The electrical conductivity was investigated for a section of the molten ternary mixture Na₃AlF₆-Li₃AlF₆-AlF₃ with molar ratio \( n(\text{Li₃AlF₆}) : n(\text{AlF₃}) = 1 : 2 \). The conductivity of this system can be described by the following equation:

\[
\kappa / \text{S cm}^{-1} = 7.22 \exp \left( - \frac{1204.3}{T(\text{K})} \right) + 0.97 \chi(\text{Li₃AlF₆}) - 1.66 \chi(\text{AlF₃}) - 9.42 \times 10^{-3} \chi(\text{Li₃AlF₆})\chi(\text{AlF₃})
\]

where \( \chi(i) \) represent the mole fractions of the additions. The influence of additions of CaF₂, MgF₂ and/or Al₂O₃ on the electrical conductivity of the binary system Na₃AlF₆-Li₃AlF₆ and the ternary system Na₃AlF₆-Li₃AlF₆-AlF₃ was also studied.

1. Introduction

Melts based on sodium cryolite (Na₃AlF₆) serve as solvent for alumina in the electrolytes used for the production of aluminium [1]. Cryolite is a high melting compound (1012°C), and the conventional bath consists of cryolite with 6-13% AlF₃, 3-8% CaF₂ and 2-5% Al₂O₃ (all percentages by mass); the temperature of the electrolyte is usually in the range 945 - 970°C. It might be of advantage to use an electrolyte with a lower temperature of primary crystallization [2-4]. By the introduction of low-melting baths one might expect an increase in the current efficiency, lower energy consumption and, possibly, prolonged cell life and easier adaption of inert electrode materials. The reason why the high temperature bath is prevailing is its unmatched high alumina solubility. The introduction of more efficient ways of feeding alumina to the cell by means of point feeders which can operate almost continuously, opens a possibility for use of baths with low alumina solubility. Some aspects of low-melting baths for aluminium electrolysis have been discussed in the literature [2-4]. The temperature of primary crystallization can be lowered by the use of more acid (AlF₃-rich) bath and/or by the introduction of certain additives, such as LiF, CaF₂, and MgF₂. As follows from the phase diagram of the system Na₃AlF₆-AlF₃ [1], a mixture containing an excess of about 35 mass % of AlF₃ has a temperature of primary crystallization of about 700°C. This means that the temperature of the electrolyte can in principle be lowered as much as 200°C [2] just by adding a large excess of AlF₃.

The electrical conductivity of the electrolyte, however, decreases both with increasing AlF₃ content and decreasing temperature [1]. This unfavourable effect can partly be compensated by the addition of LiF. The compositions of the melts investigated in this study were chosen in such a way that formally they corresponded to the system Na₃AlF₆-Li₃AlF₆-AIF₃, which may be considered as a promising basis for a low-melting electrolyte [4, 5].

There are no data on the electrical conductivity of these low melting systems in the literature. The objective of this work was to study the electrical conductivity of the molten mixtures Na₃AlF₆-Li₃AlF₆-AlF₃ and the influence of additions of Al₂O₃, CaF₂, and MgF₂.

2. Experimental details

The apparatus and the measuring procedure has been described in detail elsewhere [6]. The basic part of the conductivity cell consisted of a pyrolytic boron nitride tube (Boralloy, Union Carbide) of inner diameter about 4 mm and length 10 cm. The cell constant was about 45 cm⁻¹, and it was determined by calibration with NaCl using the data for the conductivity of molten sodium chloride published by Ketelaar and Mae- naut [7]. One electrode was made of a tungsten rod (diam. 2 mm), while the graphite crucible served as the
other electrode. The graphite crucible was placed in a vertical furnace with controlled atmosphere (argon) and heated up to the required temperature. The temperature was measured with a Pt-Pt10Rh thermocouple, and it was kept constant within 0.5 K.

A Solartron 1250 frequency response analyser was used for the measurement of the cell impedance. The ac amplitude was 10 mV. The frequency was varied from 5 to 30 kHz and the real part of the cell impedance was extrapolated to infinite frequency by plotting it as a linear function of the inverse square root of the angular frequency. A more detailed discussion of the measuring procedure can be found in our previous paper [6].

Hand-picked crystals of Greenland cryolite (Na$_3$AlF$_6$) and AlF$_3$ sublimed under low pressure (about 100 Pa) at 1100°C were used for the preparation of the samples. LiF, MgF$_2$ and Al$_2$O$_3$, and NaCl (used for the determination of the cell constant) were of analytical grade (Merck); CaF$_2$ was pure precip. (Merck).

3. Results and discussion

3.1. The system Na$_3$AlF$_6$-Li$_3$AlF$_6$-AlF$_3$

The mixtures used contained cryolite with up to 26.25 mass % of excess AlF$_3$ and 8.11 mass % of LiF. This upper concentration limit corresponded to a mixture consisting of 50.00 mol % Na$_3$AlF$_6$ + 16.67 mol % Li$_3$AlF$_6$ + 33.33 mol % AlF$_3$. The temperatures ranged from 820 to 1000°C. The molar ratio of Li$_3$AlF$_6$ and AlF$_3$ in the ternary system Na$_3$AlF$_6$-Li$_3$AlF$_6$-AlF$_3$ was chosen to be 1 : 2. This composition range was selected on the basis of investigations of losses of aluminium and current efficiency [4] and solubility of alumina [8] in electrolytes with temperatures of primary crystallization as low as 800°C.

The results obtained are summarized in Fig. 1. It was found that the experimental conductivity data can be described by the equation

$$\kappa / \text{S cm}^{-1} = 7.22 \exp (-1204.3/T(\text{K})) + 0.97 \chi(\text{Li}_3\text{AlF}_6) - 1.66 \chi(\text{AlF}_3) - 9.42 \times 10^{-3} \chi(\text{Li}_3\text{AlF}_6)\chi(\text{AlF}_3)$$

where $\chi(i)$ represents the mole fraction of the additives Li$_3$AlF$_6$ and AlF$_3$. The standard deviation was found to be 0.015 S cm$^{-1}$. The first term in Equation 1 describes the temperature dependence of the conductivity of pure molten Na$_3$AlF$_6$. Because the melting point of this salt is 1012°C [1] this term corresponds rather to the electrical conductivity of the supercooled liquid. It follows that the activation energy of the electrical conductivity is 10.01 kJ mol$^{-1}$. The model used to describe the temperature and concentration dependencies of the electrical conductivity of cryolite-based melts is based on the assumption that the activation energy of the process does not depend on composition provided that the concentration of Na$_3$AlF$_6$ exceeds 50 mol %. The linear concentration terms represent the influence of the additives as it follows from the addition rule. The parameters + 0.97 for Li$_3$AlF$_6$ and - 1.66 for AlF$_3$ correspond to the influence of these additives on the electrical conductivity in the binary mixtures Na$_3$AlF$_6$-Li$_3$AlF$_6$ and Na$_3$AlF$_6$-AlF$_3$ [6]. As can be seen, the term representing the ternary interaction is rather small, and it exceeds the experimental uncertainty limit only when the product of the molar fractions of Li$_3$AlF$_6$ and AlF$_3$ exceeds 0.15 (see Fig. 1).

Good agreement between the experimental and the calculated conductivity data justifies the use of this model. It is believed that Equation 1 can be used for estimation of the electrical conductivity for all compositions of the ternary system Na$_3$AlF$_6$-Li$_3$AlF$_6$-AlF$_3$ up to 40 mol % Li$_3$AlF$_6$ and 50 mol % AlF$_3$ under the restriction that the content of Na$_3$AlF$_6$ in the mixture should be larger than 50 mol %. These limits follow from the concentration range in which the electrical conductivity of the binary and ternary systems was investigated.

3.2. Influence of the additions of MgF$_2$ and CaF$_2$

Modified baths for electrowinning of aluminium may contain MgF$_2$ and CaF$_2$ in addition to LiF and to excess AlF$_3$ [3]. A certain concentration of CaF$_2$ (3–6 mass %) always builds up due to the content of calcium in the alumina feed. The melting points of these mixtures can be calculated according to the equations published in [8, 9]. The electrical conductivity measurements were carried out at temperatures corresponding to a minimum superheat (temperature above the liquidus) of about 10°C. Conductivity data for the compositions investigated in this work are summarized in Table 1. In Fig. 2 the experimental data obtained are compared with calculated values. The calculations were based on similar assumptions as discussed above, that is on the insensitivity of the