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CONDUCTIVITY OF KF-NaF-AlF_3 SYSTEM LOW-TEMPERATURE ELECTROLYTE

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Abstract

The continuously varying cell constant (CVCC) technique was applied to measure the conductivity of molten KF-NaF-AlF_3 electrolyte with ([NaF]+[KF])/[AlF_3] ratio (CRT) between 1.2 to 1.5. The investigated temperature range is 750 to 820 °C. The effect of CRT, temperature, NaF and alumina on conductivity was studied. An empirical formula for calculating conductivity of the KF-NaF-AlF_3 melt was derived:

$$\kappa = 0.1442\times N^2 + 0.164\times N + 16.947\times R^3 - 68.086\times R^2 + 91.534\times R + (8.812\times10^{-5}\times T - 0.0874)\times A + 1.39\times10^{-3}\times T - 41.1785$$

Where, κ is the conductivity, in $S\cdot cm^{-1}$, N is the mole fraction of NaF, R is the CRT of electrolyte, A is the mass fraction of Al_2O_3, *T* is the temperature of melt in degree centigrade.

Introduction

Producing aluminum with low temperature (below 900 °C) electrolyte has been a hot topic for many years [1-3]. One of the problems needed to be resolved is to find an electrolyte with satisfactory alumina solubility at lower operating temperatures and with suitable physicochemical properties. The NaF-KF-AlF_3-based electrolyte is a promising candidate for low-temperature aluminum reduction.

The published physical-chemical data of KF-NaF-AlF_3 system is not extensive. Belayaev et al. [4], Barton et al. [5] and Danielik and Gabcova [6] reported a partial phase diagram of KF-NaF-AlF_3 system. Tkatcheva et al. [7] and Apisarov et al. [8] measured the liquidus temperature at fixed values of CRT equal to 1.3, 1.5 and 1.7. The liquidus temperature of Na_3AlF_6-K_3A1F_6 melts was studied by Chin et al. [9] and Jiawei et al. [10]. In our previous works, the liquidus temperature on the KF-NaF-AlF_3-based electrolyte has been measured at CRT is 1.3, 1.41 and 1.5 [11], the alumina solubility in molten KF-NaF-AlF_3-based electrolyte and the effect of temperature, CaF_2 and LiF on alumina solubility was discussed [12], and the surface tension and density of molten KF-NaF-AlF_3-based electrolyte were determined as a function of the melt composition and temperature [13].

The conductivity is an important property for baths in the aluminum reduction industry because it is associates with the energy consumption. However, only few papers report the conductivity of NaF-KF-AlF_3-based melts. Youguo et al. [14] report the conductivity of Na_3AlF_6-40% K_3A1F_6-AlF_3-$A1_2O_3$ melts. Tkatcheva et al. [7] and Apisarov et al. [15] reported the conductivity of molten mixtures KF-NaF-AlF_3 at the cryolite ratio CRT = 1.3 and 1.5 in the temperature range from 800 °C to the liquidus temperature.

The purpose of this work is to measure the conductivity of KF-NaF-AlF_3-based melts with CRT = 1.2 to 1.5 in a temperature range of 750 to 820 °C and to study the effect of alumina and sodium fluoride additions on the conductivity.

Experimental

Theory of CVCC

The CVCC method was initially developed by Wang et al. [16]. In this method, the conductivity of melts can be obtained by formula (1):

$$k = \frac{1}{A(\frac{dR_m}{dl})} \tag{1}$$

Where, κ is the conductivity of the molten salts, in S/cm; R_m is the ohmic resistance of the molten electrolyte; *l* is the length of the conductivity cell in cm; *A* is the cross-sectional area of the conductivity cell in cm^2. The cell can be calibrated by standard melts or aqueous solutions.

In the measurement of conductivity, the total impedance of a measuring circuit (*Z*) can be measured by a LCR (Inductance (L), Capacitance (C), and Resistance (R)) bridge, expressed by:

$$Z = R + X_L + X_C \tag{2}$$

Where, *R* is the real resistance component of the measuring circuit; X_L is the inductive component of the impedance; X_C is the capacitive component of the impedance. The real resistance component of the impedance, *R*, may be expressed as follows:

$$R = R_m + R_p + R_w \tag{3}$$

Where, R_m is the ohmic resistance of the molten electrolyte; R_p is the polarization resistance. R_w is the contact resistance between the wires and electrodes and can be considered as a constant.

The impedance of molten salts can be measured at higher frequency range to reduce the effects of any electrode reactions. In this condition, the R_p is disregarded because of a very small value. The inductive and capacitive impedances are considered as constant when the AC signal frequency and power level are fixed. R_m is changing with the varying conductivity cell constant. Then:

$$k = \frac{1}{A(\frac{dR_m}{dl})} = \frac{1}{A(\frac{dR}{dl})} = \frac{1}{A(\frac{dZ}{dl})} \tag{4}$$

It follows that with a fixed frequency, changing the length of capillary conductivity cell and reading the total impedance (*Z*) of the measuring circuit in various lengths of the conductivity cell, the conductivity of the molten salts can be calculated by Equation (4). It has the advantage that the applied resistance has no influence on the result, resulting in good reliability of the conductivity cell and good experimental performance.

Chemicals

KF, NaF, and Al_2O_3 are analytical reagents, all from Aladdin Reagent, and the purity is higher than 99.7 %. AlF_3 is prepared from $AlF_3 \cdot 3H_2O$ (analytical grade, Aladdin Reagent) as follows: Aluminum fluoride trihydrate is dried at 120 to 200 °C under air flow for at least 8 hours, then it is mixed with ammonium hydrogen fluoride (analytical grade, Aladdin Reagent) and heated at 350 to 600 °C for about 6 hours in argon atmosphere in an air-tight furnace, the exhaust gas is absorbed by sodium hydrate solution and hydrochloric acid solution. The purity of the aluminum fluoride prepared with this method was higher than 99.5 %. Before the experiments, all reagents were dried in a vacuum oven with P_2O_5 at 150 °C for at least 4 hours.

Experimental Set-up

The schematic diagram of the experimental setup is show in Figure 1.The measuring device consist of an electric resistance furnace, a conductivity cell, a precision riser, and a digital LCR bridge. The electric resistance furnace is used to heat the melt. The cylindrical corundum furnace tube is sealed by means of a brass lid with an O-ring. A thermal radiation shield assembly is hung with the brass lid to ensure a homogeneous temperature. The brass lid is cooled by a copper cooling pipe, in which 20-25 °C cooling water flows. All of the rods and pipes through the brass lid are fixed and air-tight.

The conductivity cell is a pyrolytic boron nitride (PBN) pipe (5 mm in inner diameter, 7 mm in outer diameter) fixed in the center of the BN crucible lid. The temperature of the melt is measured by a Pt-Pt/Rh thermocouple, whose accuracy is within ±1 °C at 800 °C. The working electrode is of a 3 mm tungsten rod protected by a corundum sleeve, leaving two ends to conduct electricity. A precision riser with 300 mm stroke is provided to move the tungsten rod. The riser has an accuracy of ±0.01 mm and consists of a controller, an electric servo motor, and a precise ball screw. The digital LCR bridge (TH2819A) is used to read the electrolyte impedance. With the frequency set to 3-10 kHz, the impedance accuracy is ±0.02 ohms.

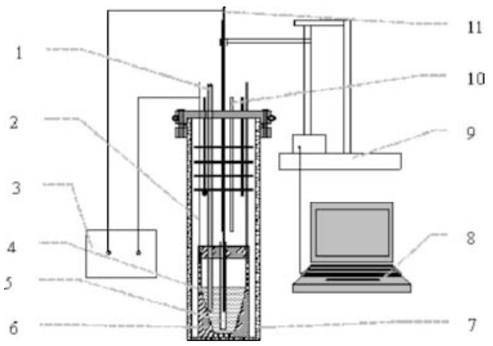

Figure 1. Schematic diagram of the conductivity measuring set-up. 1-thermocouple; 2-counter electrode; 3-digital LCR bridge; 4-melt; 5-PBN pipe; 6-high purity graphite crucible; 7-corundum furnace tube; 8-computer; 9-precision riser; 10-corundum pipe; 11-working electrode (tungsten)

Conductivity Measuring Procedure

The electrolyte is weighed and mixed in a glove box, then put into a graphite crucible with a BN lid, and then quickly transferred to corundum furnace tube. The working electrode is put into the PBN pipe. Argon is used to maintain an inert atmosphere above the sample through a corundum pipe when the furnace is heated up. The corundum sleeve, which the working electrode passes through, is fixed by a clamp to the precision riser. After the electrolyte is molten and the temperature is stable for at least 15 min, the location of the electrode in the PBN pipe is adjusted to about 2.5 cm higher than the lower end of the PBN pipe. Between each recording, the electrode is moved downward 1 mm. The total impedance (Z) monitored by the digital LCR bridge is recorded after the electrode has been moved. In most experiments the electrode is moved downward 6 to 8 times and the corresponding value of Z is recorded. The melt conductivity is calculated by Equation 4.

Result and Discussion

Calibration on the Cross-sectional Area of Conductivity Cell

According to Equation 1, the cross-sectional area of the conductivity cell can be calculated by Equation 5.

$$A = \frac{1}{k(\frac{dR_m}{dl})} \tag{5}$$

Here, A is the cross-sectional area of the conductivity cell; κ is the conductivity of standard melt or aqueous solution whose conductivity value is known; dR_m/dl is the slope of electrode distance-resistance curve.

A 1 mol/l KCl solution was used as the calibration standard solution. According to Lange's Handbook, conductivity and temperature of 1 mol/l of KCl solution meet the following relationship:

$$k_{kcl} = 0.001953 \times T + 0.062981 \tag{6}$$

Where, k_{kcl} is the conductivity of 1 mol/l KCl solution; T is the temperature of the KCl solution in degrees centigrade. The cross-sectional area of each PBN pipe is different, so the calibration of cross-sectional area is needed for each PBN tube. Graphite powder from the graphite crucible adhered to the inner wall of PBN pipe after the pipes were used once or twice, causing a drift in the measured conductivity. Hence, each PBN tube is usually only used for 1 to 2 times.

Validation on the Precision of Measured Conductivity Results

The conductivity of KCl molten salt can be calculated by an empirical formula [17]:

$$k_{m\text{-}KCl} = -3.99 + 0.009022 \times T - 0.000003 \times T^2 \tag{7}$$

Where, $k_{m\text{-}KCl}$ is the conductivity of the KCl molten salt and T is the temperature of the molten salt in K.

In order to validate the accuracy of our work, the conductivity of the KCl molten salt at 790-870 °C was measured and compared with the results calculated by Equation 7. The results are presented in Table I. The results are in good agreement with the established values with a deviation less than 1 %.

Table I. The conductivity of KCl melt

Temperature °C	Conductivity $S\cdot cm^{-1}$		Deviation %
	Ref. [17]	Our results	
790	2.211	2.197	-0.62
800	2.237	2.221	-0.71
810	2.262	2.251	-0.50
820	2.287	2.280	-0.32
830	2.312	2.313	0.06
840	2.335	2.329	-0.27
850	2.359	2.351	-0.32
860	2.381	2.374	-0.30
870	2.403	2.409	0.25

Effect of NaF Content on Conductivity of KF-NaF-AlF_3 Melts

The conductivity of KF-NaF-AlF_3 melts with CRT = 1.35 were measured with NaF content of 0 mol%, 15 mol%, 30 mol%, 45 mol% and 57.4 mol% (KF = 0 mol%), respectively, the temperature range was 750-820 °C with 10 °C interval. The results are shown in Figures 5-8.

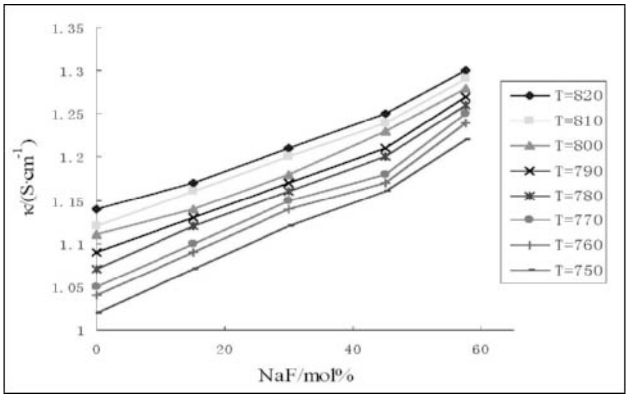

Figure 2. The effect of NaF content on the conductivity of KF-NaF-AlF_3 melts

It can be seen from Figure 2 that the conductivity of KF-NaF-AlF_3 melts with a fixed CRT tends to increase with the increasing NaF content. The conductivity increases about 0.03-0.04 $S\cdot cm^{-1}$ when NaF content increases by 15 mol%.

The reasonable explanation is: The radius of Na^+ (1.02×10^{-10} m) is smaller than the radius of K^+ (1.38×10^{-10} m). When electro-migration occurs, the migration speed of Na^+ is faster than K^+ and the number of migrating ions is larger. According to the report by Fellner et al. [18], the transport number ratio between K^+ and Na^+ in KF-NaF-AlF_3 electrolyte systems is approximately inversely proportional to the square of their ionic radius. As a result, the molar conductivity of an electrolyte with the same CRT increases with the increasing NaF content.

The effect of Al_2O_3 content on the conductivity of KF-NaF-AlF_3 melts

The conductivity of KF-NaF-AlF_3 melts with CRT = 1.41 was studied with a temperature interval of 10 °C in the range from 750 °C to 820 °C. The content of NaF was 30 mol% for all the melts, the addition of Al_2O_3 is 0 wt%, 2.2 wt%, 3.4 wt%, 4.3 wt%, 4.7 wt%, and 4.9 wt%, respectively. The results are presented in Figure 3.

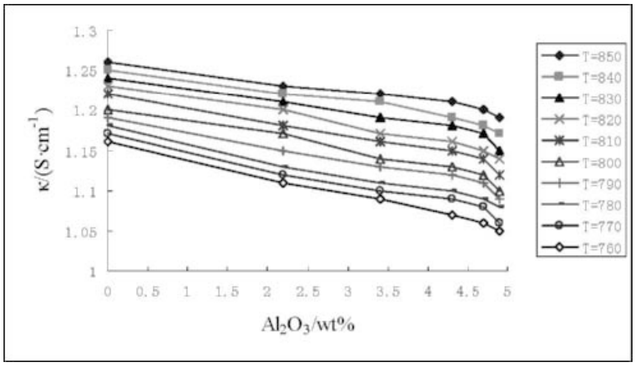

Figure 3. The effect of Al_2O_3 content on conductivity

When the CRT and temperature are kept constant, the conductivity of the KF-NaF-AlF_3-Al_2O_3 electrolyte shows a downward trend as the Al_2O_3 content increases. The conductivity exhibits a substantial linear change when the Al_2O_3 content increases from 0 wt% to 4.3 wt%. For Al_2O_3 content in the range 4.3-4.9 wt%, the conductivity of the melts tends to decrease rapidly as the alumina content increases. This is most likely because the Al-O-F complex ion which contains more than two O ions (such as $Al_3O_3F_6^{3-}$ and $Al_3O_4F_4^{3-}$) will form when the content of alumina is approaching the saturation concentration, and those larger complex ions may reduce the mobility of the Na^+ and K^+ ions.

The Effect of Cryolite Ratio (CRT) on the Conductivity of KF-NaF-AlF_3 Electrolyte

The conductivity of KF-NaF-AlF_3 melts with [NaF] = 30 mol% was investigated for CRT equal to 1.2, 1.25, 1.3, 1.35, 1.41, 1.45, and 1.5, respectively. The temperature was 750-820 °C. The results are shown in Figure 4.

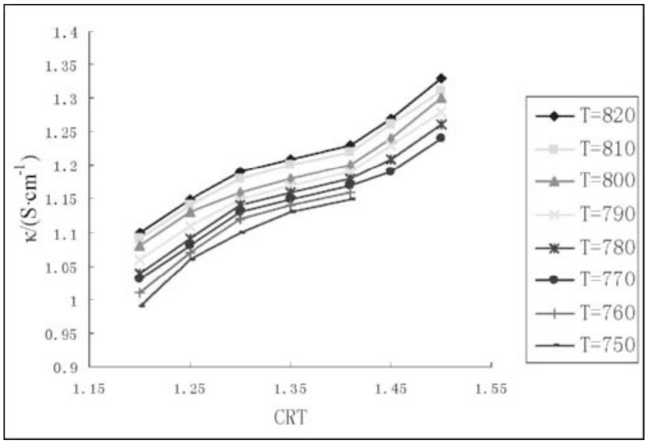

Figure 4. The effect of CRT on conductivity

The conductivity increases with increasing CRT and increasing temperature because of the increase in the number of K^+ and Na^+ ions in the melts. The CRT-conductivity curve exhibits a cubic line tendency. The conductivity has a lower increase between the CRT range of 1.3 to 1.41 than is the case for the CRT ranges between 1.2 to 1.3 and 1.41 to 1.5 where the conductivity changes more rapidly.

<u>Empirical Formula for Calculating Conductivity of the KF-NaF-AlF_3 Melts</u>

An empirical formula for calculating conductivity of the KF-NaF-AlF_3 melt was deduced from the experimental results:

$$\kappa = 0.1442\times N^2 + 0.164\times N + 16.947\times R^3 - 68.086\times R^2 + 91.534\times R + (8.812\times10^{-5}\times T - 0.0874)\times A + 1.39\times10^{-3}\times T - 41.1785 \qquad (8)$$

Where, κ is the conductivity in $S\cdot cm^{-1}$; N is the mole fraction of NaF in the range of 0 to 0.6; R is the CRT of electrolyte in the range of 1.2 to 1.5; A is the mass fraction of Al_2O_3 in the range 0 to 0.043; and T is the temperature of the melt in degree centigrade in the range 750 to 820 °C.

The results calculated by the empiric formula, Equation 8, are compared to the experimental results in Table II.

Table II. The results obtained by calculating from empiric formula and by experiments

CRT	NaF mol%	Al_2O_3 wt%	T °C	κ, $S\cdot cm^{-1}$		$\Delta\kappa_1$ $S\cdot cm^{-1}$
				Cal*	Exp#	
1.2	30	0	820	1.10	1.10	0
1.2	30	0	800	1.08	1.08	0
1.2	30	0	780	1.05	1.04	0.01
1.2	30	0	760	1.02	1.01	0.01
1.35	0	0	800	1.11	1.11	0
1.35	15	0	800	1.14	1.14	0
1.35	30	0	800	1.18	1.18	0
1.35	45	0	800	1.22	1.23	-0.01
1.41	30	0	820	1.23	1.23	0
1.41	30	2.2	800	1.17	1.17	0
1.41	30	3.4	780	1.11	1.11	0
1.41	30	4.3	760	1.06	1.07	-0.01
1.5	30	0	820	1.33	1.33	0
1.5	30	0	780	1.27	1.26	0.01

Note: Cal* means the results were calculated by the empirical formula (Equation 8), Exp# means experimental results.

It can be seen from Table II that the results calculated by the empirical formula (Equation 8) and the experimental results is within an accuracy of 0.01 $S\cdot cm^{-1}$. Hence, the empirical formula is suitable for calculating the conductivity of KF-NaF-AlF_3-Al_2O_3 for melts with CRT = 1.2 to 1.5, Al_2O_3 = 0 to 4.3 wt%. The formula has not been verified outside these ranges and may give erroneous results if used in extrapolations.

Apisarov et al. [15] reported the conductivity of molten mixtures KF-NaF-AlF_3 melts at the cryolite ratio CRT = 1.3 and 1.5, and several empirical formulas were given to calculate KF-NaF-AlF_3 melts for fixed compositions. Table III shows a comparison of our results with those of Apisarov et al. [15].

Table III. The comparison of KF-NaF-AlF_3 melts conductivity results

CRT	NaF mol%	T °C	κ, $S\cdot cm^{-1}$		$\Delta\kappa_2$ $S\cdot cm^{-1}$
			Our results	Results from [15]	
1.3	0	780	1.07	1.17	-0.10
1.3	0.81	780	1.07	1.21	-0.14
1.3	30.68	780	1.13	1.26	-0.13
1.3	44.43	780	1.17	1.30	-0.13
1.5	0	780	1.21	1.25	-0.04
1.5	43.68	780	1.31	1.43	-0.12
1.5	8	800	1.25	1.37	-0.12
1.5	8	793	1.24	1.32	-0.08
1.5	8	788	1.23	1.29	-0.06
1.5	15.7	800	1.27	1.40	-0.13
1.5	15.7	787	1.25	1.37	-0.12
1.5	30.28	799	1.30	1.46	-0.16
1.5	30.28	790	1.29	1.44	-0.15

The results show that the values calculated by our empirical formula are smaller, however, the deviation is generally less than 0.15 $S \cdot cm^{-1}$. The measured differences may be due to the the accuracy of the methods.

Conclusion

The conductivity of molten KF-NaF-AlF_3 system electrolyte with CRT ranging from 1.2 to 1.5 was measured at temperatures ranging from 750 to 820 °C. The effect of CRT, temperature, NaF and alumina on the conductivity was determined. An empirical formula for calculating conductivity of the KF-NaF-AlF_3 melt was derived.

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