Content of Sodium and Lithium in Aluminium in Equilibrium with Cryolite Melts
Experimental Data and Thermodynamic Model

V. DANIELIK and P. FELLNER

Department of Inorganic Technology, Faculty of Chemical Technology, Slovak University of Technology, SK-812 37 Bratislava

Received 30 September 1997

Equilibrium content of sodium and lithium in aluminium in contact with the melts of the system Na_3AlF_6—AlF_3—LiF—Al_2O_3 (saturated) was investigated at the temperature of 1000 °C and/or 15 °C superheat. The excess content of AlF_3 with respect to cryolite was 10 mass % and 20 mass %, respectively. The content of LiF ranged from 0 to 2.5 mass %.

A thermodynamic model describing the experimental data on the content of sodium in aluminium is proposed. The model is consistent with the literature data on the vapour pressure over the molten system Na_3AlF_6—AlF_3 and with the phase diagram of this system.

Sodium is always present in aluminium produced by the electrolysis of cryolite melts as a nondesired impurity [1]. As it has been recently shown by *Tabereaux* [2] the content of sodium in aluminium can be used as an indicator of aluminium cell performance. The higher is the content of sodium in metal, the higher is also the current efficiency of the electrowinning of aluminium. Lithium fluoride is added to the electrolyte for electrowinning of aluminium for increasing the electrical conductivity. Also lithium in aluminium is a nondesired admixture. For understanding the nonequilibrium concentrations of sodium and/or lithium in aluminium we need to have reliable equilibrium data on this parameter as a function of composition of the melt and of the temperature. In this paper we present supplementary experimental data to those which are available in the literature [3—6]. We also derive a thermodynamic model which describes the dependence of the concentration of sodium in aluminium on the composition of the melt and on the temperature.

EXPERIMENTAL

For preparation of samples following chemicals were used: cryolite of anal. grade (Merck), lithium fluoride of anal. grade (Lachema, Brno), AlF_3 was sublimed (99.5 %); aluminium was of purity 99.999 %. The measurements were realized in an inert atmosphere of nitrogen.

60 g of the homogenized mixture Na_3AlF_6—AlF_3—LiF—Al_2O_3 (saturated) was weighed into a graphite crucible together with 60 g of aluminium. Molybdenum plate on the bottom of the crucible protected contact between aluminium and graphite and in the case of electrolysis it served as current supply to the aluminium cathode. In most experiments dense alumina (corundum) lining was used and the melt was saturated with alumina. The crucible was placed into a furnace preheated to chosen temperature. After melting the sample was mixed and kept for another 30 min at that temperature. When equilibrium (or a stationary state) was achieved 0.8 g of metal was siphoned into quartz glass tube (inner diameter of 4 mm) equipped with adjusted syringe. The sample was 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.

RESULTS AND DISCUSSION

In preliminary experiments the time dependence of sodium content in aluminium was determined. In accordance with literature [3, 4] it was found that the equilibrium was achieved after 15 min. Standard deviation in determination of the content of lithium was 0.3 ppm. The standard deviation in determination of sodium depends on the content of sodium in aluminium. It equals *ca.* 5 % of the content of sodium in aluminium. The experimental data obtained in this work are summarized in Table 1.

Concentration of sodium in aluminium is related to thermodynamic properties of the melt. We will present a thermodynamic model which describes the obtained data. The model is based on the following assumptions and approximations:

1. In the first step the composition coordinates of the system NaF—AlF_3 are transformed to the system NaF—$NaAlF_4$. This transformation does not reflect

Table 1. Content of Sodium and Lithium in Aluminium as a Function of Composition of the Melt and Temperature of the Electrolyte (CR denotes the cryolite ratio)

CR	w(LiF)/mass %	Temperature/°C	w(Na)/ppm	w(Li)/ppm
2.35	0	1 000	103.50	0
2.35	0	1 000	91.24	0
2.35	0	1 000	106.33	0
2.35	0	1 000	114.13	0
2.35	0.5	1 000	100.21	2.20
2.35	0.5	1 000	98.34	2.14
2.35	0.5	1 000	95.48	2.16
2.35	0.5	1 000	90.31	2.21
2.35	0.5	1 000	100.41	2.19
2.35	0.5	1 000	88.31	2.18
2.35	0.5	1 000	105.32	3.67
2.35	0.5	1 000	102.58	3.55
2.35	1.0	1 000	97.35	6.95
2.35	1.0	1 000	96.24	6.84
2.35	1.0	1 000	95.63	2.80
2.35	1.0	1 000	94.28	2.84
2.35	1.0	1 000	95.89	2.82
2.35	1.0	1 000	95.71	2.81
2.35	1.0	1 000	89.12	2.82
2.35	1.0	1 000	88.31	2.83
2.35	1.5	1 000	73.65	3.45
2.35	1.5	1 000	72.81	3.47
2.35	1.5	1 000	70.21	3.50
2.35	1.5	1 000	76.35	3.44
2.35	1.5	1 000	75.81	3.46
2.35	1.5	1 000	73.31	3.50
2.35	2.0	1 000	84.29	11.89
2.35	2.0	1 000	83.66	12.43
2.35	2.0	995	48.04	4.28
2.35	2.0	995	47.81	4.30
2.35	2.0	995	48.23	4.33
2.35	2.0	995	49.30	4.25
2.35	2.0	995	43.58	4.24
2.35	2.0	995	51.39	4.28
2.35	2.5	990	27.33	4.95
2.35	2.5	990	25.69	4.98
2.35	2.5	990	28.48	5.03
2.35	2.5	990	29.20	5.05
2.35	2.5	990	28.34	4.96
2.35	2.5	990	25.85	4.91
1.85	0	1 000	68.96	0
1.85	0	1 000	65.31	0
1.85	0	1 000	72.10	0
1.85	0	1 000	70.43	0
1.85	0.5	940	65.94	2.54
1.85	0.5	940	64.54	2.31
1.85	0.5	940	66.16	2.28
1.85	0.5	940	65.12	2.43
1.85	1.0	937	61.42	4.33
1.85	1.0	937	60.54	4.53
1.85	1.0	937	61.45	4.28
1.85	1.0	937	60.68	4.46
1.85	1.5	935	55.58	5.78
1.85	1.5	935	54.79	5.94
1.85	1.5	935	55.01	5.85
1.85	1.5	935	54.88	5.91
1.85	2.0	933	51.78	7.54
1.85	2.0	933	52.45	7.34
1.85	2.0	933	52.14	7.41
1.85	2.0	933	51.20	7.43
1.85	2.5	930	44.42	10.11
1.85	2.5	930	45.82	9.87
1.85	2.5	930	45.54	9.94
1.85	2.5	930	44.97	10.02

the real composition of the melt but at low and high concentration of AlF_3 in the melt this approximation is close to the physical reality.

2. It is assumed that the content of sodium in aluminium which is in equilibrium with the melt can be described by the reaction scheme

$$\text{Al (l)} + 4\ \text{NaF (in the melt)} = 3\ \text{Na (in liquid Al)} + \text{NaAlF}_4\ \text{(in the melt)} \qquad (A)$$

3. The excess Gibbs energy of the system NaF—$NaAlF_4$ is expressed by the equation

$$\Delta G^{\mathrm{E}}/(\mathrm{J\ mol^{-1}}) = x(\mathrm{NaF})x(\mathrm{NaAlF_4})\ \{a_0 + a_1 x(\mathrm{NaAlF_4}) + a_2\ [x(\mathrm{NaAlF_4})]^2 + a_3\ [x(\mathrm{NaAlF_4})]^3\}$$

where

$a_0 = -104\ 810 + 34.14\ T/\mathrm{K}$
$a_1 = -195\ 235 + 198.71\ T/\mathrm{K}$
$a_2 = 568\ 372 - 453.11\ T/\mathrm{K}$
$a_3 = -412\ 538 + 305.48\ T/\mathrm{K}$

4. The parameters of the above equation were determined by a nonlinear regression analysis (the criterion of the least squares) using the experimental data for the content of sodium in aluminium, vapour pressure of $NaAlF_4$ [7], and solid—liquid equilibrium of NaF with the melt [8].

Comparison between the experimental and calculated data is plotted in Figs. 1—3. In Fig. 1, the content of sodium calculated according to the presented thermodynamic model is compared with experimental data. Composition of the molten system NaF—AlF_3 ($NaAlF_4$) is expressed by the cryolite ratio, which is the mole ratio of NaF and AlF_3 (CR = $n(\mathrm{NaF})/n(\mathrm{AlF_3})$). It can be seen that the model describes the data well. Content of sodium in aluminium for CR = 1.20 is higher than that by *Tingle et al.* [3] and that predicted by the model. This discrepancy might be caused by alumina present in the melt.

In Fig. 2, vapour pressure over the melt NaF—$NaAlF_4$ at the temperature of 1000℃ is compared with the calculation. It was assumed that the pressure is given only by $NaAlF_4$(g) species. The activity of $NaAlF_4$(l) was calculated from the presented model. The vapour pressure over the melt NaF—$NaAlF_4$ was taken from the literature [7].

In Fig. 3, the experimental and calculated phase diagram of the system NaF—$NaAlF_4$ is presented. The calculation was based on the approach used in papers [9, 10]. It has been discussed in detail in [11]. It can be seen that in this case there is a deviation of experimental data [8] from the calculation. This problem could be solved by refining the empirical coefficients of the model. However, as the primary purpose of the model is the description and refinement of the data on the content of sodium in aluminium, the agreement was considered as sufficiently good.

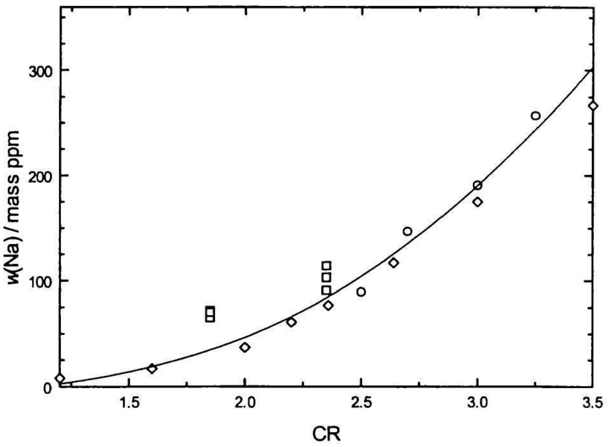

Fig. 1. Content of sodium in nonpolarized aluminium at the temperature of 1 000 °C. —— Calculated; ☐ this paper; ○ *Fellner* and *Lubyová* [4]; ◇ *Tingle*, *Petit*, and *Frank* [3].

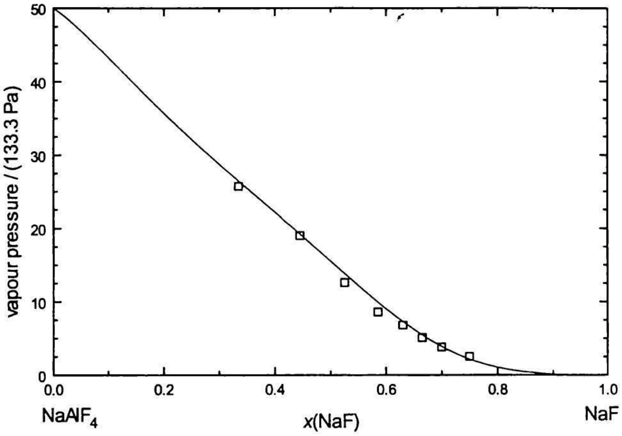

Fig. 2. Vapour pressure over the melt of the system NaF—$NaAlF_4$. —— Calculated; ☐ *Guzman*, *Grjotheim*, and *Østvold* [7].

The literature data [3] which are compared with model calculations in Fig. 1 were obtained in the systems containing no alumina. The data on sodium presented in this work were measured in the systems saturated with alumina. It follows that in the limits of error the alumina concentration has almost no influence on the equilibrium concentration of sodium in aluminium. Experiments for confirmation of the influence of alumina on the content of sodium in aluminium are under progress.

Peterson and *Tabereaux* [5] have published their data on the content of sodium and lithium in aluminium in the form of an empirical equation. We made an attempt to develop a semiempirical model based on our experimental data (see Table 1). This model is based on the reaction schemes

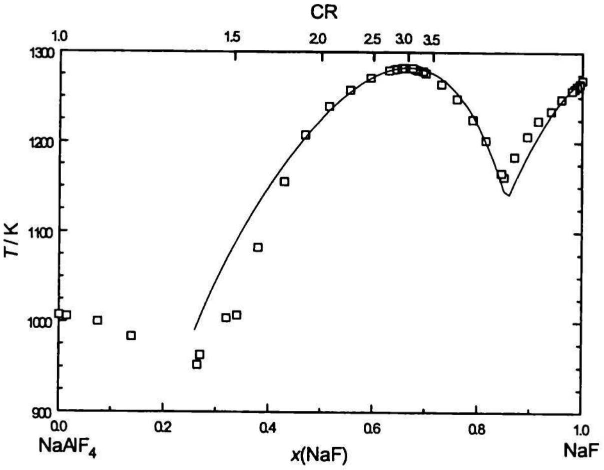

Fig. 3. Phase diagram of the system NaF—$NaAlF_4$. —— Calculated; □ *Holm* [8].

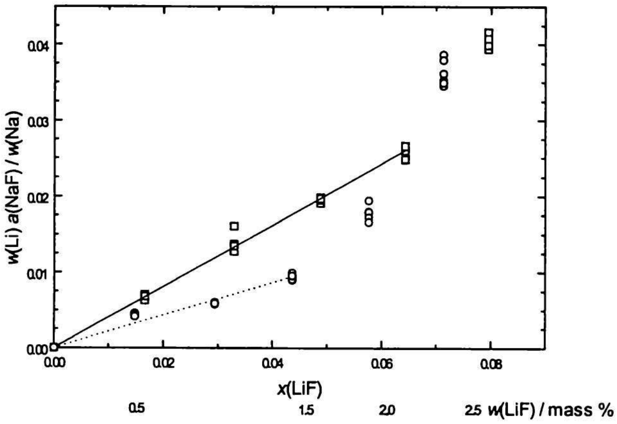

Fig. 4. Semiempirical model describing the content of sodium and lithium in nonpolarized aluminium. □ CR = 1.85; ○ CR = 2.35.

$$\begin{aligned}&3\ \mathrm{LiF}\ (\text{in the melt}) + \mathrm{NaF}\ (\text{in the melt}) + \mathrm{Al}\ (\mathrm{l}) = \\ &3\ \mathrm{Li}\ (\text{in liquid Al}) + \mathrm{NaAlF_4}\ (\text{in the melt}) \qquad (B)\end{aligned}$$

$$\begin{aligned}&\mathrm{Al}\ (\mathrm{l}) + 4\ \mathrm{NaF}\ (\text{in the melt}) = \\ &3\ \mathrm{Na}\ (\text{in liquid Al}) + \mathrm{NaAlF_4}\ (\text{in the melt}) \qquad (C)\end{aligned}$$

It follows that the relation between the content of sodium and lithium in aluminium is influenced by the equilibrium reaction

$$\begin{aligned}&\mathrm{NaF}\ (\text{in the melt}) + \mathrm{Li}\ (\text{in liquid Al}) = \\ &\mathrm{Na}\ (\text{in liquid Al}) + \mathrm{LiF}\ (\text{in the melt}) \qquad (D)\end{aligned}$$

The amounts of sodium and lithium in aluminium are relatively small so that we can assume that the activity coefficients of these species are constant. In a zero approximation we assume that for small concentrations of LiF its activity coefficient is also constant. Then it follows

$$\frac{a(\mathrm{NaF}) \cdot w(\mathrm{Li})}{w(\mathrm{Na})} = f[x(\mathrm{LiF})] \qquad (E)$$

In this approximation we further assume that the activity of NaF equals its activity in the melt without the addition of LiF. Then using the experimental data on the content of lithium and sodium in aluminium we can calculate the expression on the left hand side of eqn (E). The result is plotted in Fig. 4. It follows that the model holds reasonably well at the constant cryolite ratio for concentrations of lithium fluoride lower than 2 mass %. When the concentration of lithium fluoride increases, the activity of sodium fluoride is not constant but it increases, too. This effect is more remarkable in less acidic melts.

Acknowledgements. This work was supported by the Research Grant No. 95/5195/204 of the Slovak Grant Agency.

REFERENCES

1. Grjotheim, K., Krohn, C., Malinovský, M., Matiašovský, K., and Thonstad, J., *Aluminium Electrolysis.* Aluminium-Verlag, Düsseldorf, 1982.
2. Tabereaux, A. T., *Light Metals 1996*, 319.
3. Tingle, W. H., Petit, J., and Frank, W. B., *Aluminium 57*, 286 (1981).
4. Fellner, P. and Lubyová, Ž., *Chem. Papers, 40*, 145 (1986).
5. Peterson, R. D. and Tabereaux, A. T. *Light Metals 1986*, 491.
6. Dewing, E. W., *Met. Trans. 3*, 495 (1972).
7. Guzman, J., Grjotheim, K., and Østvold, T. *Light Metals 1986*, 425.
8. Holm, J. L., *Undersøkelser av struktur og faseforhold for delsystemer med tilknytning til aluminium elektrolysen.* Institut of uorganisk kjemi, NTH, Trondheim, 1963.
9. Foosnaes, M., Østvold, T. and Øye, H., *Acta Chem. Scand. A32*, 973 (1978).
10. Bale, C. W. and Pelton, A. D., *Met. Trans. B 14*, 77 (1983).
11. Danielik, V., Gabčová, J., and Fellner, P., *Molten Salt Forum*, Vols. *5, 6*, pp. 229—232. Trans. Tech. Publications Ltd., Switzerland, 1998.

Translated by P. Fellner