Phase Equilibria in the System $KF—AlF_3—Al_2O_3$

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The phase diagrams of the binary system $KF—AlF_3$ as well as a part of the ternary system $KF—AlF_3—Al_2O_3$ in the range up to 10 mole % Al_2O_3 at the mole ratios $n(KF)/n(AlF_3) = 2.35$, 2.2, and 1.85 were measured using the thermal analysis method.

In the system $KF—AlF_3$ the coordinates of the eutectic points are: E_1: 8 mole % AlF_3, 821.2 °C; E_2: 45 mole % AlF_3, 559.0 °C.

In the ternary system the crystallization area of K_3AlF_6 was investigated.

In the family of the systems $MF—AlF_3$ (M = alkali metal), the sodium system is by far the most interesting from an industrial point of view, and is certainly also the most studied. However, better data for the other members of this binary family give a deeper understanding of the $NaF—AlF_3$ binary system.

The phase diagram of the binary system $KF—AlF_3$ was investigated by *Fedotieff* and *Timofeeff* [1] and *Phillips et al.* [2]. In the system, the complex compound K_3AlF_6 melting congruently at 1020 °C [1] or 985 °C [2] exists. Coordinates of eutectic points are: E_1: 5 mole % AlF_3, 840 °C [1] or 7.5 mole % AlF_3, 830 °C [2]; E_2: 45 mole % AlF_3, 570 °C [1] or 560 °C [2].

Quasi-binary system $K_3AlF_6—Al_2O_3$ was studied by *Fellner et al.* [3] and *Mashovets* [4] up to 40 mole % Al_2O_3. In this concentration range alumina was soluble in potassium cryolite. *Robert et al.* [5] studied the solubility of alumina in $KF—AlF_3$ melt at 1000 °C. No other relevant data are available in the literature.

This work deals with the measurement of the phase diagram of the binary system $KF—AlF_3$ and a part of the ternary system $KF—AlF_3—Al_2O_3$ up to 10 mole % Al_2O_3 at the mole ratios $n(KF)/n(AlF_3) = 2.35$, 2.2, and 1.85. The mole ratios of $n(NaF)/n(AlF_3)$ in the range 1.85—2.35 are important from the viewpoint of the electrowinning of aluminium. Therefore the same ratios were chosen in the investigated ternary system. According to the paper by *Robert et al.* [5] the solubility of alumina in the studied range is 9—12 mole % Al_2O_3. Thermodynamically consistent activities and phase diagrams were calculated using the thermodynamic model.

THEORETICAL

Thermodynamic models of systems containing complex compounds are usually based on the assumptions of a partial dissociation of these compounds [6]. However, the structure of cryolite-based melts is not reliably known [7]. The model presented below is independent of the real structure of the melt.

The model is based on the following assumptions and approximations. The ideal melt contains only ionic pairs of the basic species. In the case of the complex compounds presented in the solid phase, it is assumed the compounds completely dissociate to the basic species. Existence of the compounds is included in real behaviour of the melt.

Let us consider the system AX—BX, in which a compound $k\mathrm{AX} \cdot l\mathrm{BX}$ exists in the solid state, where k, l denote numbers of moles of AX and BX, respectively. In the model we assume that the compound $k\mathrm{AX} \cdot l\mathrm{BX}$ completely dissociates under melting to the species AX and BX.

It is convenient to change composition of the compound $k\mathrm{AX} \cdot l\mathrm{BX}$ into compound $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$ where

$$p = \frac{k}{k+l}, \quad q = \frac{l}{k+l} \tag{1}$$

It is obvious that $p + q = 1$. Thus by melting of 1 mole of the compound $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$, which completely dissociates to AX and BX, we will get 1 mole of the melt containing species AX and BX.

The molar enthalpy of fusion of $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$ is equal to

$$\Delta_{\mathrm{fus}} H^{\circ}_{\mathrm{m}} \left[(\mathrm{AX})_p \cdot (\mathrm{BX})_q \right] = \frac{\Delta_{\mathrm{fus}} H^{\circ}_{\mathrm{m}} (k\mathrm{AX} \cdot l\mathrm{BX})}{k+l} \tag{2}$$

The activities of AX and BX are (standard state corresponds to pure component at the temperature and pressure of the melt)

$$a(\mathrm{AX}) = x(\mathrm{AX}) \cdot \gamma(\mathrm{AX}), \quad a(\mathrm{BX}) = x(\mathrm{BX}) \cdot \gamma(\mathrm{BX}) \tag{3}$$

Activity coefficients of AX and BX could be obtained from the molar excess Gibbs energy

$$RT \ln \gamma_i = \left[\frac{\partial \left(\sum n_i \Delta G_i^{\mathrm{E}} \right)}{\partial n_i} \right]_{T,p,n_{j \neq i}} \quad (4)$$

Formally, the compound $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$ divides the system AX—BX into two subsystems AX—$(\mathrm{AX})_p \cdot (\mathrm{BX})_q$ and $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$—BX. Then the molar Gibbs energy of a subsystem, $\Delta G_{\mathrm{m}}^{*}$ (*i.e.* AX—$(\mathrm{AX})_p \cdot (\mathrm{BX})_q$) is

$$\Delta G_{\mathrm{m}}^{*} = \Delta G_{\mathrm{m}} - (1 - x_i^{*}) \Delta G_{\mathrm{m}}^{\circ} \quad (5)$$

where ΔG_{m} denotes the molar Gibbs energy of the system AX—BX; x_i^{*} is mole fraction of a component i in the subsystem (*i.e.* mole fraction AX in the subsytem AX—$(\mathrm{AX})_p \cdot (\mathrm{BX})_q$); $\Delta G_{\mathrm{m}}^{\circ}$ denotes the value of the molar Gibbs energy of the system AX—BX at the composition of the pure compound $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$. Eqn (*5*) corresponds to the assumptions that the new standard state is chosen for the compound $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$. The new standard state means the melt with the composition of the pure compound $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$ at the temperature and the pressure of the melt.

When we assume that the chemical potential of the compound $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$ corresponding to its standard state is

$$\mu \left[(\mathrm{AX})_p \cdot (\mathrm{BX})_q \right] = p\mu (\mathrm{AX}) + q\mu (\mathrm{BX}) \quad (6)$$

then for the activity of $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$ it holds

$$\begin{aligned} & a \left[(\mathrm{AX})_p \cdot (\mathrm{BX})_q \right] = \\ & = x \left[(\mathrm{AX})_p \cdot (\mathrm{BX})_q \right] \cdot \gamma \left[(\mathrm{AX})_p \cdot (\mathrm{BX})_q \right] = \\ & = \frac{x(\mathrm{AX})^p \cdot x(\mathrm{BX})^q}{x(\mathrm{AX})_0^p \cdot x(\mathrm{BX})_0^q} \cdot \frac{\gamma(\mathrm{AX})^p \cdot \gamma(\mathrm{BX})^q}{\gamma(\mathrm{AX})_0^p \cdot \gamma(\mathrm{BX})_0^q} \end{aligned} \quad (7)$$

where $x(i)_0$ and $\gamma(i)_0$ are the mole fractions and activity coefficients of AX and BX in the melt with the composition of the pure compound $(\mathrm{AX})_p \cdot (\mathrm{BX})_q$, respectively.

In the binary system the composition dependence of the molar excess Gibbs energy can be described by

$$\Delta G_{\mathrm{m}}^{\mathrm{E}} = x_1 x_2 \left(g_0 + g_1 x_2 + g_2 x_2^2 + g_3 x_2^3 \right) \quad (8)$$

When the data on the enthalpy of mixing are available (which is the case of the system KF—AlF_3), we can express the molar excess Gibbs energy by the classical relationship

$$\Delta G_{\mathrm{m}}^{\mathrm{E}} = \Delta H_{\mathrm{m,mix}} - T \cdot \Delta S_{\mathrm{m}}^{\mathrm{E}} \quad (9)$$

where $\Delta H_{\mathrm{m,mix}}$ and $\Delta S_{\mathrm{m}}^{\mathrm{E}}$ were assumed to be independent of temperature and may be described by the equations

$$\Delta H_{\mathrm{m,mix}} = x_1 x_2 \left(h_0 + h_1 x_2 + h_2 x_2^2 + h_3 x_2^3 \right) \quad (10)$$

$$\Delta S_{\mathrm{m}}^{\mathrm{E}} = x_1 x_2 \left(s_0 + s_1 x_2 + s_2 x_2^2 + s_3 x_2^3 \right) \quad (11)$$

In eqns (*9*)—(*12*) g_i, h_i, s_i are the polynomial parameters.

In the case of the ternary system the molar excess Gibbs energy of the system can be described by the relationship

$$\Delta G_{\mathrm{m}}^{\mathrm{E}} = \sum \Delta G_{\mathrm{m,\,binary}}^{\mathrm{E}} + \sum g_{ijk} x_1^i x_2^j x_3^k \quad (12)$$

where i, j, k are integer values.

EXPERIMENTAL

For the preparation of the samples, the following chemicals were used: AlF_3, KF (Mikrochem, pure), Al_2O_3 and P_2O_5 (Mikrochem, anal. grade). Al_2O_3 was dried at 600 °C for 2 h, AlF_3 was purified by sublimation, and KF was dried in vacuum drying oven in the presence of P_2O_5.

The temperatures of individual phase transitions (primary, secondary, and eutectic crystallization) were determined by means of thermal analysis method, recording the cooling and heating curves of the investigated mixtures at the rate of 2—5 °C min^{-1}. The platinum crucible containing 30 g of the sample was placed into the resistance furnace with argon atmosphere provided by an adjustable cooling rate. The temperature control and the data processing were performed using a computerized measuring device. The temperature was measured using a Pt—PtRh10 thermocouple calibrated to the melting points of NaF, $BaCl_2$, NaCl, KCl, LiF, and Na_2SO_4. The measured transition temperatures were reproducible within ± 2 °C.

RESULTS AND DISCUSSION

For the system KF—AlF_3 data on vapour pressure and enthalpy of mixing are also available in the literature. *Robert et al.* [8] published data on the vapour pressure above the melt of the KF—AlF_3 system at the temperature 1000 °C. Mass spectroscopic data by *Kolosov et al.* [9] and *Guzman et al.* [10] show that mainly $KAlF_4$ and KF exist in the vapour phase above this binary system. Also the dimer of $KAlF_4$ occurs, but only in low concentrations. Data on molar enthalpy of mixing of the system KF—AlF_3 were presented in paper by *Hong* and *Kleppa* [11].

Phase diagram of the system KF—AlF_3 was calculated using the thermodynamic model described above. Molar enthalpies and temperatures of fusion of pure components used in the calculation are listed in Table 1. The model is based on the following assumptions and approximations:

1. In the first step the composition coordinates of the system KF—AlF_3 are transformed to the system KF—$KAlF_4$. This transformation does not reflect the real ionic composition of the melt, but it is suitable to describe the thermodynamic properties.

Table 1. Enthalpy and Temperature of Fusion of Pure Compounds Used for the Calculation

Component	T_{fus} / K	$\Delta_{fus}H°$ / kJ mol^{-1}
KF	1131 [13]	28.260 [13]
K_3AlF_6	1269 [this paper]	122.620 [13]

Table 2. Coefficients h_i and s_i of Eqns (*13*) and (*14*) in the System KF—$KAlF_4$

Coefficient		Coefficient	
h_0/(kJ mol^{-1})	-66.7 ± 5.3	s_0/(J mol^{-1} K^{-1})	-22 ± 2
h_1/(kJ mol^{-1})	-227.6 ± 40.3	s_1/(J mol^{-1} K^{-1})	-117 ± 10
h_2/(kJ mol^{-1})	426.2 ± 90.0	s_2/(J mol^{-1} K^{-1})	143 ± 13
h_3/(kJ mol^{-1})	-190.8 ± 60.2	s_3/(J mol^{-1} K^{-1})	0

2. The molar enthalpy of mixing of the system KF—$KAlF_4$ is expressed by the equation

$$\Delta H_{m,mix}/(\text{J mol}^{-1}) = x(\text{KF})x(\text{KAlF}_4)\{h_0 + h_1x(\text{KAlF}_4) + h_2[x(\text{KAlF}_4)]^2 + h_3[x(\text{KAlF}_4)]^3\} \quad (13)$$

The parameters of the above equation were determined by a nonlinear regression analysis (the criterion of the least squares, confidence level 99 %) using the available experimental data [11]. The parameters of eqn (*13*) are listed in Table 2. Comparison between experimental [11] and calculated data is in Fig. 1.

3. The molar excess entropy of the system KF—$KAlF_4$ is described by the relationship

$$\Delta S_m^E/(\text{J mol}^{-1}\text{ K}^{-1}) = x(\text{KF})x(\text{KAlF}_4)\{s_0 + s_1x(\text{KAlF}_4) + s_2[x(\text{KAlF}_4)]^2 + s_3[x(\text{KAlF}_4)]^3\} \quad (14)$$

The parameters of eqn (*14*) were determined by a nonlinear regression analysis (the criterion of the least squares, confidence level 99 %) using the available experimental data on vapour pressure above the melt KF—$KAlF_4$ [8] and the measured phase diagram of the system KF—$KAlF_4$. Model parameters of the molar excess entropy of the system KF—$KAlF_4$ are listed in Table 2.

Vapour pressure above the system KF—AlF_3 is shown in Fig. 2. Pressures above the pure compounds KF and $KAlF_4$ were calculated according to the paper published by *Zhou* [12]. It was assumed that partial pressure of the dimer of $KAlF_4$ was negligible. Thus, only partial pressures of KF and $KAlF_4$ were calculated. It can be seen that experimental [8] and calculated data agreed well.

Phase diagram of the system KF—AlF_3 is shown in Fig. 3. Because of lack of thermodynamic data on

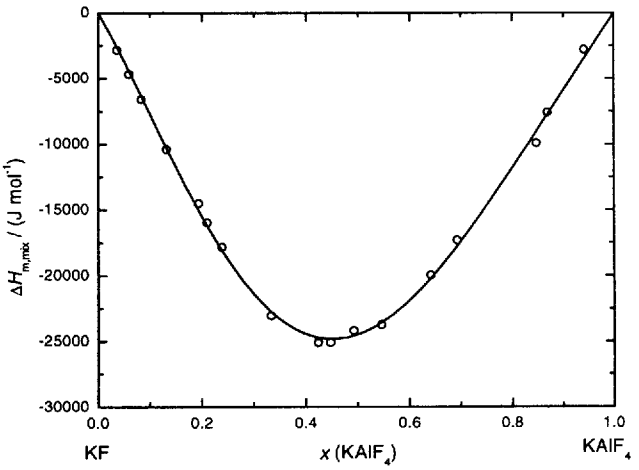

Fig. 1. Molar enthalpy of mixing of the system KF—$KAlF_4$. o Experimental data [11]; — calculated.

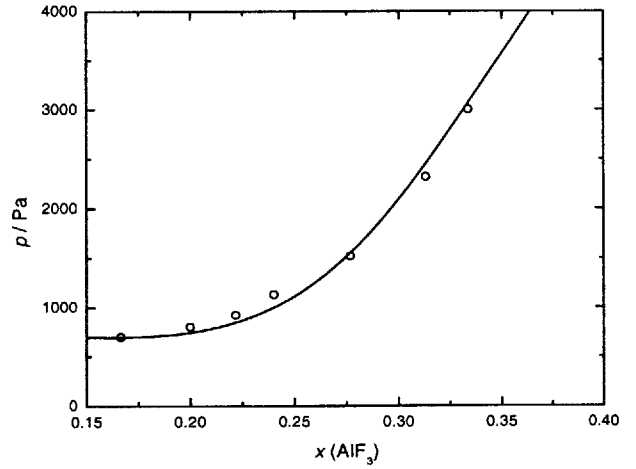

Fig. 2. Vapour pressure above the melt of the system KF—AlF_3. o Experimental data [8]; — calculated.

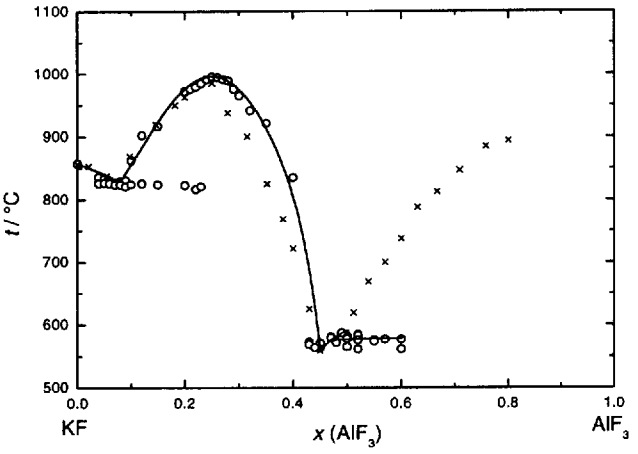

Fig. 3. Phase diagram of the system KF—AlF_3. o This paper; × experimental data [2]; — calculated.

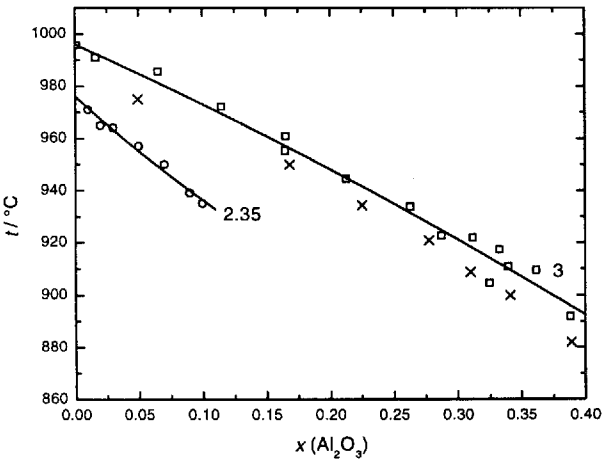

Fig. 4. Liquidus curve of K_3AlF_6 in the system KF—AlF_3—Al_2O_3 at the mole ratio $n(KF)/n(AlF_3) = 3.0$ and 2.35. ○ This paper; □ experimental data [3]; × experimental data [4]; — calculated.

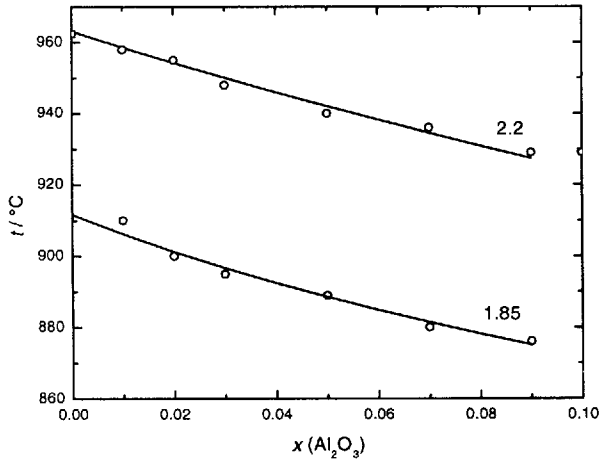

Fig. 5. Liquidus curve of K_3AlF_6 in the system KF—AlF_3—Al_2O_3 at the mole ratio $n(KF)/n(AlF_3) = 2.2$ and 1.85. ○ This paper; — calculated.

$KAlF_4$, the crystallization fields of KF and K_3AlF_6 were only calculated. It can be seen that experimental and calculated data are in a good agreement.

The calculated coordinates of the eutectic points are E_1: 8 mole % AlF_3, 821.2 °C; E_2: 45 mole % AlF_3, 559.0 °C. Temperature of fusion of K_3AlF_6 was measured as 996 °C. The obtained values are closer to the data published by *Phillips et al.* [2] than to the data by *Fedotieff* and *Timofeeff* [1]. However, there is difference about 10 °C for the temperature of fusion of pure K_3AlF_6 between values from this work and [2]. Because of better experimental technique for preparation of pure nonaqueous KF we assume that our data are more correct.

In this work new experimental data on the phase equilibria of the ternary system KF—AlF_3—Al_2O_3 are presented. Composition of the melt was up to 10 mole % Al_2O_3 at the mole ratios $n(KF)/n(AlF_3)$ = 2.35; 2.2 and up to 9 mole % Al_2O_3 at the ratio 1.85. The limiting content of Al_2O_3 in the measured area was chosen according to *Robert et al.* [5].

A part of the phase diagram of the system KF—AlF_3—Al_2O_3 was calculated using the thermodynamic model described above. Parameters of the molar enthalpy of mixing and molar excess entropy of the system KF—$KAlF_4$ were used. It was assumed that alumina has only diluting effect, *e.g.* other binary systems of the ternary system KF—AlF_3—Al_2O_3 are ideal and ternary parameters equal zero. No complex compounds in the melt were supposed.

Results are in Figs. 4 and 5. It can be seen that this simple calculation described the experimental data sufficiently.

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