

The electrical conductance and the structure of the NaF—AlF₃ melts

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The electrical conductance of the NaF—AlF₃ melts, which are the essential ingredients of the aluminium electrolyte, was measured. The experimental conductivity values were interpreted from the standpoint of the structure (ionic composition) of the melts. The assumption about the incomplete dissociation of NaF, according to which the neutral ionic pairs of Na⁺·F⁻ besides the Na⁺ and F⁻ ions are present in the melt, was confirmed. The dissociation degree of NaF was calculated and it was found that with increasing temperature the dissociation degree lowers. Also the diffusion coefficients of the Na⁺ and F⁻ ions in the NaF melt were calculated.

Измерена электропроводность расплавов NaF—AlF₃, являющихся основными ингредиентами алюминиевого электролита. Экспериментальные значения электропроводности интерпретируются с точки зрения строения (ионного состава) расплавов. Подтвердилось предположение о неполной диссоциации NaF, согласно которому в расплаве присутствуют нейтральные ионные пары Na⁺·F⁻ наряду с ионами Na⁺ и F⁻. Рассчитана степень диссоциации NaF и обнаружено, что с повышением температуры степень диссоциации уменьшается. Кроме того, рассчитаны коэффициенты диффузии ионов Na⁺ и F⁻ в расплаве NaF.

The NaF—AlF₃ system, in which the congruently melting compound Na₃AlF₆ (cryolite) is formed, is the basis of the aluminium electrolyte. From the technological point of view the electrical conductance is one of the most important physicochemical properties of the electrolyte, however its study is also interesting from theoretical point of view, as it can contribute to the explaining of the structure (ionic composition) of the investigated melts.

Between the conductivity data of the molten NaF—AlF₃ system according to various authors [1], there are relatively great differences, caused probably not only by different purity of the used reagents, but also by errors caused by the used measuring method. Therefore, the conductivity of the molten NaF—AlF₃ system was again determined in this work using high purity reagents and a new experimental technique permitting high precision of the measurement. The experimentally determined dependence of the conductivity of the melts on the

composition was compared with the theoretical one calculated according to the series model [2].

According to the classical idea the NaF, as well as the other alkali halides, should be completely dissociated after melting to Na^+ and F^- ions. With regard to the difference between the values of the molar conductance of alkali halides calculated from the diffusion coefficients and the experimental ones, which are generally lower, the assumption of the incomplete dissociation of these compounds was expressed [3, 4]. On the basis of the experimentally determined values of the conductivity of the NaF— AlF_3 melts, of the values of the density [5] and of the equilibrium composition of the melt determined from the known values of the dissociation constants of cryolite [6, 7], the dissociation degree of NaF similar to the approach in [6] was calculated. The diffusion coefficients of the Na^+ and F^- ions in the NaF melt were also calculated.

Experimental

For the measurement the following reagents were used: KNO_3 , NaNO_3 , NaCl , KCl , all of anal. grade, NaF "for single crystals" with the melting point of 995°C and AlF_3 prepared by the sublimation of technical product.

The conductivity was measured by the method of four electrodes [8, 9]. The principle of this "absolute" method lies in the measurement of the voltage between one couple of electrodes in an electrical field of known intensity created by current flowing through opposite couple of electrodes. The measurement is realized at two depths of immersion of the electrodes. The conductivity values were calculated by the equation

$$\kappa = \frac{\ln 2}{2\pi} \cdot \frac{R_1 - R_2}{R_1 \cdot R_2 \cdot \Delta W} \cdot F \quad (1)$$

where R_1 and R_2 are the values of the resistance at individual depths of immersion, ΔW is the difference between the two depths of immersion of electrodes and F is a factor near unity respecting the deviation from the ideal geometrical arrangement of the measuring system.

The detailed description of the measuring apparatus was published in [10]. The working sequence of the measuring device was controlled and the output data were processed by means of a computer SAPI 1. The measurement of the electrical conductance of the melts was realized in a resistance furnace, the temperature of which was controlled with a thyristor regulator. The temperature of the melt was measured with a Pt—Pt10Rh thermocouple, the thermoelectrical voltage was also processed and recalculated in K or $^\circ\text{C}$ in the control unit. The difference in the immersion depth of the electrodes (ΔW) was adjusted by means of a micrometric screw with a tolerance of ± 0.01 mm. The change in the immersion depth of the electrodes was realized automatically by means of an electromagnet. Pt30Rh wires with a diameter of 0.5 mm fixed in a sintered alumina four-fold capillary tube served as electrodes. The measurement was carried out with an alternating current with a frequency of 5 kHz.

The correct function of the apparatus was verified with the measurement of the conductivity of the aqueous solutions of KCl and of the NaNO₃, KNO₃, and NaCl melts. The investigated electrolyte was placed in a Pt crucible of *ca.* 25 cm³ in volume. By the measurement the used immersion depths of electrodes were $W_1 = 5$ mm and $W_2 = 10$ mm. For the mutual distance of the electrodes of 3 mm the average value of the geometrical factor determined by calibration was $F = 1.0160 \pm 2 \times 10^{-4}$.

The conductivity measurement of the melts of the system NaF—AlF₃ was realized in the temperature range of 960—1060 °C. Eight to twelve independent measurements were made at each chosen temperature. The maximum dispersion of the conductivity values at constant temperature was ± 0.4 %. From the analysis of the measurement errors, overall error of the measurement of 1 % was estimated.

The temperature dependences of the conductivity were described by polynomials of the second order, the coefficients and the standard deviations of which are given in Table 1.

Table 1

Coefficients a , b , c in the equation $\kappa = a + b \cdot \theta + c \cdot \theta^2$ for the melts of the NaF—AlF₃ system and the standard deviation σ of the experimental values from this equation

mole % AlF ₃	$-a$ S cm ⁻¹	$b \cdot 10^2$ S cm ⁻¹ °C ⁻¹	$-c \cdot 10^6$ S cm ⁻¹ °C ⁻²	$\sigma \cdot 10^2$ S cm ⁻¹
0	1.654	0.899	2.34	2.6
2.5	2.776	1.233	3.69	3.8
5	5.804	1.527	4.87	4.4
7.5	4.721	1.325	4.16	3.0
10	6.030	1.498	4.78	8.1
12.5	7.831	1.740	5.71	3.4
15	7.695	1.717	5.71	4.3
17.5	2.524	0.788	1.93	1.2
20	5.862	1.348	4.31	5.1
22.5	5.958	1.287	3.89	2.0
25	4.519	1.015	2.78	4.4
27.5	4.884	1.063	3.03	6.3
30	6.194	1.232	3.68	3.3
32.5	6.290	1.234	3.75	4.1
35	8.450	1.578	5.21	3.2
37.5	1.598	0.465	1.03	3.4
40	7.512	1.462	5.21	1.6
45	5.393	1.088	3.86	2.1

Results and discussion

In Fig. 1 the isotherm of the conductivity of the NaF—AlF₃ melts at 1000 °C, constructed on the basis of interpolated and/or extrapolated conductivity values

on the polytherms of individual melts, is shown. In comparison with the course of the concentration dependence of the conductivity calculated according to the series model [2] (dotted line in Fig. 1) the experimentally determined conductivity values are in a relatively good agreement with the series model only in the region from 20 to 40 mole % AlF_3 . It was found that the determined dependence $\kappa = f(c(\text{AlF}_3))$ is approximately up to 30 mole % AlF_3 linear, similarly as in [11], where the electrical conductance was measured using two electrodes and a Whetton bridge. In the region over 30 mole % AlF_3 the dependence lies between the courses given in [2] and [11]. The existence of an inflexion point predicted in [2] was not confirmed.

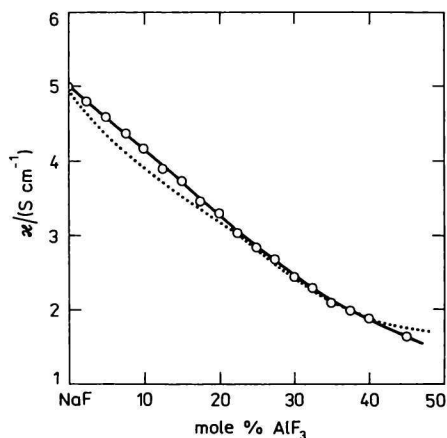


Fig. 1. The dependence of the conductivity of the NaF— AlF_3 melts on the composition (mole % AlF_3) at the temperature 1000 °C. Dotted line — after the series model [6].

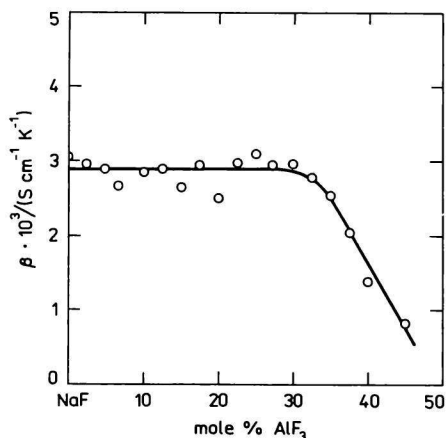


Fig. 2. The dependence of the temperature coefficient of the conductivity of the NaF— AlF_3 melts on the composition at the temperature 1000 °C (the melting point of Na_3AlF_6 is 1003 °C).

The temperature coefficient of the conductivity (Fig. 2) of the melts of the NaF— AlF_3 system is constant approximately to 30 mole % AlF_3 and then decreases. The average value in the interval of 0 to 30 mole % AlF_3 at the temperature of 1000 °C, is $2.88 \times 10^{-3} \text{ S cm}^{-1} \text{ K}^{-1}$, which is comparable with the value given for the NaF melt in [12] ($2.74 \times 10^{-3} \text{ S cm}^{-1} \text{ K}^{-1}$).

On the basis of the idea of the incomplete dissociation of NaF in the NaF— AlF_3 melts the calculation of the dissociation degree of NaF according to [6] was realized. The calculation was carried out for the concentration range which corresponds to the partial NaF— Na_3AlF_6 system. In the melts of this system also NaAlF_4 besides NaF and Na_3AlF_6 is present, which is formed by partial thermal dissociation of Na_3AlF_6 according to the scheme



The present NaF partially dissociates according to the scheme



with a dissociation degree α . It is assumed that the present NaAlF₄ and Na₃AlF₆ components fully dissociate according to the schemes



For the calculation of the dissociation degree of NaF only the values of the conductivity and the molar concentration of conducting ions (Na⁺ and F⁻) were taken into account; the participation of AlF₄⁻ and AlF₆³⁻ ions on the charge transport was neglected. Further it was assumed that the molar conductance of Na⁺ and F⁻ ions ($\lambda(\text{Na}^+)$ and $\lambda(\text{F}^-)$) does not depend on the concentration of the other components of the electrolyte. Then the conductivity of a molten mixture can be expressed by the relation

$$\kappa = c(\text{Na}^+) \cdot \lambda(\text{Na}^+) + c(\text{F}^-) \cdot \lambda(\text{F}^-) \quad (2)$$

where $c(\text{Na}^+)$ and $c(\text{F}^-)$ are the equilibrium molar concentrations of Na⁺ and F⁻ ions in the mixture.

The molar concentrations of Na⁺ and F⁻ ions were determined by the mass balance analysis. According to the above-mentioned assumptions the Na⁺ ion is formed by a complete dissociation of the fluoroaluminate components and by a partial dissociation of NaF. The F⁻ anion is formed only by the dissociation of NaF. For the molar concentrations of conducting particles Na⁺ and F⁻ in the melts of the NaF—AlF₃ system the following relations can be derived

$$c(\text{Na}^+) = \frac{\rho(3x + \alpha \cdot y + z)}{210x + 42y + 126z} \quad (3)$$

$$c(\text{F}^-) = \frac{\rho \cdot \alpha \cdot y}{210x + 42y + 126z} \quad (4)$$

where ρ is the density of the melt and x , y , z are the equilibrium mole fractions of Na₃AlF₆, NaF, and NaAlF₄ in the melt. The denominator in relations (3) and (4) corresponds to the average molar mass of the melt. Substituting eqns (3) and (4) into eqn (2) we get a set of equations for various compositions, which can be solved for the chosen values of α . The right value of α must obey the following relation

$$\frac{\lambda(\text{Na}^+)}{\lambda(\text{F}^-)} = \frac{r(\text{F}^-)}{r(\text{Na}^+)} \quad (5)$$

The ionic radii of Na^+ and F^- ions ($r(\text{Na}^+)$ and $r(\text{F}^-)$) were taken from [13]. The values of the density of the NaF—AlF_3 melts and the equilibrium mole fractions of components used in eqns (3) and (4) for the chosen values of the temperature 1000, 1050, and 1100 °C were taken from [5, 6]. For the dissociation constant of NaF then it holds

$$K_{\text{d,NaF}} = \frac{\alpha^2}{1 - \alpha^2} \quad (6)$$

The values of the dissociation degree, of the equilibrium constants, and the Gibbs energies of dissociation of NaF at temperatures of 1000, 1050, and 1100 °C are given in Table 2.

Table 2

The calculated dissociation degree, the dissociation constant, and the dissociation Gibbs energy of the NaF melt

$\frac{\theta}{\text{°C}}$	α	$K_{\text{d,NaF}}$	$\frac{\Delta G_{\text{d,NaF}}}{\text{kJ mol}^{-1}}$
1000	0.655	0.751	3.11
1050	0.641	0.697	3.96
1100	0.631	0.662	4.81

The values of the molar conductances of Na^+ and F^- ions, which correspond to the determined dissociation degrees, are given in Table 3 together with the values of molar conductances of the pure NaF melt calculated according to the relation

$$\lambda(\text{NaF}) = \alpha(\lambda(\text{Na}^+) + \lambda(\text{F}^-)) \quad (7)$$

The values of ionic mobilities are given in Table 3, too. The determined values of the molar conductance of NaF are in a good agreement with the values given in [11] and [14]. On the other hand, in comparison with the values given in [6] and [11], the molar conductances of Na^+ and F^- ions are higher, especially for the $\lambda(\text{F}^-)$ value. From the values of the dissociation degree of the NaF and the molar conductances determined in this work it follows that the participation of the F^- ions on the conductance of the NaF melt is higher than that one mentioned in [6] and [11]. On the electrical conductance of the NaF—AlF_3 melts the F^- ions participate most significantly. This is confirmed by the similarity of the temperature dependences of the conductivity of the pure NaF melt and of the molten NaF—AlF_3 mixtures, as well as the dependence of the molar concentration of Na^+ and F^- ions and of the ionic pairs $\text{Na}^+ \cdot \text{F}^-$ on the com-

Table 3

The calculated molar conductance of Na⁺ and F⁻ ions, the molar conductance of NaF, and the mobilities of the Na⁺ and F⁻ ions in the NaF melt

θ	$\lambda(\text{Na}^+)$	$\lambda(\text{F}^-)$	$\lambda(\text{NaF})$	$u_{\text{Na}^+} \cdot 10^4$	$u_{\text{F}^-} \cdot 10^4$
°C	S cm ² mol ⁻¹	S cm ² mol ⁻¹	S cm ² mol ⁻¹	cm ² s ⁻¹ V ⁻¹	cm ² s ⁻¹ V ⁻¹
1000	94.27	71.80	108.78	9.77	7.44
1050	100.47	76.73	113.59	10.41	7.95
1100	106.10	81.09	118.12	11.00	8.40

position in the NaF—AlF₃ system, given for the temperature 1000 °C in Fig. 3. At the same time this dependence hints to the fact that the shape of the conductivity isotherm of the NaF—AlF₃ melts is given first of all by the course of the concentration of the F⁻ ions. From the temperature dependences of the molar conductances of Na⁺ and F⁻ ions

$$\lambda(\text{Na}^+) = A(\text{Na}^+) \cdot \exp[-E^*(\text{Na}^+)/RT] \quad (8)$$

$$\lambda(\text{F}^-) = A(\text{F}^-) \cdot \exp[-E^*(\text{F}^-)/RT] \quad (9)$$

the values of the preexponential factors $A(\text{Na}^+) = 478.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $A(\text{F}^-) = 382.5 \text{ S cm}^2 \text{ mol}^{-1}$ and of the activation energies of the molar conductance of Na⁺ and F⁻ ions $E^*(\text{Na}^+) = E^*(\text{F}^-) = 17.46 \text{ kJ mol}^{-1}$ were determined. The equality of the activation energy values results explicitly from the condition (5). When substituting eqns (8) and (9) into eqn (2), the temperature dependence of the conductivity of the pure NaF melt can be expressed in the form

$$\frac{\kappa(\text{NaF})}{\text{S cm}^{-1}} = \frac{20.508}{\text{S cm}^2 \text{ g}^{-1}} \cdot \rho \cdot \alpha \cdot \exp\left(-\frac{2100 \text{ K}}{T}\right) \quad (10)$$

where ρ is the density and α is the dissociation degree of the NaF melt, where both depend on the temperature.

The determined values of the dissociation degree of NaF permit the interpretation of the temperature dependence of the conductivity of the NaF—AlF₃ melts on the basis of the proposed structure of the NaF melt. If the dissociation of NaF can be looked upon as the equilibrium between the ionic pairs Na⁺ · F⁻ and the “free” Na⁺ and F⁻ ions, then the values of the dissociation degree show that with increasing temperature the amount of “free” ions decreases and the amount of ionic pairs increases. This is in agreement with the Frenkel’s model of melts, in which the mean life-time of a “free” ion in the melt decreases with increasing temperature. Simultaneously the density of the melt decreases with increasing temperature. Both these factors cause the dilution of the “free” ions

in the melt. It means that the conductivity of the melt will be influenced by the mobility of the "free" ions as well as by their dilution in the melt. For the NaF melt both these factors are considered in eqn (10). From the temperature dependence of $\kappa(\text{NaF})$ it follows that at lower temperatures the influence of the "diluting" term $\rho \cdot \alpha$ is less important than at higher temperatures.

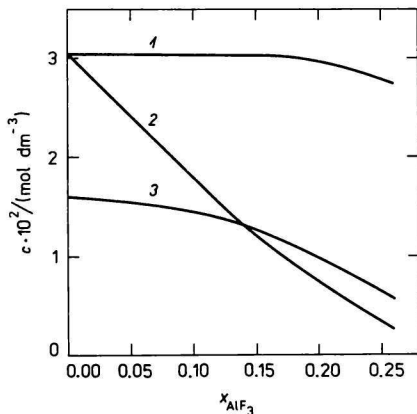


Fig. 3. The isotherms of the molar concentration of Na^+ (1) and F^- (2) ions and of the $\text{Na}^+ \cdot \text{F}^-$ (3) ionic pairs in the $\text{NaF}-\text{AlF}_3$ melts at the temperature 1000°C .

From the temperature dependence of the dissociation degree of the NaF melt it follows that at temperatures close to the melting point of NaF the dissociation degree is maximum. This refers to the "quasicrystalline" character of the melt in the proximity of the melting point. With increasing temperature the concentration of the ionic pairs in the melt increases, the coordination number of ions decreases and the extent of the perturbation of the original quasicrystalline structure increases. It may be supposed that in the proximity of the boiling point the concentration of the ionic pairs will predominate in the melt and the melt shows a "quasivapour" character.

On the basis of the values of the absolute mobilities of Na^+ and F^- ions and using the Nernst—Einstein's equation, the diffusion coefficients of the respective ions in the NaF melt were calculated (Table 4). The values of the diffusion

Table 4

The calculated values of the diffusion coefficients of Na^+ and F^- ions in the NaF melt

θ °C	$D(\text{Na}^+) \cdot 10^5$ $\text{cm}^2 \text{s}^{-1}$	$D(\text{F}^-) \cdot 10^5$ $\text{cm}^2 \text{s}^{-1}$
1000	10.72	8.16
1050	11.87	9.06
1100	13.01	9.94

coefficient of the Na⁺ ion in the molten NaF at temperatures 1000, 1050, and 1100 °C, given in Table 4, are by 8, 5, and 2 % higher than the respective values given in [15]. Harari *et al.* [16] measured the diffusion coefficients of ions in the NaF—AlF₃ melts and they show the following values for the pure NaF at 1049 °C: $D(\text{Na}^+) = 9.80 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D(\text{F}^-) = 9.67 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. For the intrinsic diffusion coefficients they give values $D(\text{Na}^+) = 12.97 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D(\text{F}^-) = 10.15 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. With regard to the error in the determination given by the authors of [16] (± 4 %) these values are in a good agreement with the values given in Table 4.

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