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LIQUIDUS TEMPERATURE OF ELECTROLYTES FOR ALUMINUM REDUCTION CELLS

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Abstract

In this paper, the liquidus temperatures of the cryolite-alumina melts containing LiF, NaCl and KF were measured. The molar ratio of NaF/AlF_3 was in the range of 2.0-3.0. A differential thermal analysis (DTA) apparatus was designed and constructed to measure the liquidus point of cryolite melts. The effect of these additives on the liquidus temperature was discussed. A multiple regression solution was obtained for the liquidus temperature of aluminum electrolytes.

Introduction

In the progress of bath chemistry of cryolite-alumina melt, other compounds, including AlF_3, CaF_2, MgF_2, NaCl, KF and LiF were added to molten cryolite to modify the physico-chemical properties in order to improve the cell performance. All additives lower the liquidus temperature. Reduction in liquidus temperature is generally considered advantageous, because the operation temperature of the reduction cell may be reduced, and this improves the current efficiency of the process. Several research groups have developed some model equations describing liquidus temperature as a function of the concentrations of alumina and additives. [1-4]

The present work describes a new equation for both conventional electrolyte compositions and low melting bath with high concentrations of AlF_3, LiF, KF and NaCl.

Phase equilibria can be studied by thermal analysis, by differential thermal analysis, by cryoscopy. In this study, a differential thermal analysis apparatus was designed and installed to measure the liquidus point of cryolite baths.

Experimental Apparatus and Process

The structure of the apparatus used in this study is shown in the Figure 1. The containers for sample and reference substance were graphite crucibles, with the inner diameter 14mm, the outside diameter 20mm, and height 35mm. The crucibles were fixed to a steel bracket.

Reagent chemicals, CaF_2(99%), LiF(99%), NaCl(99%), NaF(99%), Al_2O_3(99%), Na_3AlF_6(99%) were commercially available and used after appropriate drying treatments. KF was dried under vacuum at 400°C for 6hr. In view of the relatively large quantity of melt required and the number of samples, it is not practical to use vacuum-sublimed AlF_3. $AlF_3 \cdot 3H_2O$ mixed with NH_4F(70:30, wt%) was dried at 200°C for 3h and 500°C for 3h. All chemicals after dry treatment were kept in a dry box.

In all cases, bath sample were prepared under nitrogen gas atmosphere. A furnace was preheated to about 50°C above the melting point of the composition under investigation. The melt constituents were mixed in the dry state and placed in a graphite crucible, which was then placed inside the hot furnace. As soon as melting occurred, the crucible contents were stirred with a graphite rod to insure homogeneity and then chilled. This procedure was designed to cut down the time that the melts were at high temperature; consequently composition changes due to volatilization or hydrolysis were kept to a minimum.

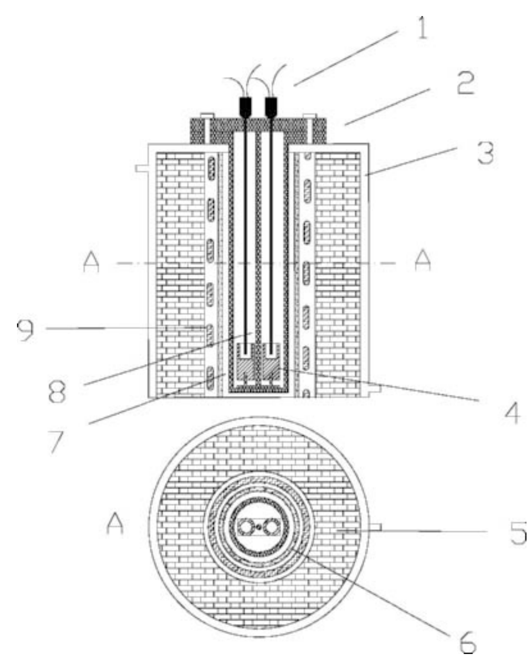

Fig.1. The DTA apparatus
1-thermocouple, 2-flange, 3-circulating water cooling furnace sets, 4-graphite crucible, 5-insulation layer, 6-the corundum insulation layer, 7-stainless steel crucible, 8-stainless steel mounting bracket, 9-heating element

The chilled melt was pulverized and sampled.

In the DTA apparatus the differential is achieved by using two type K thermocouples, one in the sample and one in the alumina, with the negative leads connected together. Approximately 2 grams of the bath is loaded into the sample crucible and alumina into the reference crucible. The weight of sample and α-Al_2O_3 as the reference substance was 2g. The sample and alumina were encapsulated in the graphite crucible with a lid to avoid volatilization. The entire system was heated at a speed of 10°C/min until the bath was molten, plus approximately 50°C superheat.

The freezing point of melt is determined from the thermograph obtained from the heating process of the DTA, as shown in

Figure 2. The first heat effect at temperature a_1 corresponds to the solid phase transformation of cryolite, following by the progressive melting of chilite up to the temperature a_2, where the amount of pure cryolite still present as a solid, undergoes isothermal peritectic transformation into soiled cryolite and a liquid. Thereafter, the next progressive melting of cryolite takes places up to the liquidus temperature a_3. Test samples were measured twice, and were usually found to be within one to two degrees of each other.

The freezing point of two standards, chemically pure NaCl (801°C) and NaF (994°C) were always measured with the DTA apparatus before the freezing points of a series of electrolytes were determined to ensure that the apparatus was functioning properly. Calibrations were found to agree with 1-2 degrees of the freezing point of the standards.

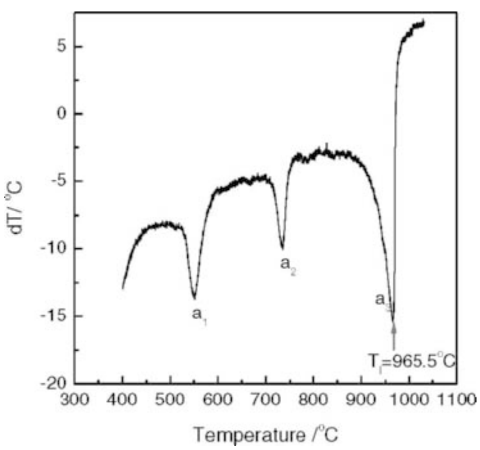

Fig. 2. A typical thermograph for cryolite-alumina bath

Results and Discussion

In this work, a multiple regression model was adopted to fit the relationship between liquidus temperature and chemical composition of cryolite bath. The general form of the model can be described as:

$$y=K+a_{11}x_1+a_{12}x_1^2+\ldots a_{1n}x_1^n+a_{21}x_2+a_{22}x_2^2+\ldots a_{2n}x_2^n+\ldots+a_{m1}x_m+a_{m2}x_m^2+\ldots+a_{mn}x_m^n \qquad (1)$$

where, y is the liquidus temperature; x_i is the chemical concentration of additive in weight percent; K, a_{11} to a_{mn} are constants.

Na_3AlF_6-5wt%Al_2O_3-AlF_3-CaF_2-KF

The regression equation of Na_3AlF_6-5wt%Al_2O_3-AlF_3-CaF_2-KF system was deduced with the data from present work (21 experimental points). There is no $[Al_2O_3]$ in the equation as its concentration is set as 5 wt% for all the samples. The equation is

$$y=1011+0.52[AlF_3]-0.21[AlF_3]^2-10.14[CaF_2]-7.4[KF]+1.27[KF]^2-0.1[KF]^3 \qquad (2)$$

Where, $[AlF_3]$ denotes the weight percent of excess aluminum fluoride with respect to cryolite; $[CaF_2]$ and [KF] denote the weight percent of CaF_2 and KF, respectively; y is the liquidus temperature. The composition limitations of Equation 2 are proposed to be $[AlF_3]<16$wt%, 3.5wt%$<[CaF_2]<5$wt%, $[KF]\leqslant 9$wt%. The coefficient of determination, r2, has a value of 0.95.

The curves in Figure 3 are plotted according to Equation 2. A comparison of Equation 2 with the liquidus equations published by Solheim [3] is also provided in Figure 3. The concentrations of CaF_2 and Al_2O_3 are 4wt% and 5 wt%, respectively.

The equation provided by Solheim is not valid for electrolytes containing KF> 5 wt%.

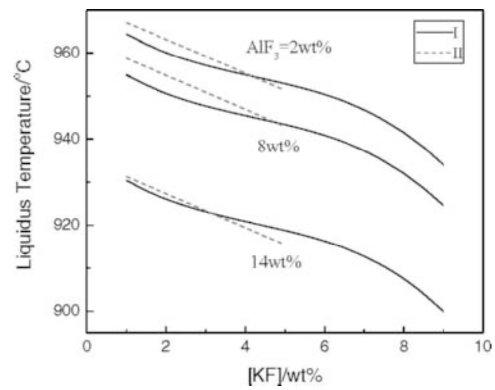

Fig. 3. Liquidus temperature for the system Na_3AlF_6-5wt%Al_2O_3- AlF_3- CaF_2- KF. I---this work, II---Solheim[3]

Na_3AlF_6-5wt%Al_2O_3-AlF_3-CaF_2-LiF

The regression equation of Na_3AlF_6-5wt%Al_2O_3-AlF_3-CaF_2-LiF system was deduced with data from the present work (23 experimental points). There is no $[Al_2O_3]$ in the equation as its concentration is set as 5 wt% for all the samples. The equation is

$$y=1011+4.3[AlF_3]-0.89[AlF_3]^2+0.03[AlF_3]^3-18.15[CaF_2]+1.27[CaF_2]^2-7.52[LiF]+0.35[LiF]^2-0.04[LiF]^3 \qquad (3)$$

The composition limitations of Equation 3 are proposed to be $[AlF_3]<16$ wt%, 3.5 wt%$<[CaF_2]<5$ wt%, $[LiF]\leqslant 9$ wt%. The coefficient of determination, r2, has a value of 0.989.

Figure 4 shows the comparison between the liquidus temperature calculated from Solheim's Equation [3] and present work. The data from Solheim are in reasonable agreement with data from the present work. Compared to KF, LiF has higher potential for decreasing liquidus temperature.

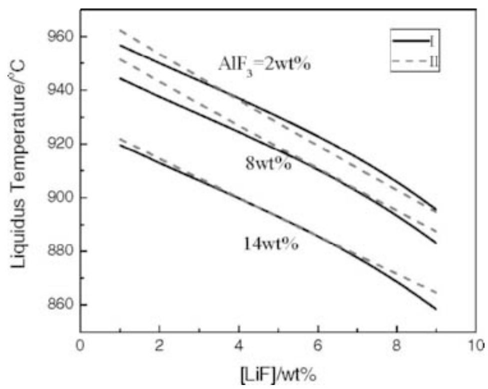

Fig.4. Liquidus temperature for the system Na_3AlF_6-5wt%Al_2O_3- AlF_3- CaF_2- LiF. I---this work, II---Solheim[3]

Na_3AlF_6-5wt%Al_2O_3-AlF_3-CaF_2-NaCl

The regression equation of Na_3AlF_6- 5wt%Al_2O_3- AlF_3- CaF_2- NaCl system was deduced with data from the present work (23 experimental points). There is no [Al_2O_3] in the equation as its concentration is set as 5 wt% for all the samples. The equation is

$$y=1011+1.71[AlF_3]-0.47[AlF_3]^2+0.01[AlF_3]^3-10.72[CaF_2]-6.78[NaCl]+0.12[NaCl]^2 \quad (4)$$

The curves of the liquidus temperature calculated from Equation 4 are shown in Figure 5. The curves are approximately linear. Compared to LiF and KF, the reduction of the freezing temperature is higher than KF, but lower than LiF.

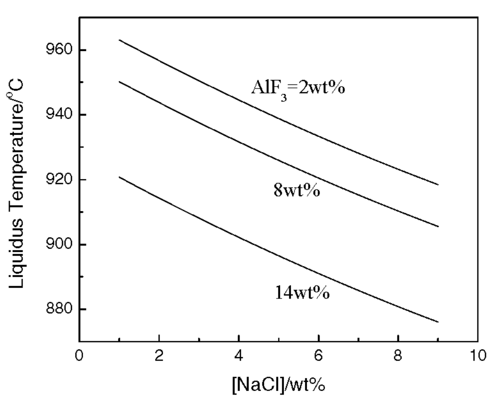

Fig.5. Liquidus temperature for the system Na_3AlF_6-5wt%Al_2O_3- AlF_3- CaF_2- NaCl.

Na_3AlF_6-5wt%Al_2O_3-AlF_3-CaF_2-KF-LiF-NaCl

A new equation is derived when all the experimental points (about 74 points) are included, as shown in equation 5.

$$y=1011+3.79[AlF_3]-0.79[AlF_3]^2+0.02[AlF_3]^3-29.84[CaF_2]+4.46[CaF_2]^2-6.05[KF]+1.14[KF]^2-0.09[KF]^3-9.07[LiF]+0.86[LiF]^2-0.077[LiF]^3-5.817[NaCl]-0.11[NaCl]^2 \quad (5)$$

the composition limitations of which are proposed to be [AlF_3]<16wt%, 3.5wt%<[CaF_2]<5wt%, [KF]≈[LiF]≈[NaCl] ≤9wt%. The standard error of the estimate is 4.2°C. Coefficient of multiple determinations, r2, has a value of 0.978. Table 1 shows some experimental and calculated (from Figure 5) liquidus temperatures for the system Na_3AlF_6- 5wt%Al_2O_3-AlF_3- CaF_2- KF- LiF- NaCl.

Table1. The experimental liquidus temperatures and liquidus temperatures calculated from Equation 5 for system Na_3AlF_6-5wt%Al_2O_3- AlF_3- CaF_2- KF- LiF- NaCl.

[AlF_3]	[KF]	[LiF]	[NaCl]	[CaF_2]	Liq. Temperature (°C).	
		Wt%			Experimental	Eq.5
15	0	0	0	5	924	919.9
11.43	0	0	0	5	944	943.3
8.18	0	0	0	5	964	962.4
5.22	0	0	0	5	975	974.4
8.77	1	0	0	4.35	946	946.5
4.42	3	0	0	4	956	955.7
6.93	5	0	0	4.16	943	946.1
3.33	7	0	0	3.92	952	950.1
8.3	9	0	0	4.12	921	925.2
7.85	0	1	0	4.21	947	946.9
8.29	0	3	0	4.12	931	930.8
5.59	0	5	0	4.03	926	929.8
9.56	0	7	0	4.12	900	897.8
6.09	0	9	0	3.85	892	892.8
14.83	0	0	1	5	913	915.2
7.84	0	0	3	4.12	938	938.1
2.27	0	0	5	3.71	939	940.1
7.93	0	0	7	3.94	921	917.7
5.83	0	0	9	3.69	916	917.4

Conclusion

The liquidus temperatures of the cryolite-alumina melts containing LiF, NaCl and KF were measured by the differential thermal analysis (DTA) apparatus. Equations were derived to calculate the freezing point temperature as a function of chemical compositions.

LiF and NaCl were found to have a linear effect on lowering the liquidus temperature of cryolite. KF did not show the similar characteristic. Regarding the temperature lowering potential of the liquidus temperature with 1% addition of additives, the rank is KF<NaCl<LiF.

Acknowledgment

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