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ELECTRICAL CONDUCTIVITY OF LOW MELTING CRYOLITE MELTS

Vasylii A. Kryukovsky[1], Anton V. Frolov[2], Olga Yu. Tkatcheva[3], Alexander A. Redkin[3], Yurii P. Zaikov[3], Vladimir A. Khokhlov[3] and Alexey P. Apisarov[3]

[1] Russian Aluminum Company RUSAL, Nikoloyamskaya st. 13, bld. 1, Moscow, 109240, Russia
[2] Engineering-Technological Center Ltd, RUSAL, Pogranichnikov st. 37/1, Krasnoyarsk, 660111, Russia
[3] Institute of High Temperature Electrochemistry, S.Kovalevskaya st. 20, Ekaterinburg, 620219, Russia

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Abstract

Modern industrial aluminum electrolysis is carried out at high temperature that leads to great energy consumption and fast corrosion of the construction materials. This situation can be improved by using low melting electrolytes such as $KF-AlF_3$ (CR=1.3) with a melting temperature below 600°C. The critical parameter in this case is the electrical conductivity because it decreases with temperature very fast. The electrical conductivity of molten system $KF-AlF_3$ (CR=1.3) has been measured in the temperature range of 680-770°C in a capillary cell by the impedance method. The electrical conductivity temperature dependence in molten systems $KF-AlF_3-Al_2O_3$ (CR=1.3), $KF-AlF_3-LiF$ (CR=1.3), $KF-AlF_3-Al_2O_3-LiF$ (CR=1.3) has been measured in Egear type cell. The Al_2O_3 concentration was varied from 0 to 4.8 wt.% and the LiF concentration was changed from 0 to 10 wt.%. The results obtained show the possibility of use of this electrolyte for industrial electrolysis.

Introduction

The interest in low-temperature baths for the electrolysis of alumina is caused by their unquestioning advantages such as smaller corrosion of the structural materials of reduction cell, smaller concentration of dissolved aluminum, which decreases the current efficiency, in the electrolyte, and a better coefficient of energy consumption. The disadvantage of the technology of low-temperature electrolysis is a decrease in the alumina solubility with decreasing temperature of the bath. However, studies of the alumina solubility in $MF-AlF_3$ melts [1] show that it strongly depends on the nature of cation and increases according to the following order: Li < Na < K. Therefore, it is of interest to examine the potassium cryolite with a low cryolite ratio as a new low-temperature electrolyte for aluminum production.

The purpose of this work was to measure the electrical conductivity of potassium cryolite with CR = 1.3 in a temperature range of 680 – 795°C and to study the effect of alumina and lithium fluoride additions on the electrical conductivity of this electrolyte.

Experimental

<u>*Constructions of the measuring cells.*</u> To determine the electrical conductivity of the electrolytes under study, we used cells of two types: a capillary cell (Figure 1) and a cell with two parallel electrodes (Figure 2).

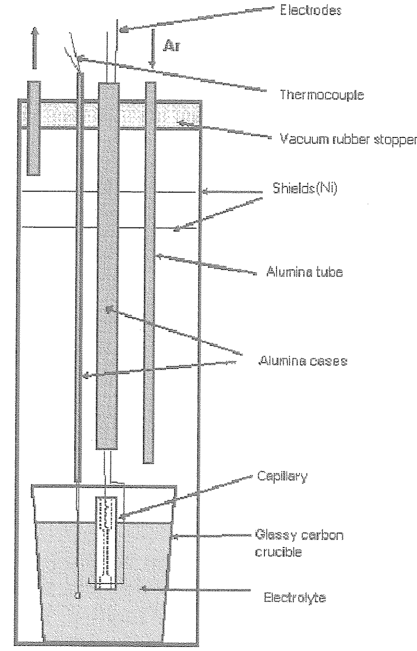

Figure 1. Capillary conductivity cell

Pyrolytic boron nitride was selected as the capillary material since it is characterized by a high corrosion resistance in cryolite melts and a small heat-expansion coefficient and is an electrical insulator even at 1000°C. The capillary unit was a pyrolytic boron nitride rod, in which a capillary of 1-3 mm in diameter was drilled. The capillary diameter in each capillary unit was selected experimentally. The platinum electrode placed into the upper part of the capillary unit was twisted into a spiral for increasing surface area of the electrode submerged into the molten electrolyte. The capillary unit was hung on the second platinum electrode, which was fastened in its lower part.

A glassy carbon crucible filled with a weighed quantity 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 cases for the thermocouple and electrodes were prepared from alundum. The platinum - platinum-rhodium thermocouple without any casing was immersed directly into the molten salt.

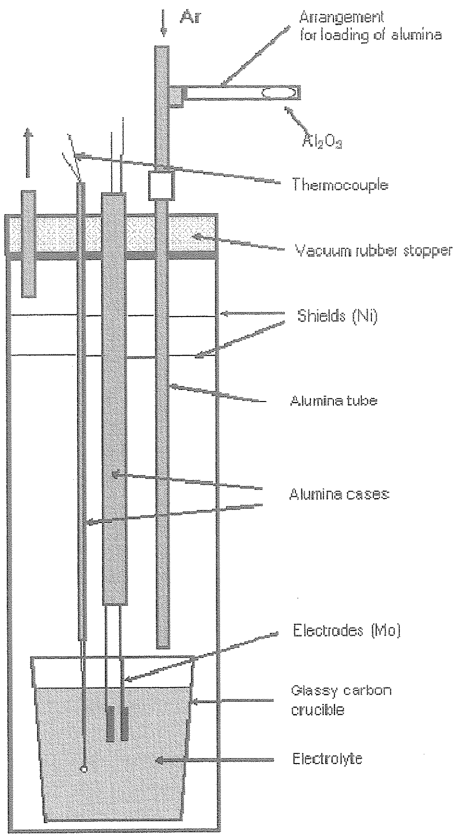

Figure 2. Conductivity cell with parallel electrodes.

The difference of the cell with the parallel electrodes from the capillary type cell was the fact that two rigidly fixed parallel cylindrical molybdenum electrodes were immersed into 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, we corrected the submersion depth of electrodes with allowance for the changed electrolyte volume and recorded the change in the electrolyte resistance. In the experiments with the $KF-AlF_3-LiF$ system, the lithium fluoride was added in the mixture with the potassium cryolite in the quantity providing an unchanged cryolite ratio.

Preparation of the electrolyte. Potassium cryolite containing (mol %) 57 KF and 43 AlF_3, which corresponds to a cryolite ratio of 1.3, was prepared from individual salts AlF_3 and KF. The KF component was taken as KF·HF. In the experiment, we used the alumina of Achinsk Alumina Plant. The preparation of potassium cryolite can be described by the following reaction:

$$6\ KF \cdot HF + Al_2O_3 \rightarrow 2\ K_3AlF_6 + 3\ H_2O \quad (1)$$

The mixture of the components was heated in the glassy carbon container in the flow of inert gas by elevating temperature to 600°C for three hours and then to 750°C. The melt was held at 750°C for two hours. Upon this holding, HF was removed from the melt due to thermal decomposition (the melting point of KF· HF is 238.7°C). The oxygen concentration in the prepared electrolyte was determined by the atomic-adsorptive method to be not higher than 0.1 wt.%.

Measurement procedure. The test tube was put into the furnace, evacuated, filled with inert gas, and heated to a temperature of 795°C. The impedance diagrams were recorded when the electrolyte resistance remained unchanged within the limits of 2 mOhm. The cell was cooled to 690°C and then heated to 795°C. The impedance measurements were performed every 15-20 degrees by using a Zahner electric IM6 impedometer in the AC frequency range between 1 Hz and 1 MHz with an AC amplitude of 5 mV. The electrolyte resistance was determined from the impedance diagrams. The electrical conductivity was calculated by the formula $\sigma = K/R$, where K is the cell constant, and R is the electrolyte resistance.

The capillary type cells were used for measuring the electrical conductivity of the molten potassium cryolite $KF-AlF_3$ (CR = 1.3). The electrical conductivity of the $KF-AlF_3-Al_2O_3$, $KF-AlF_3-LiF$, and $KF-AlF_3-LiF-Al_2O_3$ melts was measured in the cells with the parallel electrodes.

Calibration of the cells. The capillary unit was calibrated against molten potassium chloride [2] in a temperature range of 790-860°C. The temperature dependence of the capillary cell constant is described by the linear equation:

$$K_1 = 15.066 - 0.0037 \cdot T, \quad (2)$$

where T is the temperature (°C). In a temperature range of 690 – 795°C, the cell constant was 12.36±0.03 cm^{-1}.

The constant of the cell with two parallel platinum electrodes was determined from the electrical conductivity value obtained for potassium cryolite with CR = 1.3 in the capillary type cell. The electrical conductivity measured for the electrolytes under study in the cells with the parallel electrodes was calculated with allowance for the temperature dependence of the constant. The cell constant for the systems in the temperature range of 680 – 770°C system is described by the equations:

$$K_2 = 0.2008 + 0.0006\ T \quad (3)$$

for $KF-AlF_3-Al_2O_3$,

$$K_3 = 0.1484 + 0.0009 \cdot T \quad (4)$$

for $KF-AlF_3-LiF$,

$$K_4 = 0.0553 + 0.0012 \cdot T \quad (5)$$

for $KF-AlF_3-LiF-Al_2O_3$.

Results and discussion

System $KF-AlF_3$ (CR = 1.3)

The electrical conductivity of the molten $KF-AlF_3$ (CR = 1.3) system was measured in capillary type cells at a temperature of 690-795°C. The impedance diagrams obtained at different temperatures are represented in Figure 3. The electrolyte resistance was determined from the value of the real part of the impedance at the point of curve intersection with the X-axis. The measurement data on the electrical conductivity of the $KF-AlF_3$ (CR = 1.3) electrolyte are given in Table. 1.

Its temperature dependence is described by the empirical equation:

$$\ln\sigma = 1.7991 - 1238.1/T, \qquad (6)$$

where T is the temperature (°C).

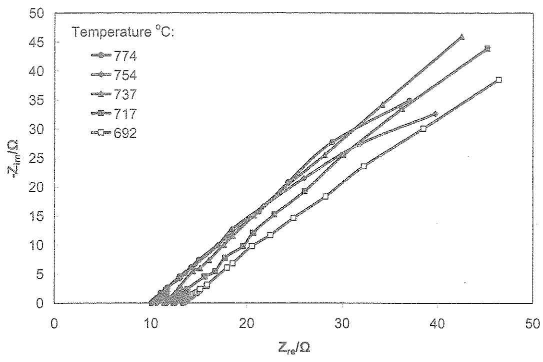

Figure 3. Impedance diagrams in the $KF\text{-}AlF_3$ (CR=1.3) system

Table I. Electrical conductivity of the $KF\text{-}AlF_3$ (CR = 1.3) melt

Temperature, °C	Conductivity, $Ohm^{-1}cm^{-1}$
692	0.94
717	1.01
737	1.06
754	1.11
774	1.16
795	1.21

Figure 4 shows the electrical conductivity obtained in [3, 4] for the potassium cryolite with different cryolite ratios. All data are in a good agreement within the experimental error.

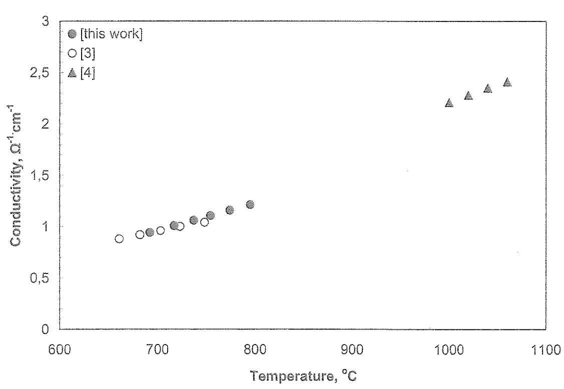

Figure 4. Temperature dependence of the potassium cryolite conductivity.

System $KF\text{-}AlF_3\text{-}Al_2O_3$

The measurement of the $KF\text{-}AlF_3$ electrolyte (CR = 1.3) electrical conductivity depending on the alumina content was performed in the cells with the parallel platinum electrodes in a temperature range of 680-770°C. The polythermal curves of the electrical conductivity of potassium cryolite with different alumina contents are given in Figure 5. As one would expect, the electrical conductivity decreases with decreasing temperature and with increasing alumina concentration. The curve of the temperature dependence of electrical conductivity in the $KF\text{-}AlF_3$ melt (CR = 1.3), which contains 4.8 wt.% alumina, exhibits a small bend in a temperature range of 700-720°C. This means that the saturation of melt by alumina occurs at temperatures below 700°C. The solubility of Al_2O_3 at 700°C is about 4.6 wt. %.

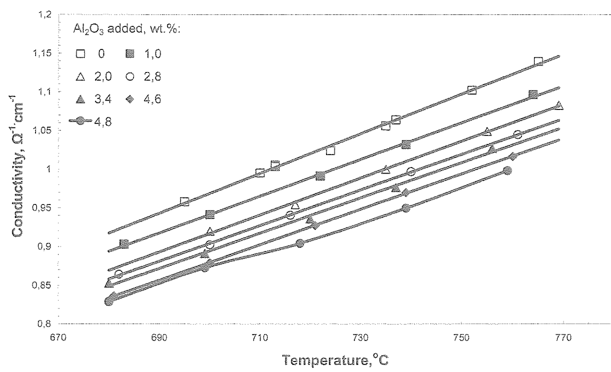

Figure 5. Conductivity of $KF\text{-}AlF_3$ (CR=1.3)+Al_2O_3 as a function of temperature

The resistance of the investigated melts at temperatures ranging from 795°C to a temperature several degrees below the solidification point was measured in the potassium cryolite with CR = 1.3 and different alumina contents. The obtained cooling curves are shown in Figure 6. The bend points in the curves correspond to the solidification points of the electrolytes under study. The determination of the solidification point in the melts with the alumina contents exceeding 3.4 wt. % was hindered because of the phenomenon of supercooling, which is frequently met in the electrolytes of such composition.

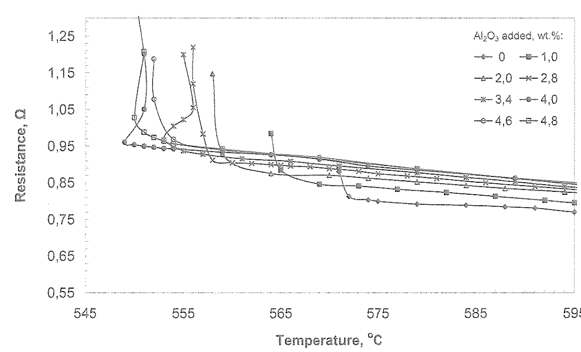

Fig. 6 Resistance of the $KF\text{-}AlF_3$ (CR=1.3)+Al_2O_3 system electrolytes as a function of temperature

Nevertheless, we attempted to schematically build the section of the phase diagram of the [$KF-AlF_3$ (CR = 1.3)] – [Al_2O_3] system (Figure 7).

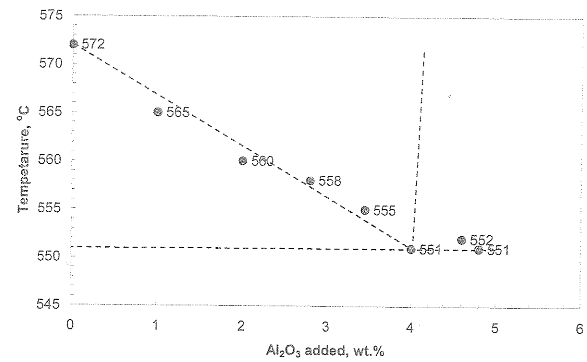

Figure 7. Melting points of $KF-AlF_3$ (CR=1.3) vs. added alumina

The left liquidus line is built according to the melting points determined from Fig. 6. The right liquidus line rises abruptly to the point with coordinates x = 4.6 wt.% Al_2O_3 and y = 700°C determined from Fig. 5. The point with the "coordinates": T = 551°C and a concentration of 4 wt.% Al_2O_3 corresponds to the eutectic.

System $KF-AlF_3$-LiF

The measurement of the electrical conductivity of the $KF-AlF_3$ electrolyte (CR = 1.3) as a function of the LiF content was performed in the cells with the parallel molybdenum electrodes. The concentration dependence of the electrical conductivity of the $KF-AlF_3$-LiF system (CR = 1.3) at temperatures of 755 and 700°C is represented in Figure 8.

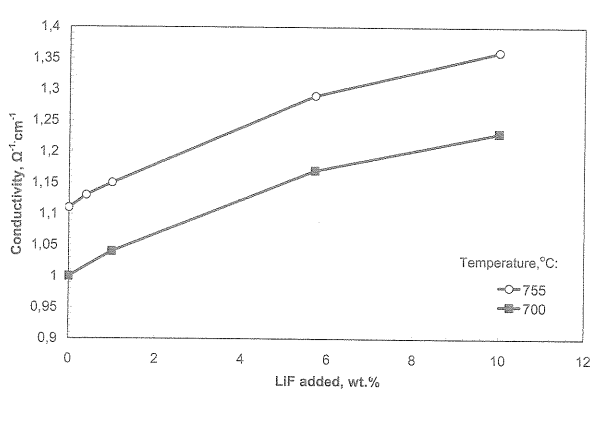

Fig. 8 Conductivity of $KF-AlF_3$-LiF (CR=1.3) as a function of added LiF

It is evident from Figure 8 that the electrical conductivity decreases with decreasing temperature and substantially increases with increasing content of added LiF.

System $KF-AlF_3-LiF-Al_2O_3$

To study the mutual effect of the additions of lithium fluoride and alumina on the electrical conductivity of the potassium cryolite, we investigated the $KF-AlF_3$-LiF (CR = 1.3) + Al_2O_3 system in a temperature range of 680-750°C. The temperature dependence of the electrical conductivity of this system is shown in Figure 9.

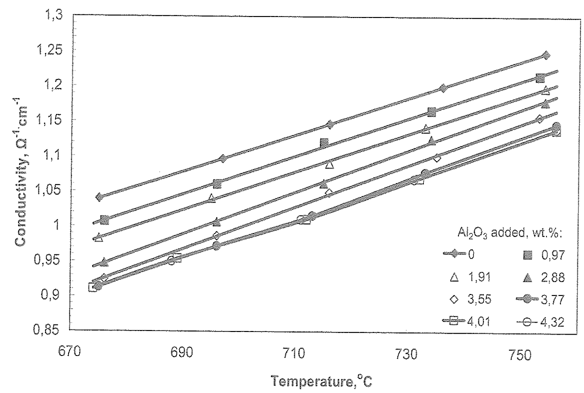

Figure 9. Conductivity of $KF-AlF_3$-LiF (CR=1.3)+Al_2O_3 as a function of temperature

For the mixtures containing 3.77, 4.01, and 4.32 wt.% alumina, the polythermal curves virtually coincide. Figure 10 shows the dependence of the electrical conductivity of the electrolyte on the concentration of the added alumina.

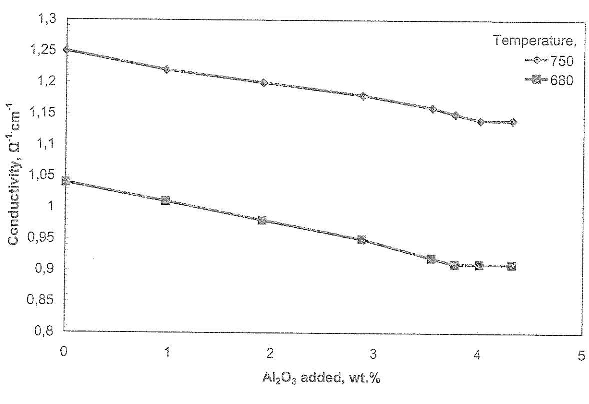

Figure 10. Conductivity of $KF-AlF_3$-LiF(CR=1,3) as a function of added alumina

The solubility of alumina in these melts is somewhat lower than its solubility in the electrolytes free from lithium fluoride additions. At 750°C, the solubility of alumina in the $KF-AlF_3-LiF-Al_2O_3$ electrolyte is about 4 wt. %. Figure 11 shows the temperature dependences obtained in the melts: $KF-AlF_3$ (CR = 1.3); $KF-AlF_3$ (CR = 1.3)+LiF (5.0 wt. %) and $KF-AlF_3$-LiF (5.0 wt. %) with the addition of 3.55 wt. % Al_2O_3.

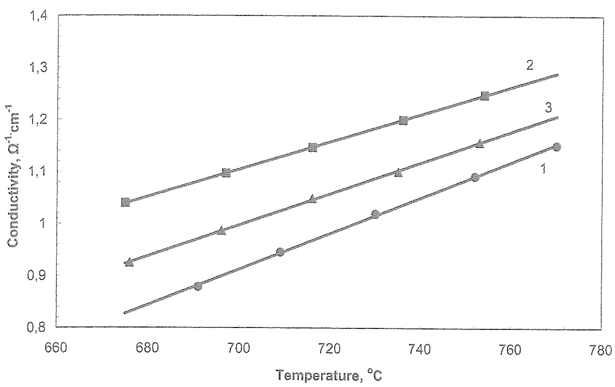

Figure 11. Temperature dependences of the conductivity of the systems:
1-KF-AlF_3 (CR=1.3);
2-KF-AlF_3 (CR=1.3) with LiF(5.0 wt.%);
3 – [KF-AlF_3-LiF (5.0 wt.%)] (CR=1.3) with 3.55 wt.% Al_2O_3

It is seen from Figure 11 that a decrease in the electrical conductivity of potassium cryolite in the presence of alumina can be compensated by lithium fluoride additions.

Conclusions

The investigation of the properties of the low-melting KF-AlF_3 (CR = 1.3) electrolyte with alumina additions in a temperature range of 680-770°C showed that its electrical conductivity is substantially lower than that of conventional electrolyte based on sodium cryolite; however, the solubility of alumina at these temperatures is sufficiently high. A decrease in the electrical conductivity in the presence of alumina can be compensated by lithium fluoride additions which significantly increase it. The potassium cryolite with a low cryolite ratio and the additions of lithium fluorides can be proposed as a new low-melting electrolyte for the production of aluminum in the event of the design of a fundamentally new electrolytic pot construction.

References

1. J. Olsen, *Dissertation*, The University of Trondheim, Norway, 1996.
2. J.Janz, *J.Phys.Chem.Ref.Data*, 17, Suppl.2, 1988.
3. J. Hives, J Thonstad, *Light metals* 49, Issue 28, 2004, p. 5111.
4. E.W. Yim and M Feinleib, *J. Electrochem. Soc.* 104, № 10, 1957, p. 626.