Liquidus Temperatures of $Na_3AlF_6-AlF_3-CaF_2-NaCl-Al_2O_3$ Melts

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Temperatures for the primary crystallization of Na_3AlF_6 in multicomponent electrolyte systems of interest for the aluminum electrolysis process were determined by thermal analysis. The molar ratio of NaF/AlF_3 ranged from 2.0 to 3.0. The melts contained up to 9 % NaCl (by mass). An empirical equation describing liquidus temperatures for the primary crystallization of Na_3AlF_6 was derived: $t/°C = 978.142 - 4.078w(AlF_3) - 13.341w(NaCl) + 0.619w(AlF_3)^2 + 1.210w(NaCl)^2 + 1.052w(AlF_3)w(NaCl) - 0.034w(AlF_3)^3 - 0.050w(NaCl)^3 - 0.040w(AlF_3)w(NaCl)^2 - 0.070w(AlF_3)^2w(NaCl)$, where $w(AlF_3)$ denotes the mass fraction of excess aluminum fluoride with respect to cryolite and $w(NaCl)$ denotes the mass fraction of sodium chloride.

Introduction

The molten systems based on cryolite (Na_3AlF_6) serve as the solvent for alumina in the electrolytes used for the production of aluminum. The high melting temperature of cryolite (1008 °C) can be lowered by the addition of other salts. The conventional system consists of cryolite with (6 to 13) % AlF_3, (3 to 8) % CaF_2, and (2 to 5) % $A1_2O_3$ (all percentages by mass). The working temperature of the electrolyte is usually in the range (945 to 970) °C. It might be of advantage to use an electrolyte with a lower melting temperature.[1−4] The temperature of primary crystallization can be lowered by use of an AlF_3-rich bath and/or by the introduction of certain additives. Besides the additions like CaF_2, LiF, KF, and MgF_2, sodium chloride may also be present in the bath. Industrial practices with electrolytes containing sodium chloride have been confirmed with good results by some Chinese aluminum reduction smelters.[5] The effect of the above additives on the temperature of primary crystallization of the system $Na_3AlF_6-AlF_3$ has been studied.[6] In the case of NaCl, the data are limited for melts with a high molar ratio of NaF/AlF_3 (higher than 2.7).[1,5] In this work we have measured the effect of NaCl on the reduction of liquidus temperatures of the molten system $Na_3AlF_6-AlF_3-CaF_2-Al_2O_3$.

Experimental Section

AlF_3 was purified in our laboratory by sublimation, while CaF_2, NaF, NaCl, and alumina were high-quality chemicals containing very small amounts of impurities and were dried at 400 °C for 48 h. Na_3AlF_6 was prepared by mixing NaF and AlF_3 at a molar ratio of 3 and melting at 1050 °C.

The thermal analysis was performed under an atmospheric pressure of argon in an apparatus consisting of a 6.0 cm diameter stainless steel (310s) chamber with ports for thermocouple and argon gas inlet. The chamber was heated by a vertical alumina tube furnace. The crucibles were usually made of high-quality graphite. The cooling rate was 1 °C·min^{-1}. The temperature of the melt was measured by immersing a Pt−Pt/Rh 10 % thermocouple connected to a digital thermometer with a resolution of 0.1 °C, and all experiments were done by placing the crucible in the constant temperature zone of the furnace. The Pt−Pt/Rh 10 % thermocouple was calibrated to the melting points of pure compounds NaCl, LiCl, and NaF. The measured transition temperatures were reproducible to within ± 2 °C. Argon gas was passed through the chamber at a rate of 100 cm^3·min^{-1}.

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Table 1. Experimental Liquidus Temperatures and Liquidus Temperatures Calculated from Equation 1 for the Molten System $Na_3AlF_6-AlF_3-NaCl-4$ % CaF_2 (by Mass)−3 % Al_2O_3 (by Mass)

$w(AlF_3)$	w(NaCl)	t	calc. t	Δt	$w(AlF_3)$	w(NaCl)	t	calc. t	Δt
%	%	°C	°C	°C	%	%	°C	°C	°C
15.33	1.00	929.1	926.1	3.0	5.33	1.00	962.5	960.1	2.4
15.00	3.00	906.4	906.4	−0.0	5.22	3.00	946.0	947.3	−1.3
14.67	5.00	885.5	889.5	−4.0	5.10	5.00	940.6	938.9	1.7
14.33	7.00	872.7	873.4	−0.7	4.99	7.00	933.6	932.7	0.9
14.00	9.00	854.6	855.5	−0.9	4.87	9.00	925.2	926.2	−1.0
11.68	1.00	945.6	951.1	−5.5	2.56	1.00	963.0	961.1	1.9
11.43	3.00	938.4	936.0	2.4	2.50	3.00	946.9	946.5	0.4
11.17	5.00	928.1	924.1	4.0	2.44	5.00	935.2	937.0	−1.8
10.92	7.00	918.0	913.1	4.9	2.39	7.00	932.2	930.5	1.7
10.67	9.00	905.4	900.8	4.6	2.33	9.00	926.4	924.4	2.0
8.36	1.00	959.0	958.9	0.1	0	1.00	964.0	966.0	−2.0
8.18	3.00	944.6	946.1	−1.5	0	3.00	948.6	947.7	0.9
8.00	5.00	936.0	936.9	−0.9	0	5.00	935.4	935.5	−0.1
7.82	7.00	924.6	929.2	−4.6	0	7.00	925.6	927.0	−1.4
7.64	9.00	915.5	920.7	−5.2	0	9.00	920.3	919.8	0.5

Results and Discussion

Thirty $Na_3AlF_6-AlF_3-NaCl-4$ % CaF_2 (by mass)−3 % Al_2O_3 (by mass) mixtures were investigated (some of them repeatedly). The molar ratio of NaF/AlF_3 ranged from 2.0 to 3.0. The melts contained up to 9 % NaCl (by mass). The results are summarized in Table 1. It was found that the experimental results could be described by the following equation:

$$t/°C = 978.142 - 4.078w(AlF_3) - 13.341w(NaCl) + 0.619w(AlF_3)^2 + 1.210w(NaCl)^2 + 1.052w(AlF_3)w(NaCl) - 0.034w(AlF_3)^3 - 0.050w(NaCl)^3 - 0.040w(AlF_3)w(NaCl)^2 - 0.070w(AlF_3)^2w(NaCl) \quad (1)$$

where t is the temperature of primary crystallization. The coefficients of the equation were determined using a multiple-nonlinear regression. The composition is given in mass fraction.

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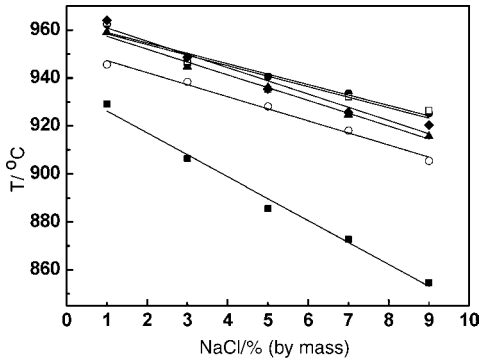

Figure 1. Liquidus temperatures at different amounts of NaCl content in the system $Na_3AlF_6-AlF_3-CaF_2-NaCl-Al_2O_3$. ■, CR = 2.0; ○, CR = 2.2; ▲, CR = 2.4; ●, CR = 2.6; □, CR = 2.8; ◆, CR = 3.0.

$w(AlF_3)$ denotes the mass fraction of excess aluminum fluoride with respect to cryolite; w(NaCl) denotes the mass fraction of sodium chloride. The relationship between $w(AlF_3)$ and CR (CR is the molar ratio of NaF/AlF_3) can be described by eq 2

$$w(AlF_3) = (3 - CR)(100 - SA)/(3 + 1.5CR) \quad (2)$$

where $SA = w(CaF_2) + w(Al_2O_3) + w$(NaCl).

Equation 1 is based on our experimental data. The experimental and calculated data are compared in Table 1. The coefficient of determination, R^2, has a value of 0.989.

On the basis of the present study, the composition limitations of eq 1 are proposed to be $w(AlF_3) < 16$ % (by mass) and w(NaCl) up to 9 % (by mass). The standard error of the estimate is about 3.23 °C. The overall uncertainty was estimated to be below 1 %.

Figure 1 shows the liquidus temperatures for the primary crystallization of cryolite in the system $Na_3AlF_6-AlF_3-CaF_2-NaCl-Al_2O_3$. The data were fiited to single lines as shown in Figure 1. The slope of the line with CR = 2.0 is about 9.1 °C/% NaCl (by mass). The slopes of lines with CRs of 2.2 to 3.0 are in the range of (4.3 to 5.5) °C/% NaCl (by mass). The reduction of the freezing temperature is much more pronounced in electrolyte with CR = 2.0 than in electrolytes with CR > 2.2 if 1 % NaCl (by mass) is added to the electrolyte.

Literature[6,7]data indicate a reduction of liquidus temperature of (7 to 9) °C/% LiF (by mass) in electrolytes with a CR of 2.2 to 3.0, and 6 °C/% (by mass) in electrolytes with CR = 2.0. Therefore, sodium chloride has more reduction potential of the liquidus temperature for electrolytes with a lower CR than lithium fluoride. Considering the significantly low cost, NaCl is perhaps the best additive for a low-temperature electrolyte with a CR lower than 2.0.

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