E.Th. van der Kouwe, in 'Light Metals' edited by P.G. Campbell (Proceedings of 118th TMS Annual Meeting, 1989), p. 297.
4. E.W. Dewing and E.Th. van der Kouwe, *Met. Trans. B* **20B** (1989) 671.
5. R.D. Peterson and A.T. Tabereaux, in 'Light Metals' edited by R.E. Miller (Proceedings of 115th TMS Annual Meeting, 1986), p. 491.
6. P. Fellner and V. Danielik, Proceedings of The International Harald A. Øye Symposium Trondheim-Norway (1995) 389.
7. V. Danielik, P. Fellner and J. Thonstad, *J. Appl. Electrochem.* **28** (1998) 1265.
8. V. Danielik and P. Fellner, *Chem. Papers* **52**(4) (1998) 195.
9. E.W. Dewing and M.J. Gilbert, in 'Light Metals' edited by C.J. McMinn (Proceedings of 109th TMS Annual Meeting, 1980), p. 221.
10. J. Thonstad, A. Slättavik and J. Abrahamsen, *Aluminium* **49** (1973) 674.
11. R.N. Prasad, G. Varhegy and J. Horvath, *Banyasz. Kohasz. Lapok* **112**(10) (1979) 475.
12. E.W. Dewing, *Met. Trans.* **3**(2) (1972) 495.
13. P. Fellner and Ž. Lubyová, *Chem. Papers* **40**(2) (1986) 145.
14. E.W. Dewing, *Met. Trans. B* **18B** (1987) 409.
15. A. Solheim, E. Rolseth, L. Skybakmoen, Å. Støen, Å. Sterten and T. Støre, *Met. Trans. B* **27B** (1996) 739.
16. E.W. Dewing, in 'Light Metals' edited by P.G. Campbell (Proceedings of 118th TMS Annual Meeting, 1989), p. 303.
17. D.R. Stull and H. Prophet, 'JANAF Thermochemical Tables 2nd, edn (Nat. Bur. Stand. (USA), coden NSRDA 1971).
18. Å. Sterten and I. Mæland, *Acta Chem. Scand.* **A39** (1985) 241.
19. G.K. Sigworth and T.A. Engh, *Scand. J. Met.* **11** (1982) 143.
20. J. Guzman, K. Grjotheim and T. Østvold, in 'Light Metals' edited by R.E. Miller (Proceedings of 115th TMS Annual Meeting, 1986), p. 425.
21. A. Solheim and Å. Sterten, Proceedings of Ninth Int. Symp. on Light Metals Production Tromsø-Trondheim, Norway, August 19–21 (1997) 225.
22. J.L. Holm, 'Thermodynamic properties of molten cryolite and other fluoride mixtures', Institute of Inorganic Chemistry, NTH (Trondheim, Norway, 1971).
23. K.C. Hong and O.J. Kleppa, *High Temp. Science* **8** (1976) 299.
24. M. Chrenková, V. Daněk and A. Silný, Proceedings of Ninth Int. Symp. on Light Metals Production Tromsø-Trondheim, Norway, August 19–21 (1997) 1.
25. P. Fellner, K. Grjotheim and H. Kvande, *Acta Chem. Scand. A* **38A** (1984) 699.
26. B. Gilbert, E. Robert, E. Tixhon, J.E. Olsen and T. Østvold, *Inorg. Chem.* **35**(14) (1996) 4198.