Density of the $NaAlF_4 + KAlF_4$ Electrolyte, Saturated with Alumina

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Density data were determined for melts with the equimolar composition $NaAlF_4 + KAlF_4$, saturated with alumina, over the temperature range (650 to 750) °C. The density measurements were performed in a platinum crucible with 5 % alumina added, as well as in a sintercorundum crucible with the same amount of alumina, to ensure alumina saturation. From both overall regression equations obtained from the measurements in sintercorundum and platinum crucibles, the density values were very close, indicating that the system in the platinum crucible with 5 % alumina added was saturated. By combining the equations for both sets of measurements, the final equation was: $\rho/g\cdot cm^{-3} = 2.5321 - (9.598\cdot10^{-4})t/°C$.

Introduction

Aluminum is being produced industrially by the so-called Hall−Héroult process, which is based on electrolytic decomposition of alumina from a molten $NaF + AlF_3 + Al_2O_3$ electrolyte at about 960 °C. The composition of the electrolyte is one of the most important technological parameters of this process. It is closely related to the current efficiency (CE) of the process. The optimal composition of the electrolyte depends on other technological parameters such as temperature, interelectrode distance, current density, physicochemical properties of the electrolyte, etc. To find the optimal electrolyte composition, mainly concerning the contents of alumina and aluminum fluoride, is a priority to achieve high CE.

The electrolyte composition also plays a key role when using so-called inert anodes. In industrial aluminum production only consumable carbon anodes are used, evolving greenhouse gases (mainly CO_2). Many attempts have been made to replace the carbon anodes by inert anodes.[1] The anode gas will then be oxygen. The inert anode material can be a ceramic oxide material or a metal substrate covered by an adherent oxide layer.[1] The present industrial electrolyte might also be suitable for inert anodes, but the application of more low-melting electrolytes is desirable. All oxide materials exhibit some solubility in the electrolyte; therefore, a certain rate of dissolution of the anode material into the electrolyte must be tolerated. The use of a low electrolyte temperature should then be advantageous. When using a metal substrate as an inert anode material, a low electrolyte temperature is of particular interest, because the rate of oxidation of metals drops sharply by decreasing temperature. In order to lower the melting point of the electrolyte, AlF_3 is the most commonly used additive. However, addition of this component lowers the alumina solubility and the electrical conductivity.[2,3] As an alternative additive to lower the operating temperature, the use of KF can be considered, allowing electrolyte temperatures down to the range of (600 to 700) °C.

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The phase diagrams of the binary system $KF + AlF_3$ were measured by several workers as summarized in ref 2. There are some minor differences between those sets of data. Published coordinates of the eutectic point, e_2, were found to be 54 % AlF_3 and 560 °C[4−6] and (49 to 54) % AlF_3 and 570 °C,[7,8] respectively. The solubility of alumina in $KF + AlF_3$ melts at 1000 °C was measured by Robert et al.[9] Concerning the density of the relevant systems, no data are available in the literature.

The present work focused on density analysis of the potentially interesting systems based on NaF, KF, and AlF_3. Experimentally determined values of density are important not only from a technological but also from a theoretical point of view since they characterize volume properties of the electrolytes. From this information, it is possible to consider the "structure" of the electrolyte. Density measurements were performed for the ternary fluoride systems $(NaF + KF) + AlF_3$ with the addition of alumina.

Experimental Section

To prepare the mixtures, the following chemicals were used: NaF (Merck), purity grade; KF (Fluka), purity grade; AlF_3, sublimated; alumina BDH, chemicals grade p.a. The NaF, AlF_3, and alumina were dried at 500 °C for 2 h. KF was dried under vacuum at 130 °C for 24 h in the presence of P_2O_5. The handling of all salts was done in a glovebox under dry nitrogen atmosphere (Messer, 99.99 %). Samples were homogenized before each experiment.

The measurements were carried out within a temperature interval of (100 to 150) °C, starting at approximately 620 °C. The density of the melts was measured using the Archimedean method. A platinum vessel suspended in a platinum wire of 0.3 mm diameter, attached below an electronic balance unit, was used as the measuring body. The dependence of the volume of the vessel on temperature was determined by calibration, using molten NaCl, KCl, and $(LiF + NaF + KF)_{eut}$, all of reagent grade purity. The temperature was measured using a Pt−Pt(10 % Rh) thermocouple calibrated at the melting points of NaCl, KCl, and Na_2SO_4. An online PC computer was used for control of the measuring device and for evaluation of the experimental data. The experimental error in the density measurement did not exceed ± 0.5 %.

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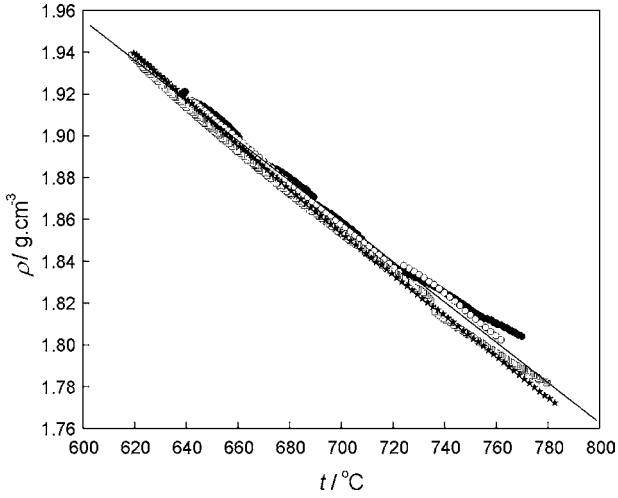

Figure 1. Results from four runs of density measurements made in a sintercorundum crucible: ●, 1st cooling; ○, 1st heating; □, 2nd cooling; ★, 2nd heating; line, overall trendline.

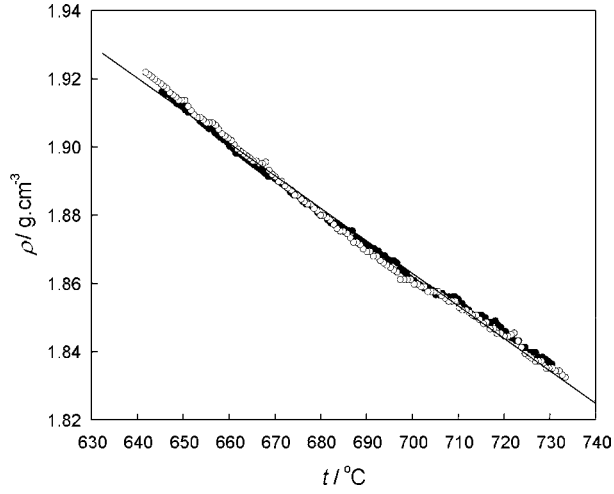

Figure 2. Results from four runs of density measurements made in a platinum crucible: ●, cooling; ○, heating; line, overall trendline.

A platinum (or sintercorundum) crucible containing the sample was placed inside an electric resistance furnace in a controlled dried nitrogen atmosphere, having adjustable cooling and heating rates of ~(2 to 3) °C·min^{-1}. A detailed description of the measuring device can be found in ref 10.

The measurements were carried out within a temperature interval of approximately 100 °C, starting at (20 to 30) °C above the temperature of primary crystallization. The density data were automatically measured and registered by the measuring device every 10 s, yielding approximately 300 density data for each run.

Prior to the density measurements, the melting point of the system was estimated. By the cryoscopic method, a value of 616.5 °C was obtained for the temperature of primary crystallization.

The temperature dependence of the density was expressed in the form of a linear equation

$$\rho/\mathrm{g\cdot cm^{-3}} = a - b\cdot t/°\mathrm{C} \qquad (1)$$

where ρ is the density and t is the temperature. For each measurement in heating and cooling modes, the curves were recorded.

Results and Discussion

The density measurements were performed in a platinum crucible with 5 % alumina being added to the mixture, as well as in sintercorundum crucibles with the same amount of alumina, to ensure that the melt was saturated with alumina. Excess undissolved alumina would settle at the bottom of the crucible and did not interfere with the measurements. It was found that it was not necessary to make any corrections for changes in composition with time, caused by evaporation. This was most probably so because the duration of the measurements was short and also because small composition changes do not have any pronounced influence on the density values.

Densities measured at the same temperature at the beginning and at the end of a measuring cycle did not differ by more than 0.5 %. The temperature dependence of the density, measured in the sintercorundum crucible, when presented in the form of linear equations, differed only marginally for the heating and cooling periods. The measured data and its overall trendline are presented in Figure 1. The results obtained by the measurement in the platinum crucible are presented in Figure 2. The regression equations for different runs in the sintercorundum and platinum crucibles as well as regression equations based on all the data gathered in the measurements in both crucibles are summarized in Table 1. The values of the constants together with the standard deviations (SD) of approximations were obtained by linear regression analysis of the experimental data. From both overall regression equations obtained from the measurements in sintercorundum and Pt crucibles, it follows that the density values are very close, indicating that the system in the platinum crucible with 5 % alumina was saturated. A comparison of the density data for three selected temperatures, calculated according to both overall equations (equations (C) in Table 1), are given in Table 2. From density values it follows that the differences in density values for both systems did not exceed 0.3 %. When combining both overall equations, we get the final equation (Table 1), which describes very well the

Table 1. Coefficients *a* and *b* in Equation 1 and the Standard Deviations (SD) of the Fit for the Investigated System ((NaF + KF) + AlF_3) (1) + Al_2O_3 (2)[a]

x_1	x_2	a / (g·cm^{-3})	$b\cdot10^{-4}$ / (g·cm^{-3}·°C)	SD·10^{-3} / (g·cm^{-3})	t / °C
		Sintercorundum Crucible			
1.00	0.05	2.5204[A]	9.4360	2.7	620 to 770
1.00	0.05	2.5754[A]	10.3000	4.2	620 to 770
0.95	0.05	2.4970[B]	9.1000	0.9	620 to 770
0.90	0.05	2.5390[B]	9.7785	1.8	620 to 770
0.90	0.05	2.5323[C]	9.6397	4.3	620 to 770
		Platinum Crucible			
0.90	0.05	2.5474[A]	9.7833	2.5	620 to 770
0.90	0.05	2.5144[B]	9.3028	2.9	620 to 770
0.90	0.05	2.5309[C]	9.5430	1.7	620 to 770
		Final Equation			
0.90	0.05	2.5321	9.5980	2.9	620 to 770

[a] A, heating period; B, cooling period; C, overall relation.

Table 2. Density for Three Selected Temperatures, Measured in Sintercorundum (1) and Platinum (2) Crucibles

t / °C	$\rho(1)$ / g·cm^{-3}	$\rho(2)$ / g·cm^{-3}
650	1.9059	1.9106
700	1.8577	1.8629
750	1.8094	1.8152

density of the equimolar composition of the $NaAlF_4 + KAlF_4$ system saturated with alumina.

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Supporting Information Available:

Sintercorundum crucible and platinum crucible data. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Galasiu, I.; Galasiu, R.; Thonstad, J. *Inert Anodes for Aluminium Electrolysis*; Aluminium-Verlag: Düsseldorf, Germany, 2007.
(2) Grjotheim, K.; Krohn, C.; Malinovský, M.; Matiašovský, K.; Thonstad, J. *Aluminium Electrolysis. Fundamentals of the Hall-Héroult Process*, 2nd ed.: Aluminium-Verlag: Düsseldorf, Germany, 1982.
(3) Thonstad, J.; Fellner, P.; Haarberg, G. M.; Híveš, J.; Kvande, H.; Sterten, Å. *Aluminium Electrolysis*, 3rd ed.; Aluminium-Verlag: Düsseldorf, Germany, 2001.
(4) Barton, C. J.; McVay, T. N.; Bratcher, L. M.; Grimes, W. R. *Phase Diagrams of Nuclear Reactor Materials*; Thoma, R. E., Ed.; Oak Ridge National Laboratory report ORNL-2548, USA, 1959.
(5) Jenssen, B. Phase Factors Conditions for Any Alkali Aluminum Fluoride Complexes; Thesis, The University of Trondheim, NTH, Trondheim, 1969.
(6) Phillips, B.; Warshaw, C. M.; Mockrin, I. Equilibria in $KAlF_4$-containing System. *J. Am. Ceram. Soc.* **1966**, *49*, 631–634.
(7) Pushin, N. A.; Baskov, A. V. Equilibrium in Binary Systems of Fluorides. *Zh. Russ. Fiz. Khim. Obshch.* **1913**, *135*, 82–84.
(8) Fedotieff, P. P.; Timofeeff, K. The Melting Diagram of the Systems $KF-AlF_3$ and $LiF-AlF_3$. *Z. Anorg. Allg. Chem.* **1932**, *206*, 263–266.
(9) Robert, E.; Olsen, J. E.; Daněk, V.; Tixton, E.; Ostvold, T.; Gilbert, B. Structure and Thermodynamics of Alkali Fluoride-Aluminum Fluoride-Alumina Melts. Vapor Pressure, Solubility, and Raman Spectroscopic Studies. *J. Phys. Chem.* **1997**, *101* (46), 9447–9457.
(10) Silný, A. Equipment for Density Measurements of Liquids. *Advising Technics (Sdelovací Technika)* **1990**, *38*, 101–103.

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