

# Equilibrium between aluminium and the cryolite melt containing lithium fluoride

P. FELLNER and Ž. LUBYOVÁ

*Institute of Inorganic Chemistry, Centre for Chemical Research,  
Slovak Academy of Sciences, CS-842 36 Bratislava*

Received 11 September 1985

*Dedicated to the memory of Professor Ing. M. Malinovský, DrSc.,  
April 2, 1926—December 15, 1984*

Content of lithium and sodium in aluminium which is in equilibrium with cryolite melt containing lithium fluoride was measured. It was found that the content of lithium depends mainly on the content of LiF in the melt, while its dependence on the ratio  $x(\text{NaF})/x(\text{AlF}_3)$  is rather small. On the other hand, content of sodium is determined largely by the ratio  $x(\text{NaF})/x(\text{AlF}_3)$ . The obtained experimental data are interpreted on the basis of thermodynamic model.

Измерено содержание лития и натрия в алюминии, находящемся в равновесии с расплавом криолита, содержащем фторид лития. Было найдено, что содержание лития зависит, главным образом, от содержания LiF в расплаве, в то время, как зависимость от отношения  $x(\text{NaF})/x(\text{AlF}_3)$  относительно невысока. С другой стороны, содержание натрия в большой мере определяется отношением  $x(\text{NaF})/x(\text{AlF}_3)$ . Полученные экспериментальные данные интерпретированы на основе термодинамической модели.

Addition of lithium fluoride to the electrolyte used for electrowinning of aluminium influences the operational parameters of electrolysis [1, 2]. This admixture decreases the temperature of primary crystallization of the electrolyte and increases its electrical conductivity. Temperature of the bath can be decreased, which influences positively current efficiency of the electrolysis and decreases the total amount of fluoride emissions. On the other hand, lowering of the temperature unfavourably influences kinetics of dissolution of aluminium oxide. The addition of LiF causes also contamination of aluminium with lithium. In order to make it possible to optimize composition of the electrolyte (this depends on technological conditions of the electrolysis [3]) it is desirable to know the relation between composition and properties of the melt. Dewing has recently published

results of the investigation of the equilibrium between aluminium and melt of the system  $\text{Na}_3\text{AlF}_6\text{—Li}_3\text{AlF}_6$  [4]. This work is devoted to the investigation of the equilibrium between aluminium and the cryolite-based melts containing lithium fluoride, the composition of which is close to the composition of industrial bath. The relation between composition of the electrolyte and the content of lithium and sodium in aluminium is interpreted on the basis of thermodynamic model, which may contribute to deeper understanding of thermodynamic properties of cryolite-based melts.

## Experimental

For preparation of samples following chemicals were used. Cryolite,  $\text{Na}_3\text{AlF}_6$  of anal. grade (Merck), lithium fluoride and sodium fluoride of anal. grade (Lachema, Brno),  $\text{AlF}_3$  sublimated (99.7 %) and aluminium of purity 99.999 %.

30 g of homogenized mixture  $\text{NaF—AlF}_3\text{—LiF}$  was weighed in sinter-alumina or graphite crucible together with 30 g of aluminium. The ratio  $x(\text{NaF})/x(\text{AlF}_3)$  was 2.70, 3.00, and 3.25, respectively. The crucibles were placed into a furnace preheated to 1000 °C. After melting the sample was mixed and kept for 30 min at the temperature of  $(1000 \pm 2)$  °C. Then the metal (ca. 4 g) was sampled into quartz glass tube ( $\varnothing = 4$  mm) equipped with adjusted syringe and quenched in water mixed with ice. The cooled sample was mechanically cleaned, dissolved in HCl (diluted 1:1) and analyzed. Content of sodium and lithium was determined by AAS (Perkin—Elmer 305 A).

In this paper only the results obtained with sinter-alumina crucibles are presented. These results were more consistent than those obtained with graphite crucibles. Analysis of the melt after experiment showed that the melt contained 5—10 mass %  $\text{Al}_2\text{O}_3$ . The experiments carried out in the graphite crucibles proved that part of alumina originates from oxidization of aluminium dissolved in the melt.

## Results and discussion

The experimental results on the equilibrium between aluminium and melt of the system  $\text{LiF—NaF—AlF}_3$  are summarized in Table 1. Weighed-in composition is given. It follows that in the investigated interval of composition the content of lithium in aluminium depends markedly on the content of lithium fluoride in the melt while cryolite ratio (CR) (defined as  $n(\text{NaF})/n(\text{AlF}_3)$ ) has a small influence. On the other hand, content of sodium in aluminium depends mainly on CR and the influence of LiF is less important.

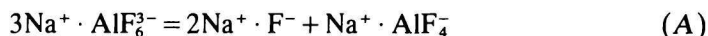
We will show that these relationships can be explained on the basis of thermodynamic model. The model presented here is based on the assumption that at low concentrations of LiF the molten system  $\text{LiF—NaF—AlF}_3$  consists of ionic pairs  $\text{Li}^+ \cdot \text{F}^-$ ,  $\text{Na}^+ \cdot \text{F}^-$ ,  $\text{Na}^+ \cdot \text{AlF}_4^-$ , and  $3\text{Na}^+ \cdot \text{AlF}_6^{3-}$ . In contradistinction to the

Table 1

Dependence of mass concentration of lithium and sodium in aluminium on composition of the melt

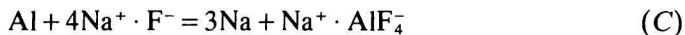
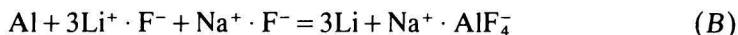
Melt			Metal	
$\frac{x(\text{LiF})}{\text{mole \%}}$	$\frac{x(\text{NaF})}{\text{mole \%}}$	$\frac{x(\text{AlF}_3)}{\text{mole \%}}$	$\frac{\rho(\text{Li})}{\text{ppm}}$	$\frac{\rho(\text{Na})}{\text{ppm}}$
0	75.00	25.00	0	191
1.30	74.03	24.67	6	176
2.70	72.97	24.33	10	138
4.22	71.83	23.95	17	150
5.89	70.58	23.53	19	156
9.68	67.74	22.58	33	164
14.29	64.28	21.43	44	158
0	72.97	27.03	0	147
1.32	72.01	26.67	5	147
2.74	70.97	26.28	10	105
4.29	69.84	25.87	19	115
5.98	68.61	25.41	25	130
9.82	65.81	24.37	31	150
14.48	62.41	23.11	54	115
1.28	75.49	23.23	6	—
2.67	74.43	22.90	12	—
4.18	73.28	22.55	20	—
5.82	72.02	22.16	23	—
14.14	65.66	20.20	70	—

Temkin model [5] we do not consider that the cations  $\text{Li}^+$  and  $\text{Na}^+$  are distributed randomly in the melt. The proposed model assumes that randomly are mixed the ionic pairs stated above. The relationships between “weighed-in” and “model” composition of the investigated system follow from material balance of  $\text{LiF}$ ,  $\text{NaF}$ , and  $\text{AlF}_3$  and from the equilibrium of thermal dissociation of the anion  $\text{AlF}_6^{3-}$



It has been shown [6] that this model describes very well the temperature of primary crystallization of  $\text{Na}_3\text{AlF}_6$  in the system  $\text{Na}_3\text{AlF}_6$ — $\text{LiF}$  up to mole fraction  $\text{LiF } x(\text{LiF}) \leq 0.4$ . Thus it can be assumed that this model will be suitable also for correlation of the composition of the system  $\text{LiF}$ — $\text{NaF}$ — $\text{AlF}_3$  with the content of lithium and sodium in aluminium which is in the equilibrium with the melt. Method of calculation of the model composition of the melt is outlined in appendix. It was assumed [7] that the equilibrium constant of reaction (A) equals 0.06.

According to proposed model content of lithium and sodium in aluminium can be calculated from equilibria of the following reactions



The equilibrium between components of the melt is given by eqn (A). Then it follows

$$\rho(\text{Li}) = k_{\text{Li}} \cdot x(\text{Li}^+ \cdot \text{F}^-) \sqrt[3]{\frac{x(\text{Na}^+ \cdot \text{F}^-)}{x(\text{Na}^+ \cdot \text{AlF}_4^-)}} \quad (1)$$

$$\rho(\text{Na}) = k_{\text{Na}} \sqrt[3]{\frac{(x(\text{Na}^+ \cdot \text{F}^-))^4}{x(\text{Na}^+ \cdot \text{AlF}_4^-)}} \quad (2)$$

$\rho$  denotes the concentration of lithium or sodium in aluminium and ranges from 0 to 200 ppm. Thus we may assume that the activity of lithium and sodium, respectively, is proportional to their concentrations. According to literature, the activity coefficient of lithium in aluminium at the temperature of 1000 °C equals 0.624 [8] and the activity coefficient of sodium equals  $(173 \pm 30)$  [9].  $k_{\text{Li}}$  and  $k_{\text{Na}}$  are proportionality constants.

In Fig. 1 the dependence of experimental concentration of lithium in aluminium vs.  $x(\text{Li}^+ \cdot \text{F}^-) [x(\text{Na}^+ \cdot \text{F}^-)/x(\text{Na}^+ \cdot \text{AlF}_4^-)]^{1/3}$  is plotted. Numerical value of the slope of the line is  $(155.9 \pm 5.4)$ . For confidence interval 95 % we obtain the

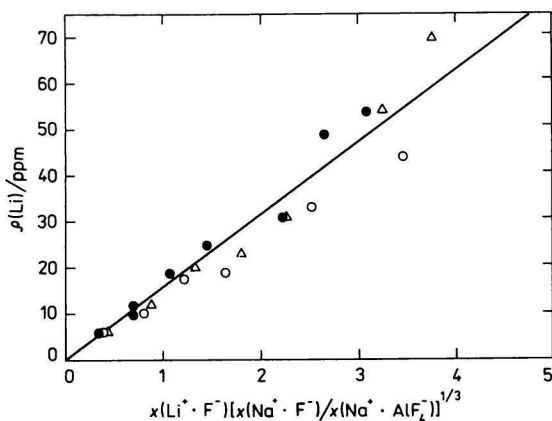


Fig. 1. Dependence of the content of lithium in aluminium on the "model" composition of the melt.

● CR = 2.70; ○ CR = 3.00; △ CR = 3.25.

equilibrium constant of the reaction (B)  $4.49 \times 10^{-11} - 6.45 \times 10^{-11}$ . Using literature data on Gibbs energy of formation of NaF and LiF [10] we can calculate Gibbs energy of formation of  $\text{Na}^+ \cdot \text{AlF}_4^-$  (l) at 1273 K. It follows  $\Delta G_f^\circ(\text{Na}^+ \cdot \text{AlF}_4^-, \text{l}, 1273 \text{ K}) = -(1681.8 - 1685.7) \text{ kJ mol}^{-1}$ , which is in good agreement with recently published value [11, 12]. It should be noted, however, that numerical values of the above discussed quantities may be partly influenced by the choice of thermodynamic model and/or by the presence of  $\text{Al}_2\text{O}_3$  in the melt. When a more complex model (taking into account the existence of  $\text{Li}^+ \cdot \text{AlF}_4^-$ ,  $3\text{Li}^+ \cdot \text{AlF}_6^{3-}$ , and  $5\text{Na}^+ \cdot \text{Al}_3\text{F}_{14}^-$ ) has been considered the value of  $\Delta G_f^\circ(\text{Na}^+ \cdot \text{AlF}_4^-, \text{l}, 1273 \text{ K})$  partly changed. This problem will be discussed elsewhere.

In Fig. 2 the dependence of the content of sodium in aluminium vs. the term  $[(x(\text{Na}^+ \cdot \text{F}^-))^4/x(\text{Na}^+ \cdot \text{AlF}_4^-)]^{1/3}$  is plotted. The numerical value of the slope of this

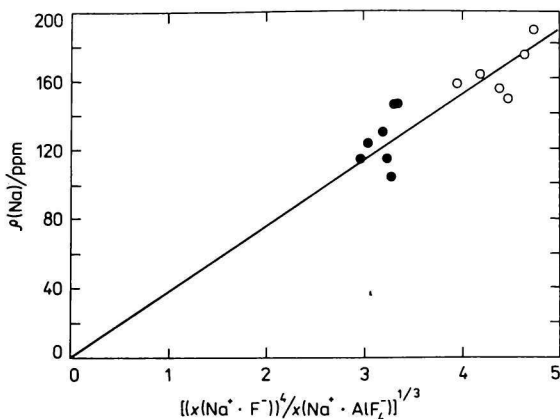


Fig. 2. Dependence of the content of sodium in aluminium on the "model" composition of the melt.

● CR = 2.70; ○ CR = 3.00.

line equals  $k_{\text{Na}} = (380.1 \pm 12.1)$ . For confidence interval 95 % (and  $\gamma_{\text{Na}} = 173$ ) it follows  $\Delta G_f^\circ(\text{Na}^+ \cdot \text{AlF}_4^-, \text{l}, 1273 \text{ K}) = -(1664.0 - 1667.6) \text{ kJ mol}^{-1}$ . In this case the value of  $k_{\text{Na}}$  (and consequently of  $\Delta G_f^\circ(\text{Na}^+ \cdot \text{AlF}_4^-)$ ) depends on the chosen model more markedly than in the case of  $k_{\text{Li}}$  (equilibrium of lithium). Also the value of the activity coefficient of sodium in aluminium has a greater standard deviation than in the case of lithium in aluminium and therefore one should consider the value of  $\Delta G_f^\circ(\text{Na}^+ \cdot \text{AlF}_4^-, \text{l})$  evaluated on the basis of distribution of lithium between melt and metal as more reliable. The agreement between the value of  $\Delta G_f^\circ(\text{Na}^+ \cdot \text{AlF}_4^-, \text{l})$  obtained in this work and that reported in literature [11, 12]

suggests that the simplified model of the molten system  $\text{LiF—NaF—AlF}_3$  describes thermodynamic behaviour of this system in the concentration region close to the composition of an industrial electrolyte sufficiently well.

## Appendix

### Calculation of the "model" composition of the system

#### $\text{LiF—NaF—AlF}_3$

The simplified model assumes that the melt contains the ionic pairs  $\text{Li}^+ \cdot \text{F}^-$ ,  $\text{Na}^+ \cdot \text{F}^-$ ,  $\text{Na}^+ \cdot \text{AlF}_4^-$ , and  $3\text{Na}^+ \cdot \text{AlF}_6^{3-}$ . Let us denote the weighed-in amount of substances as  $n(\text{LiF})$ ,  $n(\text{NaF})$ , and  $n(\text{AlF}_3)$ . (Numerical values of these quantities may equal the mole fractions of the components.) From material balance it follows

$$n(\text{NaF}) = n(\text{Na}^+ \cdot \text{F}^-) + n(\text{Na}^+ \cdot \text{AlF}_4^-) + 3n(3\text{Na}^+ \cdot \text{AlF}_6^{3-}) \quad (3)$$

$$n(\text{AlF}_3) = n(\text{Na}^+ \cdot \text{AlF}_4^-) + n(3\text{Na}^+ \cdot \text{AlF}_6^{3-}) \quad (4)$$

$$n(\text{LiF}) = n(\text{Li}^+ \cdot \text{F}^-) \quad (5)$$

When we choose the value of  $n(3\text{Na}^+ \cdot \text{AlF}_6^{3-})$  we can calculate from eqn (4) the value of  $n(\text{Na}^+ \cdot \text{AlF}_4^-)$  and in the next step the value of  $n(\text{Na}^+ \cdot \text{F}^-)$  from eqn (3). The value of  $n(3\text{Na}^+ \cdot \text{AlF}_6^{3-})$  must be chosen so as to satisfy the condition

$$\frac{[x(\text{Na}^+ \cdot \text{F}^-)]^2 \cdot x(\text{Na}^+ \cdot \text{AlF}_4^-)}{x(3\text{Na}^+ \cdot \text{AlF}_6^{3-})} = K = 0.06 \quad (6)$$

This task was solved numerically by iteration method using a programmable calculator HP 9821A.

## References

1. Pawlek, R., *Übersicht über das Verhalten lithiumhaltiger Salze in der Tonerdeschmelzflusselektrolyse*. Schweizerischen Aluminium AG, 1981.
2. Grjotheim, K., Kvande, H., and Matiašovský, K., *Light Metals 1983*. Conference Proceedings. The Metallurgical Society of AIME.
3. Grjotheim, K. and Kvande, H., *Erzmetall* 35, 597 (1982).
4. Dewing, E. W., *Light Metals 1985*. Conference Proceedings. The Metallurgical Society of AIME.
5. Temkin, M., *Acta Physicochim.* (URSS) 20, 411 (1945).
6. Fellner, P., Grjotheim, K., and Lubyová, Ž., *V. Al-Sympózium*. Extended abstracts, p. 61. Banská Bystrica, 1984.
7. Paučířová, M., Matiašovský, K., and Malinovský, M., *Rev. Roum. Chim.* 15, 201 (1970).
8. Dewing, E. W., *Met. Trans.* 11B, 245 (1980).

9. Kvande, H., *Thesis*. The University of Trondheim, 1979.
10. *JANAF Thermochemical Tables*. The Dow Chemical Co., Midland, Michigan, 1970.
11. Grjotheim, K., Krohn, C., Malinovský, M., Matiašovský, K., and Thonstad, J., *Aluminium Electrolysis. Fundamentals of the Hall—Héroult Process*. Aluminium-Verlag, Düsseldorf, 1982.
12. Sterten, A. and Meland, I., *Acta Chem. Scand.* A39, 241 (1985).

Translated by P. Fellner