

# Light Metals 2011

**ALUMINUM REDUCTION  
TECHNOLOGY**

**Energy Savings by  
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Hydro Aluminum

## ELECTRICAL CONDUCTIVITY OF THE KF – NaF - AlF<sub>3</sub> MOLTEN SYSTEM AT LOW CRYOLITE RATIO WITH CaF<sub>2</sub> ADDITIONS

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### Abstract

The effect of calcium fluoride on the electrical conductivity of low temperature electrolytes for aluminum electrolysis has been investigated. Calcium fluoride addition was found to decrease the electrical conductivity of the molten mixtures of potassium and sodium cryolite melts.

### Introduction

The electrical conductivity is a crucial property for the electrolytic process because it influences the charge and heat transfer in the electrolytic cell. The electrical conductivity decreases in the sequence of cryolites  $\text{Li}_3\text{AlF}_6 > \text{Na}_3\text{AlF}_6 > \text{K}_3\text{AlF}_6$  at the temperature of 1000°C (1). Calcium fluoride usually decreases conductivity but the precise influence has not yet been investigated well. According to different authors the electrical conductivity drops with  $\text{CaF}_2$  additions to sodium cryolite [2-4]. The increase of electrical conductivity with calcium fluoride additions was found for KF-LiF-AlF<sub>3</sub> mixtures [5].

### Experimental

The investigation of the electrical conductivity of fluoride-oxide melts is very difficult due to their high corrosion activity. In order to obtain reliable experimental data special requirements to the construction materials of the conductivity cell must be kept.

#### Experimental cell

The investigations were carried in an experimental cell with two parallel electrodes [6]. A glassy carbon crucible filled with a weighed amount of the electrolyte to be investigated was put at the bottom of the quartz test tube, which was tightly closed by a vacuum rubber plug with holes for the electrodes, thermocouple, and the inert gas inlet and outlet. Small tubes for the gas inlet and outlet and the protection shields for the thermocouple and electrodes were made of alundum. The platinum - platinum-rhodium thermocouple without any shield was immersed directly into the molten salt.

Two rigidly fixed parallel molybdenum electrodes were immersed in the melt.

A unit for the load of the additives to be charged to the molten electrolyte in the flow of inert gas was attached to the small alundum gas-feeder tube. After each addition, the submersion depth was corrected.

#### Chemicals

The electrolytes under investigation were prepared from individual salts (chemically pure) AlF<sub>3</sub>, NaF and KF (taken as KF·HF). First, the electrolytes KF-AlF<sub>3</sub> and NaF-AlF<sub>3</sub> with the molar ratio required were prepared. AlF<sub>3</sub> was initially heated in a mixture with NH<sub>4</sub>F and kept for 6 hours at 450-500°C for performing oxide fluorination. In order to obtain KF-AlF<sub>3</sub> electrolyte the mixture of KF·HF and AlF<sub>3</sub> was heated up to 700°C in the glassy carbon container and kept at this temperature over four hours. HF was removed from the melt as a result of the thermal KF·HF decomposition ( $T = 238.7^\circ\text{C}$ ). The NaF-AlF<sub>3</sub> system was prepared by melting the mixture of AlF<sub>3</sub> and NaF in presence of NH<sub>4</sub>F. The ternary system KF-NaF-AlF<sub>3</sub> was obtained by mixing binaries NaF-AlF<sub>3</sub> and KF-AlF<sub>3</sub>. Before conducting the experiments the electrolytes obtained were analyzed on potassium, sodium and aluminum content by an ICP method.

#### Measurement procedure

Zahner electric IM6E was used for impedance measurements. Impedance diagrams were recorded in a frequency range from 100 Hz to 100 KHz using a signal with amplitude of 5 mV. The electrolyte resistance determined from the impedance diagrams was used for calculation of the electrical conductivity. The constant of the cell was determined from the electrical conductivity values obtained for potassium cryolite with CR 1.3 or 1.5 in the capillary type cell. The electrical conductivity was calculated taking into consideration the cell constant temperature dependence.

## Results and Discussion

The experimental values of the electrical conductivity obtained in the KF-NaF-AlF<sub>3</sub>-CaF<sub>2</sub> system with CR 1.3 and 1.5 at different temperatures are presented in Figures 1-3. The results were treated in the form of temperature dependence equations:

$$\ln \chi = A - B/T \quad [1]$$

here  $\chi$  – specific conductivity, Sm·cm<sup>-1</sup>; T – temperature, K; A and B – empirical coefficients.

The results obtained for different electrolyte compositions in a broad temperature range (> 50°) are presented in Table 1.

Table 1. The empirical coefficients of the electrical conductivity temperature dependences.

CR	NaF mol. %	KF mol. %	AlF <sub>3</sub> mol. %	CaF <sub>2</sub> mol. %	A	-B
1.5	60.00		40.00	0.00	2.86	2507
1.5	57.25		38.16	4.59	4.42	4292
1.5	56.31		37.54	6.14	3.74	3607
1.5	55.37		36.91	7.72	4.15	4091
1.5	54.41		36.27	9.31	5.45	5538
1.5	53.45		35.63	10.92	6.65	6885
1.5	52.48		34.98	12.54	7.27	10784
1.5	43.86	16.14	40.00	0.00	2.05	1861
1.5	43.17	15.89	39.37	1.58	2.13	1971
1.5	42.47	15.63	38.73	3.17	2.73	2634
1.5	41.41	15.24	37.77	5.59	2.23	3223
1.3	44.44	12.09	43.48	0.00	2.05	1963
1.3	43.73	11.89	42.78	1.60	2.09	1930
1.3	43.01	11.70	42.08	3.21	2.23	2173
1.3	41.92	11.40	41.02	5.66	2.47	2471

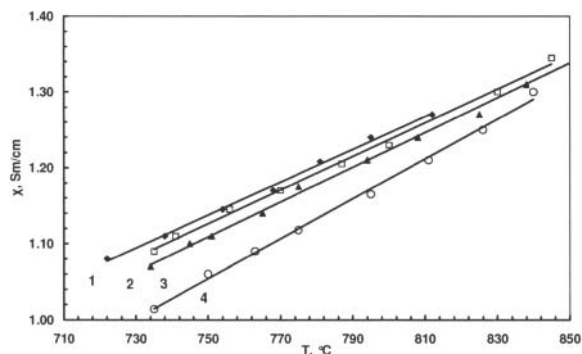


Figure 1. Electrical conductivity of the (KF-NaF-AlF<sub>3</sub>)-CaF<sub>2</sub> mixtures (CR=1.3) depending on CaF<sub>2</sub> (mol.%) concentration: 1 - 0; 2 - 1.6; 3 - 3.2; 4 - 5.7. The NaF concentration in the initial salt was 44.44 mol. %.

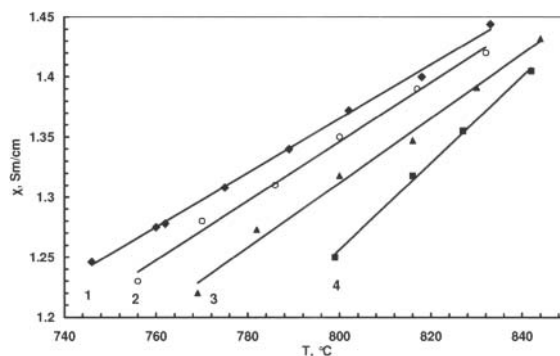


Figure 2. Electrical conductivity of the (KF-NaF-AlF<sub>3</sub>)-CaF<sub>2</sub> mixtures (CR=1.5) 1 - 0 mol. % of CaF<sub>2</sub>, 2 - 1.6 mol. % CaF<sub>2</sub>, 3- 3.2 mol. % of CaF<sub>2</sub>, 4- 5.7 mol. % CaF<sub>2</sub>. The NaF concentration in the initial salt was 43.86 mol. %.

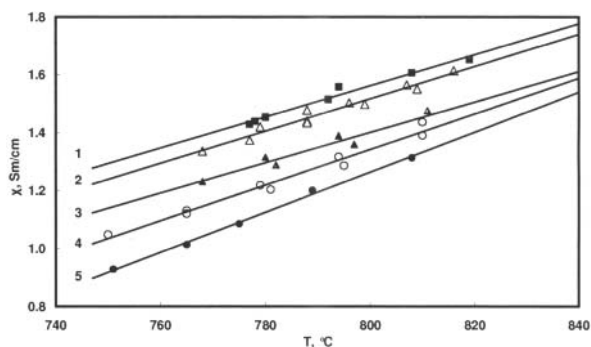


Figure 3. Electrical conductivity of the (NaF-AlF<sub>3</sub>)-CaF<sub>2</sub> mixtures (CR=1.5) depending on CaF<sub>2</sub> (mol.%) concentration: 1 – 2.3; 2 – 4.6; 3 – 7.8; 4 – 9.4; 5 - 11.

The CaF<sub>2</sub> additive reduced the electrical conductivity of the melts under investigation. The specific conductivity change with calcium fluoride content in the NaF-AlF<sub>3</sub> system (CR=1.5) at T=800°C is shown in Fig. 4.

The conductivity polytherms presented in Figures 1-3 for different electrolyte compositions show the temperature slope increase with increasing calcium fluoride concentration. The specific conductivity temperature coefficient change with CaF<sub>2</sub> in the NaF-AlF<sub>3</sub>-CaF<sub>2</sub> system (CR=1.5) is shown in Fig. 5.

The electrical conductivity activation energy for the binary NaF-CaF<sub>2</sub> system was investigated too. It slightly changes with CaF<sub>2</sub> additions. Aluminum fluoride additions significantly change the state of the melt, complicating its structure due to the joint presence of the two strongly complexing ions Al<sup>3+</sup> and Ca<sup>2+</sup>. Both of these do not exist as single cations, but are bound to fluoride ions in the melt.

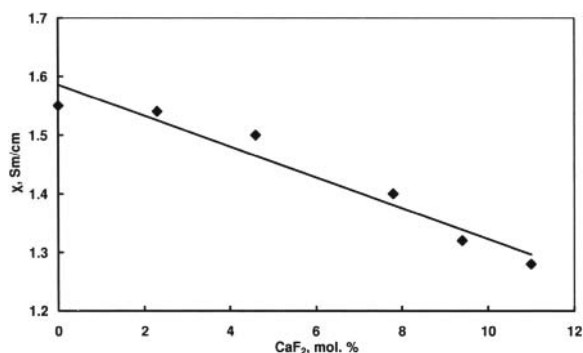


Figure 4. Electrical conductivity of the NaF-AlF<sub>3</sub> system (CR=1.5) at T=800°C.

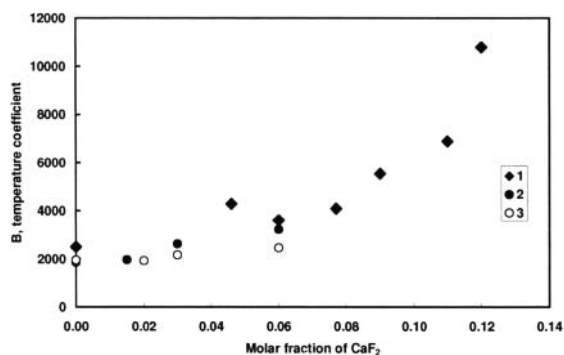


Figure 5. Electrical conductivity temperature coefficient, B. 1 - NaF-AlF<sub>3</sub>-CaF<sub>2</sub> (CR=1.5); 2 - (KF-NaF-AlF<sub>3</sub>)-CaF<sub>2</sub> (CR=1.5), the NaF concentration in the initial salt was 43.86 mol.%; 3 - (KF-NaF-AlF<sub>3</sub>)-CaF<sub>2</sub> (CR=1.3), the NaF concentration in the initial salt was 44.44 mol. %.

It leads to the great increase of activation energy with calcium fluoride additions in the NaF-KF-AlF<sub>3</sub>-CaF<sub>2</sub> system. XRD analysis of the solid samples showed the presence of elpasolite K<sub>2</sub>NaAlF<sub>6</sub>, NaCaAl<sub>2</sub>F<sub>9</sub> and KCaAl<sub>2</sub>F<sub>9</sub>. Most likely, such huge complexes can be present in the liquid state leading to ion mobility decrease.

### Conclusions

1. The CaF<sub>2</sub> additives decrease the specific conductivity of the KF-NaF-AlF<sub>3</sub> mixtures with CR=1.3 and 1.5.
2. The temperature coefficients of the specific conductivity of the melts under study increase with calcium fluoride additions.
3. The electrical conductivity decrease with CaF<sub>2</sub> in the mixed sodium-potassium cryolite systems can be explained by the formation of large complex ions containing calcium ions.

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