Physico-Chemical Properties of the System Na_3AlF_6—NaCl—TiO_2

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The phase equilibria, density and specific electrical conductivity in the system Na_3AlF_6—NaCl—TiO_2 were studied. The phase diagram, the density and the electrical conductivity isotherms at 1050°C are presented.

On addition of TiO_2, a decrease in the values of density and conductivity was observed.

An attempt was made to calculate the liquidus curve and to compare it with the experimentally determined curve for the system Na_3AlF_6—NaCl.

The molar volumes of the binary Na_3AlF_6—NaCl mixtures, as well as partial molar volumes and the excess molar volumes were calculated from the density data.

The ternary system Na_3AlF_6—NaCl—TiO_2 was studied with regard to the potential possibility of application of these mixture as electrolytes in the electrodeposition of titanium, especially in the electroplating. Similarly as in the electrolytic Al-production, also in this case cryolite is supposed to be used as a solvent for titanium dioxide, TiO_2. The addition of NaCl into the Na_3AlF_6—TiO_2 mixtures was applied with intention to decrease the density and mainly to increase the specific electrical conductivity of the fundamental electrolyte.

As regards the partial binary system, in the system Na_3AlF_6—NaCl so far the phase equilibria [1, 2] were established, and in the concentration range 0—20 weight % NaCl the density [3, 4] and the specific conductivity [5—7] were studied. In the system Na_3AlF_6—TiO_2 only the phase equilibria were determined [8].

In the present work, the phase diagram of the system Na_3AlF_6—TiO_2 and the liquidus diagram of the system Na_3AlF_6—NaCl were reexamined and the density and specific conductivity of ternary Na_3AlF_6—NaCl—TiO_2 mixtures were measured. On the basis of the experimentally determined values the phase diagram of the system Na_3AlF_6—TiO_2 and the isotherms of the density and of the specific conductivity of the ternary system at 1050°C were constructed. In the system Na_3AlF_6—NaCl, the experimental liquidus curve was compared with the calculated one in order to determine the deviation from an ideal behaviour. Furthermore, on the basis of the experimentally determined density values the molar volume of the Na_3AlF_6—NaCl mixtures as well as the partial molar volumes of components and the excess molar volume were calculated.

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Experimental

The temperature of the primary crystallization was determined by the thermal analysis method. In the measurement, the cooling curves were registrated using a recorder of the type eKBT1EN. For the measurement of the temperature a Pt/Pt10Rh thermocouple calibrated against the melting points of NaCl, Na_2SO_4, NaF and K_2SO_4 over a temperature range of 800—1000°C was used. Any *ac* signals from the furnace were filtered off and it was possible to determine the temperature with an accuracy of ± 1°C. A standard-type silite resistance furnace was used, the cooling rate being 4—6°C/min.

The analytical grade TiO_2 and NaCl and hand-picked natural Greenland cryolite containing 54.72 weight % F with a melting point of 1004°C were used. The samples were placed in a Pt crucible. The weight of a sample was 20 g.

The density was measured by the well-known buoyancy method described by *Matiašovský et al.* [4]. A Pt sinker of 25 mm diameter and 48 g mass suspended by a Pt wire of 0.3 mm diameter from the right pan of a balance was used. By a special arrangement it was possible to maintain a constant depth of immersion throughout the measurements. The sphere was calibrated over the temperature range of 800—1100°C by NaCl and KCl of which the density values are accurately known [9]. The higher temperature values of the volume of the sphere were obtained by extrapolation of the calculated volume *vs.* temperature curve. The thermocouple was calibrated previously over a temperature range of 800—1100°C.

The density ϱ, was given by the expression:

$$\varrho = \frac{M_1 - M_2}{V}, \qquad (1)$$

where M_1 and M_2 — the masses of the sphere in air and in the melt, respectively, at a particular temperature,

V — the volume at the same temperature.

The correction due to the surface tension was found to be negligible.

The apparatus and the method used in the measurement of the specific conductivity are described by *Daněk et al.* [10]. The cell was made of pure platinum with two independent Pt disc electrodes of 5 mm diameter with Pt30Ir leads. By a micrometric screw it was possible to lower the electrodes in all experiments to the same depth into the melt (7 mm). The measurements were performed with 10 mA current at a frequency of 18 kHz. The temperature was measured with a Pt/Pt10Rh thermocouple. The cell constant was determined by calibration with Na_3AlF_6. For the specific conductivity of Na_3AlF_6, the value reported by [11—13] was accepted (the extrapolated value $\sigma^{1000°C}_{Na_3AlF_6} = 2.80\ \text{ohm}^{-1}\,\text{cm}^{-1}$).

Results and Discussion

In Fig. 1 the phase diagram of the system Na_3AlF_6—TiO_2 is presented. With regard to the analogy with the system Na_3AlF_6—Al_2O_3 it may be assumed that this is also a simple eutectic system, the eutectic composition being 8.75 mole % TiO_2 and the temperature of the eutectic crystallization being 981.5°C. The decrease of the measured values corresponding to the eutectic crystallization in the field of the primary crystallization of Na_3AlF_6, when compared with those of cryo-

lite, is due most probably to the relatively low value of the heat of fusion of TiO_2, similarly as in the case of the system Na_3AlF_6—Al_2O_3. Further additions of TiO_2 rapidly increase the temperature of the primary crystallization and the liquidus curve is very steep. No evidence of formation of solid solutions in the field of high Na_3AlF_6 concentrations was found. The relatively lower temperature of the primary crystallization reported by *Mayakawa* and *Kido* [8] is most probably due to impurities in used cryolite.

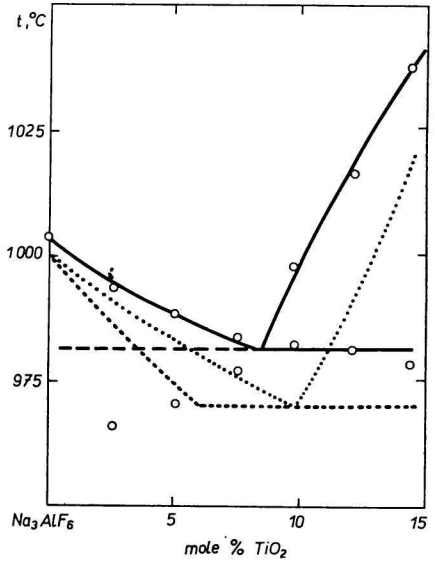

Fig. 1. The phase diagram of the system Na_3AlF_6—TiO_2.
Pointed line — according to [8], full line — this work.

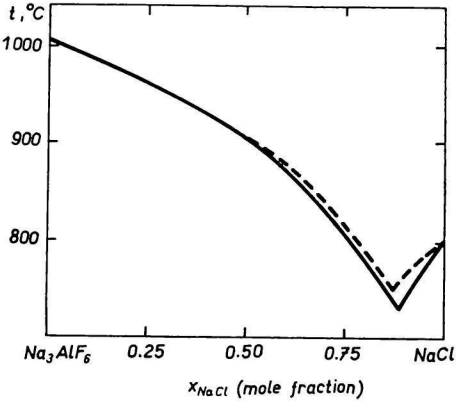

Fig. 2. The phase diagram of the system Na_3AlF_6—NaCl.
Full line — experimental, dotted line — calculated.

The calculations of the theoretical liquidus curve were done according to the Le Chatelier—Schröder formula [14]:

$$\ln x = \Delta H \cdot R^{-1} \left(\frac{1}{T_t} - \frac{1}{T} \right), \qquad (2)$$

where x — the mole fraction of cryolite,
ΔH — the heat of fusion of cryolite, 20.8 kcal/mole,
T_t — the melting point of cryolite (1277°K),
T — the liquidus point of the mixture (°K).

The data relevant for calculation were taken from [15].

Fig. 2 shows a comparison between the theoretical and experimental liquidus curves for the binary system Na_3AlF_6—NaCl. The system has an eutectic at 89 mole % of NaCl with a metling point of 731°C [2]. The experimental and the

calculated liquidus are identical at the concentrations up to 50 mole % NaCl. Thereafter there is a considerable deviation, due most probably to the interaction between the components. The calculated values corresponding to the eutectic are 87 mole % NaCl and 751°C.

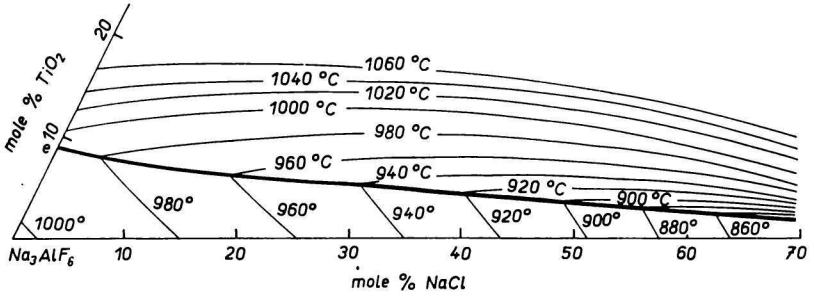

Fig. 3. The phase diagram of the system Na_3AlF_6—NaCl—TiO_2.

The phase diagram of the ternary system is given in Fig. 3. It is evident that within the studied concentration area there are two fields of the primary crystallization, one corresponding to Na_3AlF_6, the second one to TiO_2. The isotherms of this system show that in the field of the primary crystallization of TiO_2 the addition of TiO_2 increases the temperature of primary crystallization to a considerable extent.

The density isotherm of the ternary system at 1050°C is presented in Fig. 4. It is evident that both NaCl and TiO_2 affect a decrease in the density of cryolite, the influence of NaCl being more pronounced, especially at high concentrations.

From the measured values of densities of the system Na_3AlF_6—NaCl the molar volumes of the mixtures have been calculated. A graphical representation of the results is given in Fig. 5. The presented curve is the calculated one using the method of least squares. The computer calculated curve is described by the equation:

$$V = 102.117 - 56.428\,x_2 - 34.901\,x_2^2 + 71.348\,x_2^3 - 40.921\,x_2^4, \qquad (3)$$

where x_2 — the mole fraction of NaCl.

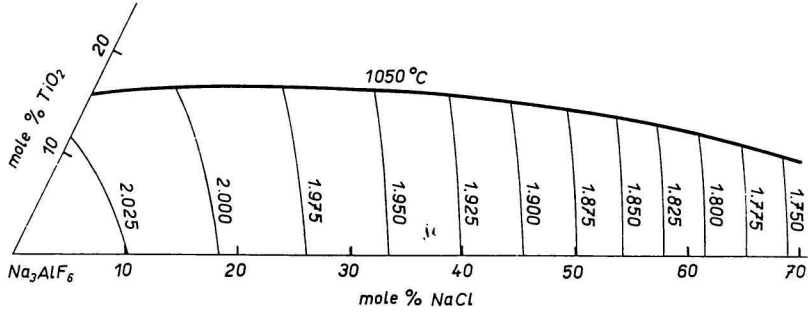

Fig. 4. The isotherm of the density of the ternary system Na_3AlF_6—NaCl—TiO_2 at 1050°C.

In Fig. 5 the calculated partial molar volumes of the components are presented *vs.* the composition. The partial molar volumes of Na_3AlF_6 ($\bar{V}_1$) and NaCl ($\bar{V}_2$) were calculated using the formulas:

$$\bar{V}_1 = V - x_2 \left(\frac{\partial V}{\partial x_2}\right)_{T,\,P}, \tag{4}$$

$$\bar{V}_2 = V - (1 - x_2) \cdot \left(\frac{\partial V}{\partial x_2}\right)_{T,\,P}, \tag{5}$$

where V — the molar volume,
x_2 — the mole fraction of NaCl at a particular point.

The partial molar volumes of the components of the system Na_3AlF_6—NaCl can be represented as a function of the mole fraction of NaCl as follows:

$$\bar{V}_{Na_3AlF_6} = 102.117 + 34.802\, x_2^2 - 142.696\, x_2^3 + 122.763\, x_2^4, \tag{6}$$

$$\bar{V}_{NaCl} = 45.689 - 69.802\, x_2 + 248.846\, x_2^2 - 306.380\, x_2^3 + 122.763\, x_2^4. \tag{7}$$

The excess molar volumes of the above system are calculated according to the equation:

$$\Delta V^E = V - V_{id}, \tag{8}$$

where V_{id} — the additive volume of the mixture in the case of an ideal system.

The fraction $\dfrac{\Delta V^E}{x_2(1 - x_2)}$ has also been calculated. The results are presented graphically in Fig. 6.

The non-ideality of this system is also evident from the ΔV^E *vs.* concentration plot which shows a deviation from the additivity from 50 mole % onwards. The

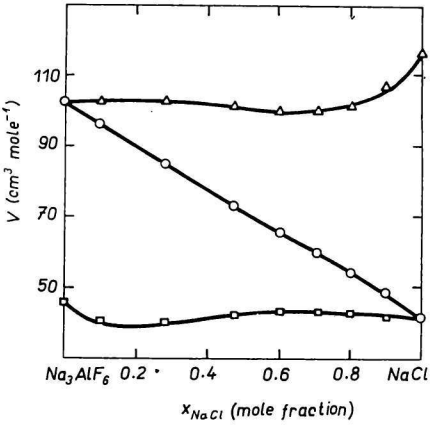

Fig. 5. The molar volume and the partial molar volumes against concentration of the system Na_3AlF_6—NaCl at 1050°C. ○ molar volume V; △ partial molar volume $\bar{V}_{Na_3AlF_6}$; □ partial molar volume $\bar{V}_{NaCl}$.

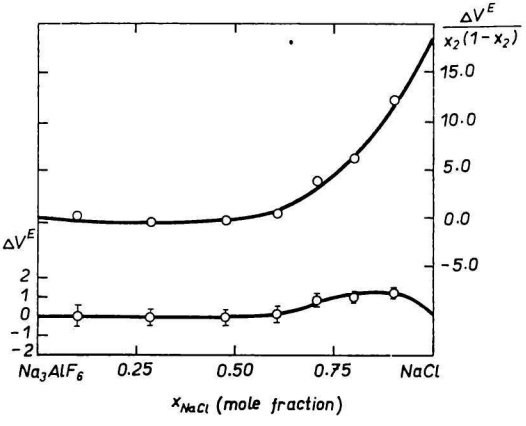

Fig. 6. Plot of excess molar volume and the fraction $\dfrac{\Delta V^E}{x_2(1 - x_2)}$ against concentration of the system Na_3AlF_6—NaCl at 1050°C.

positive deviation of the excess molar volumes in the range of higher concentrations of NaCl can be explained as due to the addition of large AlF_6^{3-} and AlF_4^- ions to NaCl. However, it is to be pointed out, that in the range of small concentrations of NaCl a decrease in the observed volume does not take place.

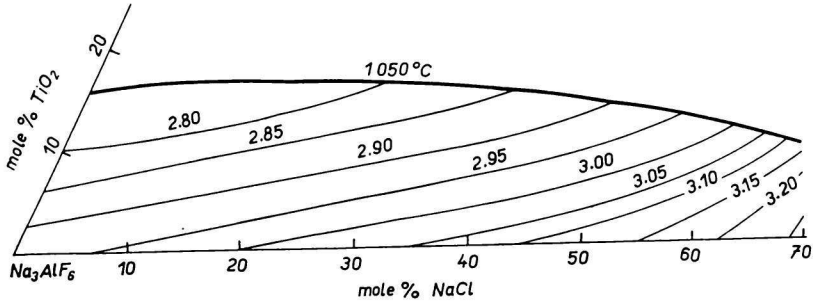

Fig. 7. The isotherm of the specific conductivity of the ternary system $Na_3AlF_6-NaCl-TiO_2$ at 1050°C.

The conductivity isotherms of the ternary system $Na_3AlF_6-NaCl-TiO_2$ are given in Fig. 7. It is evident that in the system $Na_3AlF_6-TiO_2$ the specific conductivity decreases with increasing concentration of titanium dioxide, whilst an addition of NaCl effect an increase in the electrical conductivity of $Na_3AlF_6-TiO_2$ mixtures throughout the whole studied concentration area. It may be also seen that the solubility of TiO_2 in cryolite up to the concentration of 40 mole % NaCl is not substantially affected by the addition of sodium chloride. This is advantageous with regard to the potential utilization of this system in the electrolytic deposition of titanium.

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