

# Cryolite Corner of the Phase Diagram of the Ternary System NaF—AlF<sub>3</sub>—KF

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Experimental data on solid—liquid phase equilibria of sodium cryolite corner of the ternary system NaF—AlF<sub>3</sub>—KF are presented. Composition was changed in the following range:  $x(\text{NaF})/\text{mole } \% = 40\text{—}80$ ;  $x(\text{AlF}_3)/\text{mole } \% = 20\text{—}40$ ;  $x(\text{KF})/\text{mole } \% = 0\text{—}20$ . A formal model of molten cryolite-based mixtures was used for description of the obtained experimental data. The model assumes that all KF reacts with AlF<sub>3</sub> under formation of K<sub>3</sub>AlF<sub>6</sub> and all remaining AlF<sub>3</sub> reacts with sodium cryolite under formation of NaAlF<sub>4</sub>. For the temperature of primary crystallization it holds

$$\theta(\text{tpc})/^{\circ}\text{C} = 1009.17 - 235.44 \gamma(\text{K}_3\text{AlF}_6) - 10.95 \gamma(\text{NaAlF}_4) - 638.91 [\gamma(\text{NaAlF}_4)]^4$$

This equation holds in the following range of compositions: 25—35 mole % AlF<sub>3</sub>, 0—20 mole % KF. Standard deviation equals 1.86 K.

Melts based on sodium cryolite (Na<sub>3</sub>AlF<sub>6</sub>) serve as solvent for alumina in the electrolyte used in the production of aluminium [1]. Cryolite is a high-melting compound (1011 °C), and it is advantageous to use a low-melting electrolyte [2—4]. This can be done by the use of the AlF<sub>3</sub>-rich bath. Besides of the additions like CaF<sub>2</sub>, LiF, MgF<sub>2</sub>, potassium fluoride may be present in the bath. For investigation of the physico-chemical properties the equilibrium solid—liquid temperatures of the system in question have to be known. In literature [5, 6] only the data on the melting of the system Na<sub>3</sub>AlF<sub>6</sub>—K<sub>3</sub>AlF<sub>6</sub> have been published. In monograph [7] phase diagram of the system NaF—KF—AlF<sub>3</sub> has been presented. The data in the quoted work [7] are not detailed enough in the region of cryolite corner which is used as electrolyte for aluminium smelting.

In this paper the data on solid—liquid equilibria of the ternary system NaF—AlF<sub>3</sub>—KF are presented. The composition of the bath is as follows:  $x(\text{NaF})/\text{mole } \% = 40\text{—}80$ ;  $x(\text{AlF}_3)/\text{mole } \% = 20\text{—}40$ ;  $x(\text{KF})/\text{mole } \% = 0\text{—}20$ .

## EXPERIMENTAL

Solidus—liquidus equilibrium was determined by the method of thermal analysis (cooling curves method). The chemicals used were of anal. grade (Lachema, Brno). Sodium cryolite was synthesized from AlF<sub>3</sub> purified by sublimation. Potassium fluoride was dried in a vacuum drying oven in the presence of P<sub>2</sub>O<sub>5</sub>.

Temperature of the sample was measured by the PtRh10—Pt thermocouple. Comparing point (cool junction) of the thermocouple was kept at the temperature

of  $25.00 \pm 0.01$  °C. Two experimental arrangements were used:

- Mass of the sample in the platinum crucible ( $\varnothing = 40$  mm) was 20 g, rate of cooling did not exceed  $2 \text{ K min}^{-1}$ . The cooling curves have been registered using a recorder EZ-11. Repeated measurements of the temperature of the primary crystallization of the same sample were in the interval narrower than 1 K.
- The investigated samples (10 g) were placed in a platinum crucible ( $\varnothing = 15$  mm). The cooling rate was  $2.0\text{—}2.5 \text{ K min}^{-1}$  and the thermoelectric voltage of the thermocouple was sampled at 10 s intervals and stored in computer memory. The "cooling curves" obtained were numerically treated and the reproducibility in determination of equilibrium temperatures was about 0.3 K.

The thermocouple was calibrated using the melting points of pure salts: NaF,  $\theta_{\text{fus}} = 993.5$  °C (this standard was supplied by the Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava); BaCl<sub>2</sub>,  $\theta_{\text{fus}} = 955$  °C [8]; Na<sub>2</sub>SO<sub>4</sub>,  $\theta_{\text{fus}} = 884.8$  °C [9]; LiF,  $\theta_{\text{fus}} = 848.8$  °C [10]; NaCl,  $\theta_{\text{fus}} = 800.8$  °C [10]; KCl,  $\theta_{\text{fus}} = 771$  °C [10]; and the melting temperatures of eutectic mixtures: NaCl—Na<sub>2</sub>SO<sub>4</sub>,  $\theta_{\text{eut}} = 628$  °C [11]; KCl—K<sub>2</sub>SO<sub>4</sub>,  $\theta_{\text{eut}} = 685$  °C [12]. Repeated measurements of temperature of primary crystallization of the samples for the calibration were in the interval narrower than 1 K and 0.3 K, respectively.

## RESULTS AND DISCUSSION

The obtained experimental data are summarized in Table 1 and Fig. 1. The literature data on the tempera-

**Table 1.** Temperature of the Primary Crystallization of the Ternary System NaF—AlF<sub>3</sub>—KF

$x(\text{NaF})$	$x(\text{AlF}_3)$	$x(\text{KF})$	$\theta_{\text{exp}}/^\circ\text{C}$	$\theta_{\text{calc}}/^\circ\text{C}$
0.80	0.20	0.00	980.8*	—
0.75	0.25	0.00	1011.2	1009.2
0.70	0.30	0.00	998.9	997.7
0.65	0.35	0.00	928.0*	935.0
0.60	0.40	0.00	799.3	798.8
0.75	0.20	0.05	961.3*	—
0.70	0.25	0.05	993.3	993.2
0.65	0.30	0.05	985.4	984.6
0.60	0.35	0.05	922.6	924.4
0.70	0.20	0.10	943.0*	—
0.65	0.25	0.10	976.3	978.1
0.60	0.30	0.10	971.6	971.8
0.55	0.35	0.10	912.5	912.9
0.65	0.20	0.15	930.3*	—
0.60	0.25	0.15	962.0	962.1
0.55	0.30	0.15	956.6	958.3
0.50	0.35	0.15	900.8	901.3
0.60	0.20	0.20	926.9*	—
0.55	0.25	0.20	949.5	946.3
0.50	0.30	0.20	943.7	945.5
0.45	0.35	0.20	895.1	891.0
0.80	0.20	0.00	981.0*	—
0.75	0.25	0.00	1008.0	1009.2
0.70	0.30	0.00	999.5	997.7
0.65	0.35	0.00	988.0*	935.0
0.60	0.40	0.00	741.5*	798.8
0.75	0.20	0.05	955.0*	—
0.70	0.25	0.05	992.5	993.2
0.65	0.30	0.05	985.5	984.6
0.60	0.35	0.05	912.0*	924.4
0.55	0.40	0.05	759.0*	789.8
0.70	0.20	0.10	942.0*	—
0.65	0.25	0.10	977.5	978.1
0.60	0.30	0.10	970.5	971.8
0.55	0.35	0.10	926.0*	912.9
0.65	0.20	0.15	927.0*	—
0.60	0.25	0.15	961.0	962.1
0.55	0.30	0.15	950.5*	958.3
0.50	0.35	0.15	898.5	901.3
0.60	0.20	0.20	924.0*	—
0.55	0.25	0.20	956.0*	946.3
0.50	0.30	0.20	935.5*	945.5
0.45	0.35	0.20	892.5	891.0
0.40	0.40	0.20	814.0*	761.4

\*Temperatures not used for fitting of parameters of eqn (1).

ture of primary crystallization of the system NaF—AlF<sub>3</sub>—KF published by Abramov *et al.* [7] are only in the graphical form. The data published in the cited paper are much lower in the region with a high content of excess AlF<sub>3</sub> and KF content (20—50 K) than our experimental data. However, the data for the binary systems Na<sub>3</sub>AlF<sub>6</sub>—AlF<sub>3</sub> and Na<sub>3</sub>AlF<sub>6</sub>—KF agree reasonably well.

The experimental data obtained in this work were described by a formal equation. Independent parameters in the equation are the mole fractions of K<sub>3</sub>AlF<sub>6</sub> and NaAlF<sub>4</sub> in the melt. It was assumed that:

1. All KF added to the melt reacts under formation of K<sub>3</sub>AlF<sub>6</sub>.
2. All remaining AlF<sub>3</sub> reacts with Na<sub>3</sub>AlF<sub>6</sub> and forms NaAlF<sub>4</sub>.

The proposed model is only formal and it does not reflect real nature of the melt. It can be applied only to the systems with excess of AlF<sub>3</sub> with respect to Na<sub>3</sub>AlF<sub>6</sub>. As we will see application of this model allows to describe experimental data with sufficient precision.

The experimental data were treated by a regression analysis using a program Statgraphics. It was found that the temperatures of the primary crystallization in the composition range can be described by the equation

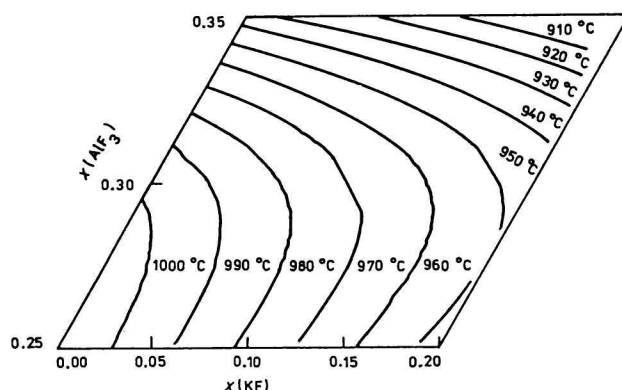
$$\theta(\text{tpc})/^\circ\text{C} = a_0 + a_1 y(\text{K}_3\text{AlF}_6) + a_2 y(\text{NaAlF}_4) + a_3 [y(\text{NaAlF}_4)]^4 \quad (1)$$

$$a_0 = 1009.17 \pm 0.88$$

$$a_1 = -235.44 \pm 5.23$$

$$a_2 = -10.95 \pm 3.29$$

$$a_3 = -638.91 \pm 17.40$$

**Fig. 1.** Experimental isotherms of the part of the ternary system NaF—AlF<sub>3</sub>—KF.

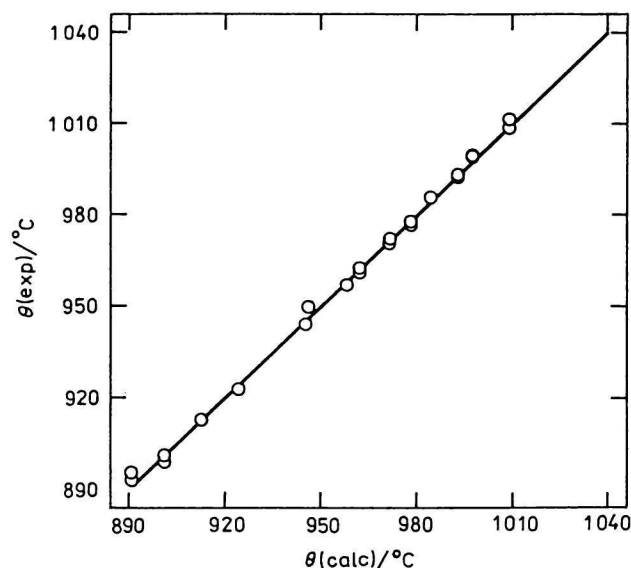


Fig. 2. Comparison of the experimental and calculated data on the temperature of primary crystallization of the ternary system NaF—AlF<sub>3</sub>—KF.

This equation holds in the following range of compositions: 25—35 mole % AlF<sub>3</sub>, 0—20 mole % KF. Standard deviation equals 1.86 K. This error is influenced mainly by the evaporation of AlF<sub>3</sub> and impurities of alumina which may be present in sublimed AlF<sub>3</sub> and/or KF. Comparison of the experimental and calculated data is given in Table 1 and Fig. 2. The temperatures of primary crystallization of samples containing excess of NaF with respect to sodium cryolite and those with excess of AlF<sub>3</sub> 40 mole % were not used for fitting of parameters of eqn (1). In Table 1 they are denoted

with asterisk. It can be seen that the agreement between the experimental and calculated data is reasonable. The constant  $a_0$  corresponds to the melting point of pure Na<sub>3</sub>AlF<sub>6</sub>. In this model this constant was obtained as an adjusted parameter. It is close to the experimentally found quantity, which supports suitability of the proposed formal model for description of the phase diagram of the studied system. Since the equation is empirical it should not be used beyond the investigated concentration limits.

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