Low-Melting Electrolyte for Aluminum Smelting

V. Danielik* and J. Híveš

Department of Inorganic Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-81237 Bratislava, Slovakia

A tube-type cell was used to determine the electrical conductivity of low-melting electrolytes (AlF_3-rich) by applying AC−techniques with a sine wave signal with small amplitude in the high-frequency range. The tested melt contained 55 mol % KF and 45 mol % AlF_3 (molar ratio $KF/AlF_3 = 1.22$) with and without the addition of 2 mass % alumina in the temperature range from 660 °C to 750 °C. The electrical conductivity κ in this system can be described by the equation $\kappa/(\Omega^{1-}\cdot cm^{-1}) = 6.458 \exp(-1858.91/T/K) - 0.01876(w(Al_2O_3))$, where $w(Al_2O_3)$ is the alumina concentration in the melt (mass %). Phase diagrams of the systems KF + AlF_3 and KF + AlF_3 + Al_2O_3 up to 10 mol % Al_2O_3 for molar ratios $KF/AlF_3 = 2.35$, 2.2, 1.85, and 1.22 (30, 31, 35, 45 mol % AlF_3) were measured. In the melt with composition 55 mol % KF and 45 mol % AlF_3, the solubility of alumina was aproximately 4 mol % (2.8 mass %) at 540 °C.

1. Introduction

The aluminum industry has long been interested in improving the energy efficiency of the electrowinning process. The methods under study are based on the using of inert anodes and on the development of low-temperature electrolytes. Using inert anodes would permit lower-cost, more efficient cell designs, and of course, there is the potential for solving environmental problems (emissions of CO_2, CF_4, etc.).

To lower the melting point of an electrolyte, aluminum fluoride is the most commonly used additive. The addition of ca. 25 mass % excess AlF_3 allows operation between (850 and 900) °C.[1] However, the addition of AlF_3 decreases alumina solubility and electrical conductivity.[2]

One of the possible components of low-temperature electrolytes is KF. Properties of the systems containing KF and a high content of AlF_3 (density and surface tension) are known and summarized in ref 2 up to 50 mol % AlF_3.

In this paper, data on electrical conductivity and phase equilibria of the system KF + AlF_3 + (Al_2O_3) are presented. The electrical conductivity for the system KF + AlF_3 + Al_2O_3 in the temperature range of interest for low-melting electrolytes is not well known. The phase diagram of the binary system KF + AlF_3 was investigated by Fedotieff and Timofeeff[3] and Phillips et al.[4] There is no agreement between those sets of data. Quasi-binary system K_3AlF_6 + Al_2O_3 was studied by Fellner et al.[5] and Mashovets[6] up to 40 mol % Al_2O_3. In this concentration range, alumina was soluble in potassium cryolite. Robert et al.[7] studied the solubility of alumina in a KF + AlF_3 melt at 1000 °C. No other relevant data are available in the literature.

2. Experimental Section

2.1. Electrical Conductivity. The apparatus for measuring the electrical conductivity of molten salts is based on a tube-type cell,[8] as shown in Figure 1. The cell consists of a pyrolytic boron nitride tube (8) (Sintec Keramik, U.K.) of inner diameter 5 mm, outer diameter 6 mm, and length 100 mm and a graphite crucible (11) of outer diameter 53 mm and height 120 mm, which is used as one electrode. A tungsten rod (9) with a stainless steel ring (7) placed in a BN tube (8) is used as the other electrode. The crucible, containing a 13-g sample of the salt mixture, is placed in a vertical laboratory furnace with a controlled atmosphere (argon 99.996%). The temperature is measured with a Pt−Pt10Rh thermocouple (3).

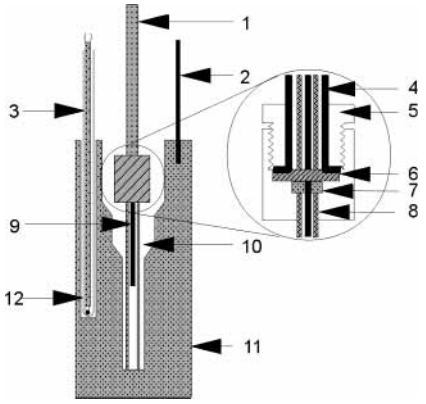

Figure 1. Cross section of the conductivity cell: 1 and 4, stainless steel tube; 2, stainless steel contact rod; 3, thermocouple; 5, BN body of the electrode attachment; 6, BN insulating ring; 7, stainless steel ring; 8, pyrolytic BN tube; 9, tungsten electrode; 10, melt; 11, graphite crucible; 12, alumina tube.

An impedance/gain-phase analyzer (Solartron 1260) was used for the measurements of the cell impedance. The ac amplitude was 10 mV, the frequency was varied from (1 to 100) kHz, and 60 readings were taken within this range. A personal computer was used to control the Solartron 1260 and collect the data. The value of the electrolyte resistance obtained was used for the evaluation of the electrical conductivity of the melt,

$$\kappa/(\Omega^{-1}\cdot cm^{-1}) = \frac{C/cm^{-1}}{R_{el}/\Omega} \quad (1)$$

where C is the cell constant (25.1 cm^{-1}) and R_{el} is the electrolyte resistance. More details can be found in the previous paper.[8]

* Corresponding author. E-mail: vladimir.danielik@stuba.sk. Fax: ++421 2 529 20 171.

10.1021/je049880d CCC: $27.50
Published on Web 07/27/2004

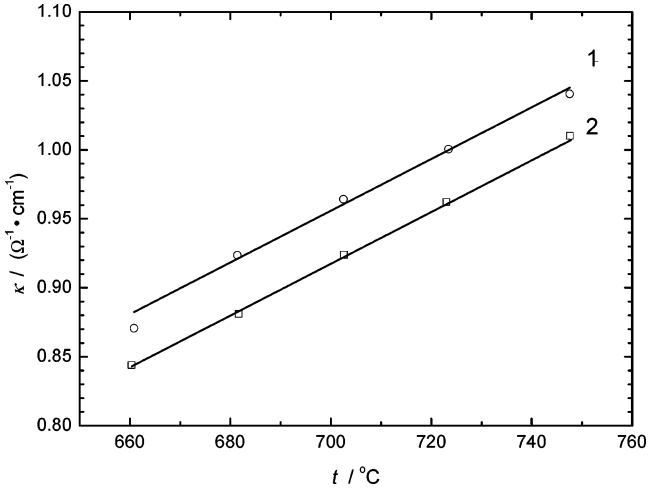

Figure 2. Electrical conductivity of the system KF + AlF_3 + Al_2O_3 as a function of temperature and composition: ○, 55 mol % KF + 45 mol % AlF_3; □, same melt plus 2 mass % alumina; line 1, eq 3; line 2, eq 5.

2.2. Phase Equilibria. The temperatures of individual phase transitions (primary, secondary, and eutectic crystallization) were determined by means of a thermal analysis method, recording the cooling and heating curves of the investigated mixtures at the rate of (2 to 5) K·min^{-1}. The platinum crucible containing (30 ± 0.005) g of the sample was placed into the resistance furnace provided by an adjustable cooling rate. Temperature control and data processing were performed using a computerized measuring device. The temperature was measured using a Pt−PtRh10 thermocouple calibrated to the melting points of pure compounds NaF, $BaCl_2$, NaCl, KCl, LiF, and Na_2SO_4. The measured transition temperatures were reproducible to within ±2 K.

2.3. Chemicals. NaCl (puratronic, 99.999%, J&M); NaF (p.a., Merck); KF (p.a., Merck); AlF_3 (sublimed, min. 99.8%); γ-Al_2O_3 (p.a., Merck); and P_2O_5 (analytical grade, Mikrochem) were used.

All chemicals were dried for several hours at 600 °C before use. KF was dried in a vacuum drying oven in the presence of P_2O_5 and kept in a drybox.

3. Results and Discussion

3.1. Electrical Conductivity. The melt contained 55 mol % KF and 45 mol % AlF_3. Alumina (2 mass %) was also added to the melt. The operating temperature ranged from 660 °C to 750 °C.

Figure 2 shows plots of the experimental conductivity data as a function of temperature for the KF + AlF_3 and KF + AlF_3 + Al_2O_3 systems. The electrical conductivity data in the molten system can be described by a simple Arrhenius-type equation:

$$\kappa/(\Omega^{-1}\cdot\mathrm{cm}^{-1}) = A\ \exp[B/(T/\mathrm{K})] \quad (2)$$

where A and B are constants for the measured system. The electrical conductivity in the alumina-free system could be described by the equation (temperature range from 660 °C to 750 °C)

$$\kappa/(\Omega^{-1}\cdot\mathrm{cm}^{-1}) = (6.458 \pm 0.0068)\ \exp[(-1858.91 \pm 20.77)/(T/\mathrm{K})] \quad (3)$$

The influence of additives can be expressed by the equation (following the additivity rule)

$$\kappa/(\Omega^{-1}\cdot\mathrm{cm}^{-1}) = A\ \exp[B/(T/\mathrm{K})] + C_i/(\Omega^{-1}\cdot\mathrm{cm}^{-1})\ w_i \quad (4)$$

where C_i represents a constant and w_i represents the mass concentration of additives.The electrical conductivity in the melt with 2 mass % alumina could be described by the equation (temperature range from 660 to 750 °C, concentration range of Al_2O_3 from 0 to 2 mass %)

$$\kappa/(\Omega^{-1}\cdot\mathrm{cm}^{-1}) = 6.458\ \exp[-1858.91/(T/\mathrm{K})] - (1.876 \pm 0.033)\ w(Al_2O_3) \quad (5)$$

The electrical conductivities for the measured system at 750 °C are presented in Table 1. The solid lines in Figure 2 represent eqs 3 and 5.

3.2. Phase Equilibria. 3.2.1. System KF + AlF_3. The phase diagram of the system KF + AlF_3 was calculated using the thermodynamic model based on the following assumptions and approximations:

(1) In the first step, the composition coordinates of the system KF + AlF_3 are transformed to those of the system KF + $KAlF_4$. This transformation does not reflect the real ionic composition of the melt, but it is suitable for the description of the thermodynamic properties.[2]

(2) The molar enthalpy of mixing of the system KF(1) + $KAlF_4$(2) is expressed by the equation

$$\Delta H_{\mathrm{m,mix}}/(\mathrm{J}\cdot\mathrm{mol}^{-1}) = x_1x_2\cdot(h_0 + h_1x_2 + h_2x_2^{\,2} + h_3x_2^{\,3}) \quad (6)$$

The parameters of the above equation were determined by a nonlinear regression analysis (least-squares criterion, confidence level 99%) using the available experimental data.[9]

(3) The molar excess entropy of the system KF(1) + $KAlF_4$(2) is described by the relationship

$$\Delta S_{\mathrm{m}}^{\mathrm{E}}/(\mathrm{J}\cdot\mathrm{mol}^{-1}\,\mathrm{K}^{-1}) = x_1x_2(s_0 + s_1x_2 + s_2x_2^{\,2} + s_3x_2^{\,3}) \quad (7)$$

The parameters of eq 7 were determined by a nonlinear regression analysis (least-squares criterion, confidence level 99%) using the available experimental data on vapor pressure above the KF + $KAlF_4$ [10] melt 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.

The thermodynamic model is described in more detail in ref 11.

The phase diagram of the system KF + AlF_3 is shown in Figure 3. Because of the lack of thermodynamic data for $KAlF_4$, only the crystallization fields of KF and K_3AlF_6 were 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 mol % AlF_3, 821.2 °C and E_2: 45 mol % AlF_3, 559.0 °C. The temperature of fusion of K_3AlF_6 was measured to be 996 °C. The obtained values are closer to the data published in ref 4 than data by Fedotieff and Timofeeff.[3] However, there is difference of about 10 °C for the temperature of fusion of pure K_3AlF_6 between the value from this work and the value from ref 4.

3.2.2. System KF + AlF_3 + Al_2O_3. In this work, new experimental data on the phase equilibira of the ternary system KF + AlF_3 + Al_2O_3 are presented. The composition of the melt was up to 10 mol % Al_2O_3 at molar ratios of KF/AlF_3 = 2.35 (30 mol % AlF_3) and 2.2 (31 mol % AlF_3) and up to 9 mol % Al_2O_3 for a molar ratio of 1.85 (35 mol % AlF_3). The range of the content of Al_2O_3 in the measured area was chosen according to Robert et al.[7] For a ratio of

Table 1. Electrical Conductivities for the System KF(1) + AlF_3(2) + Al_2O_3(3) at 750 °C[a]

x_1	x_2	w_3	$\kappa/(\Omega^{-1}\cdot cm^{-1})$
0.55	0.45	0.0	1.050 ± 0.007
0.55	0.45	0.02	1.012 ± 0.008

[a] Mole fractions are based on the binary mixture KF + AlF_3.

Table 2. Coefficients h_i and s_i of Equations 6 and 7 in the System KF + $KAlF_4$

coefficient		coefficient	
$kJ\cdot mol^{-1}$	value	$kJ\cdot mol^{-1}\cdot K^{-1}$	value
h_0	−66.7 ± 5.3	s_0	−22 ± 2
h_1	−227.6 ± 40.3	s_1	−117 ± 10
h_2	426.2 ± 90.0	s_2	143 ± 13
h_3	−190.8 ± 60.2	s_3	0

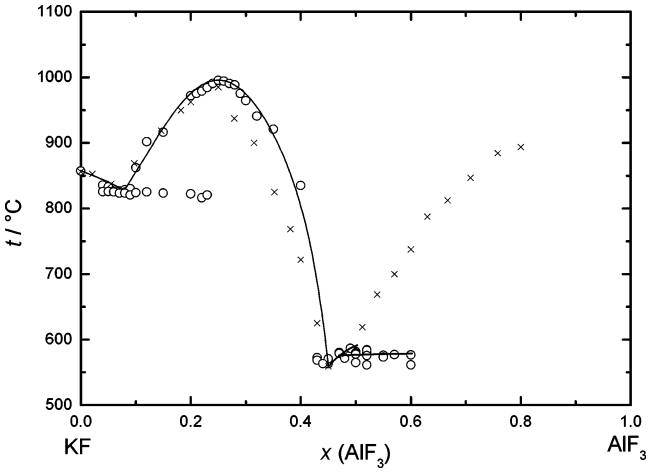

Figure 3. Phase diagram of the system KF + AlF_3: ○, experimental data; ×, Phillips et al.;[4] −, calculated.

1.22 (45 mol % AlF_3), the checked composition range of the melt was up to 7 mol % Al_2O_3, but only ca. 4 mol % Al_2O_3 was soluble in the melt at the measured temperature.

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 equalled zero). We assumed that there were no complex compounds in the melt.

Results are summarized in Figures 4−6. It can be seen that this simple calculation describes the experimental data sufficiently well. In Figure 6, it can be seen that for the molar ratio KF/AlF_3 = 1.22 (45 mol % AlF_3) the measured temperature of primary crystallization does not decrease for Al_2O_3 content of more than 4 mol %. It is assumed that the limiting solubility of Al_2O_3 in the melt was achieved. For the ratio KF/AlF_3 = 2.2 (31 mol % AlF_3), the maximum soluble content of Al_2O_3 in the melt was 9 mol % (Figure 5).

4. Conclusions

The electrical conductivity for the system KF + AlF_3 + Al_2O_3 (KF/AlF_3 molar ratio 1.22, Al_2O_3 at 0 and 2 mass %) was not known. Equation 5 allows us to calculate the electrical conductivity for the system KF + AlF_3 + Al_2O_3 at a given composition in the temperature range of (660 to 750) °C. The electrical conductivity for the conventional electrolyte of composition Na_3AlF_6 + 11 wt % AlF_3 + 5 wt % CaF_2 + 3 wt % Al_2O_3 at 950 °C is 2.130 Ω^{-1} cm^{-1}.[2] The conductivity is approximately half that of the standard bath

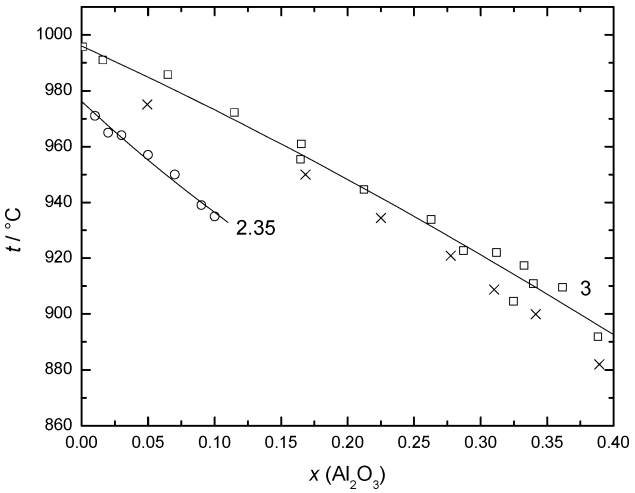

Figure 4. Lines of primary crystallization of K_3AlF_6 in the system KF + AlF_3 + Al_2O_3 at molar ratios KF/AlF_3 = 3.0 (25 mol % AlF_3) and 2.35 (30 mol % AlF_3): ○, experimental data; □, Fellner et al.;[5] ×, Mashovets;[6] −, calculated.

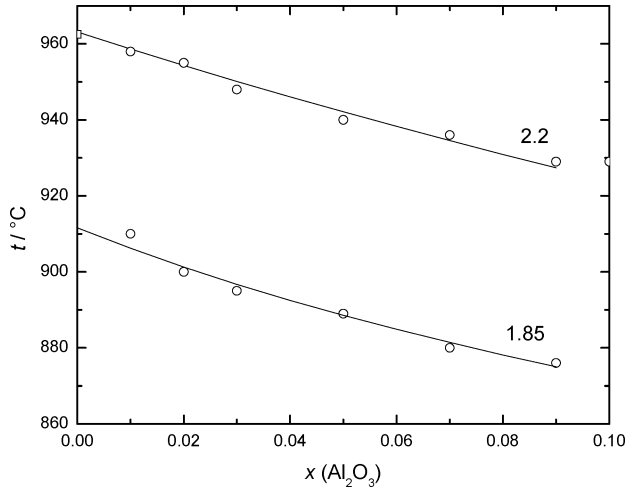

Figure 5. Lines of primary crystallization of K_3AlF_6 in the system KF + AlF_3 + Al_2O_3 at molar ratios KF/AlF_3 = 2.2 (31 mol % AlF_3) and 1.85 (35 mol % AlF_3): ○, experimental data; −, calculated.

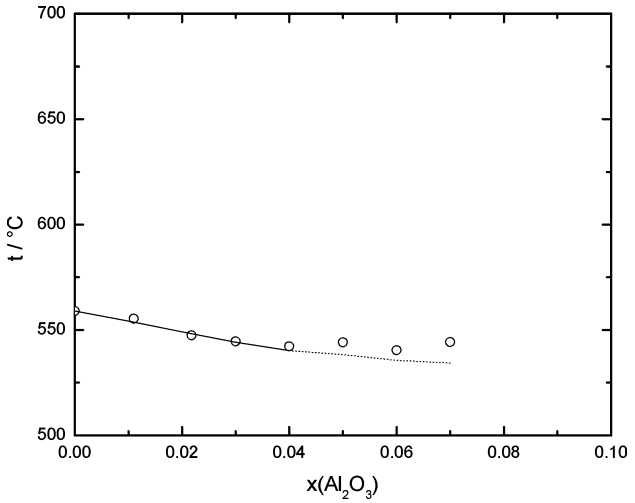

Figure 6. Line of primary crystallization of K_3AlF_6 in the system KF + AlF_3 + Al_2O_3 at molar ratio KF/AlF_3 = 1.22 (45 mol % AlF_3): ○, experimental data; −···, calculated.

(mentioned above) used in aluminum electrowinning. A higher electrolyte voltage drop (100% increase) might be expected in the case of a low-melting-point electrolyte. This can be reduced by the addition of LiF or decreasing the interelectrode distance.

The phase diagram of the system $KF + AlF_3$ was verified. The obtained values of the eutectic points are closer to the data published by Phillips et al.[4] However, there is a difference of about 10 °C for the temperature of fusion of pure K_3AlF_6, and the liquidus line of K_3AlF_6 in the concentration range of (25 to 40) mole % AlF_3 is different than that in ref 4.

Some lines at a constant KF/AlF_3 ratio with the addition of Al_2O_3 were measured. A simple thermodynamic calculation described the experimental data sufficiently. For the molar ratio $KF/AlF_3 = 1.22$, the limiting solubility of Al_2O_3 in the melt was achieved at ca. 4 mol % Al_2O_3 (2.8 mass % Al_2O_3) at 540 °C (Figure 6).

Literature Cited

(1) Sleppy, W. C.; Cochran, C. N. Bench Scale Electrolysis of Alumina in Sodium Fluoride−Aluminium Fluoride Melts below 900 °C. In *Light Metals*; Peterson, W. S., Ed.; AIME: New York, 1979; p 385.

(2) Thonstad, J.; Fellner, P.; Haarberg, G. M.; Híveš, J.; Kvande, H.; Sterten, Å. *Aluminium Electrolysis*, 3rd ed.; Verlag: Düsseldorf, Germany, 2001.

(3) Fedotieff, P. P.; Timofeeff, K. The Melting Diagram of the Systems: $KF-AlF_3$ and $LiF-AlF_3$. *Z. Anorg. Allg. Chem.* **1932**, *206*, 263.

(4) Phillips, B.; Warshaw, C. M.; Mockrin, I. Equilibria in $KAlF_4$-Containing Systems. *J. Am. Ceram. Soc.* **1966**, *49*, 631.

(5) Fellner, P.; Chrenková, M.; Gabčová, J.; Matiašovský, M. Physicochemical Properties of the Molten System $Na_3AlF_6-K_3AlF_6-Al_2O_3$. *Chem. Pap.* **1990**, *44*, 677.

(6) Mashovets, V. P. *Elektrometallurgiya Alyuminiya*; ONTI: Moscow, 1938.

(7) Robert, E.; Olsen, J. E.; Daněk, V.; Tixhon, E.; Østvold, T.; Gilbert, B. Structure and Thermodynamics of Alkali Fluoride−Aluminum Fluoride−Alumina Melts. Vapor Pressure, Solubility, and Raman Spectroscopic Studies. *J. Phys. Chem. B* **1997**, *101*, 9447.

(8) Híveš, J.; Thonstad, J.; Sterten, Å; Fellner, P. Electrical Conductivity of the Molten Cryolite-Based Ternary Mixtures $Na_3AlF_6-Al_2O_3-CaF_2$ and $Na_3AlF_6-Al_2O_3-MgF_2$. *Electrochim. Acta* **1993**, *38*, 2165.

(9) Hong, K. C.; Kleppa, O. J. Thermochemistry of the Liquid Mixtures of Aluminum Fluoride with Alkali Fluorides and with Zinc Fluoride. *J. Phys. Chem.* **1978**, *82*, 176.

(10) Robert, E.; Olsen, J. E.; Gilbert, B.; Østvold, T. Structure and Thermodynamics of Potassium Fluoride−Aluminium Fluoride Melts. Raman Spectroscopic and Vapour Pressure Studies. *Acta Chem. Scand.* **1997**, *51*, 379.

(11) Danielik, V.; Gabčová, J. Phase Diagram of the System $Na_3AlF_6-NaF-Na_2SO_4$. *Thermochim. Acta* **2001**, *366*, 79.

Received for review March 25, 2004. Accepted June 14, 2004. Part of this work was supported by the Slovak Grant Agency (VEGA 1/9426/02).

JE049880D