

## LIQUIDUS TEMPERATURES OF $\text{Na}_3\text{AlF}_6$ - $\text{AlF}_3$ - $\text{CaF}_2$ - $\text{KF}$ - $\text{LiF}$ - $\text{Al}_2\text{O}_3$ MELTS

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### Abstract

Temperatures for the primary crystallization of  $\text{Na}_3\text{AlF}_6$ - $\text{AlF}_3$ - $\text{CaF}_2$ - $\text{KF}$ - $\text{LiF}$ - $\text{Al}_2\text{O}_3$  system adopted in aluminum electrolysis process were determined by thermal analysis. An empirical equation was derived to describe the liquidus temperatures for the primary crystallization of this multicomponent electrolyte system:  $t/^\circ\text{C} = 1011 + 0.7w(\text{AlF}_3) - 0.232w(\text{AlF}_3)^2 - 7.65w(\text{Al}_2\text{O}_3) + 0.523w(\text{Al}_2\text{O}_3)^2 - 8.96w(\text{LiF}) + 0.043w(\text{LiF})^2 - 3.32w(\text{KF}) - 0.12w(\text{KF})^2 - 3.28w(\text{CaF}_2) + 0.037w(\text{CaF}_2)^2 + 0.091w(\text{AlF}_3)w(\text{LiF}) + 0.074w(\text{AlF}_3)w(\text{KF}) + 0.084w(\text{AlF}_3)w(\text{CaF}_2) - 0.27w(\text{Al}_2\text{O}_3)w(\text{LiF})$ , where  $w(\text{AlF}_3)$  denotes the mass fraction of excess aluminum fluoride with respect to cryolite. While  $w(\text{Al}_2\text{O}_3)$  ranges from 2% to 4%,  $w(\text{LiF})$ ,  $w(\text{KF})$  and  $w(\text{CaF}_2)$  from 0 to 7%, and the molar ratio of  $\text{NaF}/\text{AlF}_3$  from 2.2 to 3.

**Keywords:** Liquidus temperatures; Electrolyte system; Aluminum electrolysis

### 1. Introduction

The electrolyte used in Hall-Héroult is molten sodium-based cryolite ( $\text{Na}_3\text{AlF}_6$ ). It is usually modified with the addition of aluminum fluoride ( $\text{AlF}_3$ ), calcium fluoride ( $\text{CaF}_2$ ) and other additives to obtain better operation conditions and physicochemical properties, such as solubility for alumina ( $\text{Al}_2\text{O}_3$ ), conductivity and viscosity. These properties also vary with operation temperatures which are based on the primary crystallization temperatures of the electrolyte [1]. Thus it is important to study the primary crystallization temperatures of the  $\text{Na}_3\text{AlF}_6$ - $\text{Al}_2\text{O}_3$ - $\text{XF}_n$  system. However, what necessitates our work most is the existence of lithium oxide ( $\text{Li}_2\text{O}$ ) and potassium oxide ( $\text{K}_2\text{O}$ ) impurities in the alumina used in some Chinese aluminum smelters [2]. In some cases, the content of lithium fluoride ( $\text{LiF}$ ) and potassium fluoride ( $\text{KF}$ ) may have been enriched to 7% (percentage by mass) in the electrolytes, besides the conventional components of  $\text{AlF}_3$  (5% to 13%),  $\text{CaF}_2$  (1% to 7%) and  $\text{Al}_2\text{O}_3$  (2% to 4%). Thus, in these aluminum reduction cells, the molten system of  $\text{Na}_3\text{AlF}_6$ - $\text{AlF}_3$ - $\text{CaF}_2$ - $\text{KF}$ - $\text{LiF}$ - $\text{Al}_2\text{O}_3$  develops. Based on this new molten system, the influences of  $\text{KF}$  and/or  $\text{LiF}$  on electrolyte conductivity and on cathode block expansion were studied [3, 4]. Unfortunately, there is

fewer experimental data of the liquidus temperatures reported for the multicomponent molten system up to now. In our work, the effects of  $\text{LiF}$  and  $\text{KF}$  on reduction of liquidus temperatures of the molten system were studied, and an equation was derived based on the present measurement and our previous work [5] with  $\text{LiF}$  and  $\text{KF}$ , as well as other groups' researches [6, 7] on melts without  $\text{LiF}$  or  $\text{KF}$ .

### 2. Experimental

$\text{Na}_3\text{AlF}_6$ ,  $\text{CaF}_2$ ,  $\text{KF}$ ,  $\text{LiF}$  and  $\text{Al}_2\text{O}_3$  in our experiments were high-purity chemicals containing very small amounts of impurities, while  $\text{AlF}_3$  was purified by sublimation. All chemicals were dried at  $200^\circ\text{C}$  for 12h before being used in the experiments.

The liquidus temperatures of the electrolytes were measured by thermal analysis, which has been proven to give accurate freezing point depression data [8]. The thermal analysis was performed in a stainless steel chamber under an argon atmosphere. A vertical alumina tube furnace was used with a cooling rate of  $1^\circ\text{C}/\text{min}$ . The crucibles were made of platinum. A  $\text{NiCr}/\text{NiSi}$  thermocouple was immersed to detect the temperatures and connected to a digital thermometer. The thermocouple was calibrated to the melting point of pure  $\text{NaCl}$ . All electrolytes were melted in the constant temperature zone of the furnace at  $1010^\circ\text{C}$ .

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### 3. Results and discussion

For the electrolyte system of  $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-CaF}_2\text{-KF-LiF-Al}_2\text{O}_3$ , the molar ratio of  $\text{NaF/AlF}_3$  (CR) ranged from 2.2 to 3.0. The melts contained up to 7% of  $\text{LiF} \setminus \text{KF} \setminus \text{CaF}_2$  and 2% to 4%  $\text{Al}_2\text{O}_3$ , which agree with the electrolyte compositions of the aluminum smelters. All the 42 experimental temperatures measured are list in Table 1.

Based on the present study and the experimental results of  $\text{Na}_3\text{AlF}_6\text{-CaF}_2$  by Holm [6], those of  $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-CaF}_2\text{-LiF-Al}_2\text{O}_3$  by Røstum et al. [7] and our previous work [5], the empirical model for the liquidus temperatures of  $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-CaF}_2\text{-KF-LiF-Al}_2\text{O}_3$  melts was derived as follows,

$$t / ^\circ\text{C} = 1011 + 0.7w(\text{AlF}_3) - 0.232w(\text{AlF}_3)^2 - 7.65w(\text{Al}_2\text{O}_3) + 0.523w(\text{Al}_2\text{O}_3)^2 - 8.96w(\text{LiF}) + 0.043w(\text{LiF})^2 - 3.32w(\text{KF})$$

$$- 0.12w(\text{KF})^2 - 3.28w(\text{CaF}_2) + 0.037w(\text{CaF}_2)^2 + 0.091w(\text{AlF}_3)w(\text{LiF}) + 0.074w(\text{AlF}_3)w(\text{KF}) + 0.084w(\text{AlF}_3)w(\text{CaF}_2) - 0.27w(\text{Al}_2\text{O}_3)w(\text{LiF}) \quad (1)$$

where  $t$  is the temperature of primary crystallization. All compositions are given in mass fraction. And  $w(\text{AlF}_3)$  is excess aluminum fluoride relative to the cryolite composition;  $w(\text{Al}_2\text{O}_3)$ ,  $w(\text{LiF})$ ,  $w(\text{KF})$  and  $w(\text{CaF}_2)$  denotes the mass fraction of alumina, lithium fluoride, potassium fluoride and calcium fluoride, respectively. The standard deviation is  $1.97^\circ\text{C}$  for our experimental points with melt containing  $\text{LiF}$  and/or  $\text{KF}$  and for the 78 points from the literatures [6, 7]. The overall uncertainty was estimated to be below 1%. Table 1 also lists the liquidus temperatures calculated by eq (1) in comparison with the experimental data. Figure 1 shows the influence of  $\text{AlF}_3$  and  $\text{CaF}_2$  on the freezing temperature, respectively. It can be seen that the present calculation can well describe the experimental data.

**Table 1.** Experimental and calculated liquidus temperatures for the molten system of  $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-CaF}_2\text{-KF-LiF-Al}_2\text{O}_3$

$w(\text{AlF}_3)$	$w(\text{Al}_2\text{O}_3)$	$w(\text{LiF})$	$w(\text{KF})$	$w(\text{CaF}_2)$	$t$	Calc. $t$	$\Delta t$
/%	/%	/%	/%	/%	/°C	/°C	/°C
2.53	3	0	3	3	975.1	973.7	1.4
5.28	3	0	3	3	973.1	972	1.1
2.5	3	1	3	3	966.5	964.2	2.3
2.47	2	3	3	3	950.7	951.3	-0.6
5.22	3	1	3	3	963.5	962.8	0.7
8.18	3	1	3	3	961	957.4	3.6
2.47	3	2	3	3	955.4	954.8	0.7
2.42	4	3	3	3	941.4	940.6	0.8
5.16	3	2	3	3	951.3	953.7	-2.4
8.09	3	2	3	3	947.8	948.7	-0.9
2.39	3	3	5	3	932.3	937.2	-4.9
5.16	2	3	3	3	948.4	950.5	-2.1
2.44	3	3	3	3	944.8	945.4	-0.6
2.47	3	3	2	3	949.1	949.2	0
2.5	3	3	1	3	952	952.7	-0.7
2.5	3	3	3	1	950	951.3	-1.3
2.53	3	3	3	0	953.6	954.3	-0.7
4.99	3	3	3	5	938.1	939.6	-1.5
8.09	2	3	3	3	943.6	945.8	-2.2
4.99	3	3	5	3	935.9	936.9	-1
5.1	3	3	3	3	941	944.7	-3.7

table continued on the next page

w(AlF <sub>3</sub> )	w(Al <sub>2</sub> O <sub>3</sub> )	w(LiF)	w(KF)	w(CaF <sub>2</sub> )	t	Calc.t	Δt
/%	/%	/%	/%	/%	/°C	/°C	/°C
5.22	3	3	1	3	951.7	951.4	0.3
5.22	3	3	3	1	949.8	949.9	-0.1
5.28	3	3	3	0	951.1	952.7	-1.5
5.04	4	3	3	3	935.2	939.9	-4.7
5.28	3	3	0	3	951.9	954.4	-2.5
7.82	3	3	3	5	935	935.9	-0.8
8	3	3	3	3	938.3	940.1	-1.8
8.09	3	3	2	3	938	943.2	-5.2
8.18	3	3	1	3	943.4	946.1	-2.7
8.18	3	3	3	1	947.1	944.6	2.5
7.91	4	3	3	3	935.3	935.5	-0.2
8.27	3	3	3	0	950.2	946.9	3.2
8.27	3	3	0	3	943.9	948.7	-4.8
10.92	3	3	3	5	931.2	927.5	3.7
11.17	3	3	3	3	931.8	930.7	1
11.3	3	3	2	3	936	933.3	2.7
11.43	3	3	1	3	940.3	935.7	4.6
11.56	3	3	0	3	941.5	937.7	3.8
4.99	3	5	3	3	925.1	926.8	-1.7
7.82	3	5	3	3	923.1	923.1	0
10.92	3	5	3	3	915.9	914.8	1.2

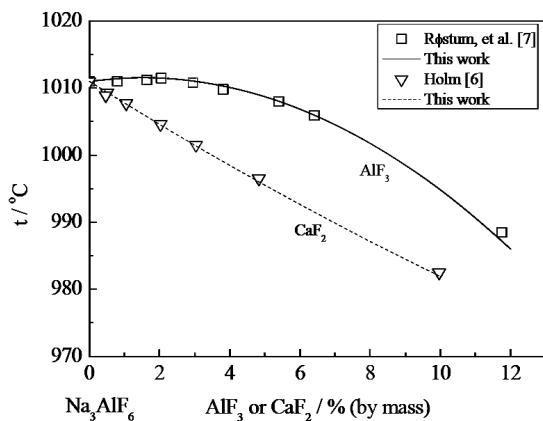


Figure 1. Lowering of liquidus temperatures of cryolite

Figure 2 shows part of the Na<sub>3</sub>AlF<sub>6</sub>-5% CaF<sub>2</sub>-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> phase diagram and a comparison was made between the results from eq (1) and from the equations published by Lee et al. [9], by Dewing [10] and by Solheim et al. [11] within the range of conventional electrolyte compositions. It must be pointed that the CaF<sub>2</sub> ranged from 3.8% to 11.25% and AlF<sub>3</sub> ranged from 5% to 20% in Lee's model. It is

indicated in Figure 1 that the model in this work is no significantly different from Dewing's and Solheim's models to calculate the liquidus temperatures for the electrolyte system without LiF or KF. However, the model developed on the basis of melts with only LiF and KF by our previous work [5] is not fit for

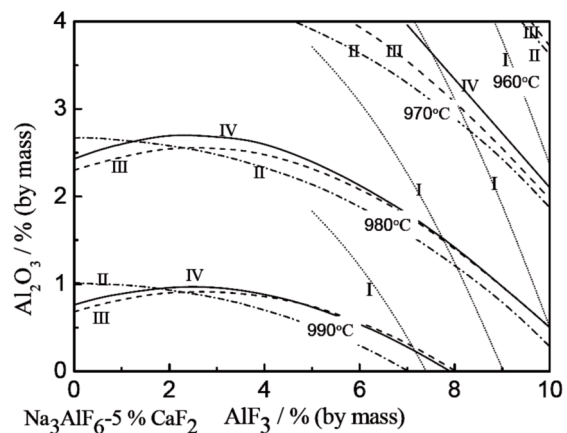


Figure 2. Part of the Na<sub>3</sub>AlF<sub>6</sub>-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-5% CaF<sub>2</sub> phase diagram as calculated from different liquidus equations. I-Lee [9], II-Dewing [10], III-Solheim [11] and IV-this work

conventional electrolytes.

Figure 3 presents the influences of LiF and KF on the liquidus temperatures of  $\text{Na}_3\text{AlF}_6$ -3%  $\text{CaF}_2$ -3%  $\text{Al}_2\text{O}_3$ - $\text{AlF}_3$  system, respectively. It indicates a reduction of the freezing temperature of 2.8°C by the addition of 1% KF with CR=2.2, a reduction of 3.5°C with CR=2.5 and 4.0°C with CR=2.8. While for addition of 1% LiF, it lowers the freezing temperature by 7.9°C, 8.7°C and 9.2°C, respectively.

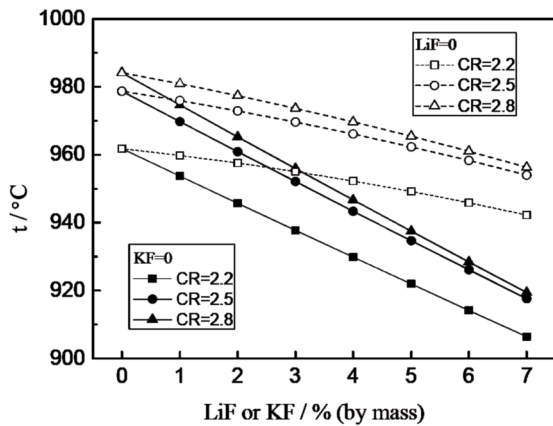


Figure 3. Lowering of liquidus temperatures when LiF or KF are added in the  $\text{Na}_3\text{AlF}_6$ -3%  $\text{CaF}_2$ -3%  $\text{Al}_2\text{O}_3$ - $\text{AlF}_3$  system

For most Hall-Héroult cells using alumina containing some impurity of  $\text{Li}_2\text{O}$  and  $\text{K}_2\text{O}$ , the contents of LiF and KF may be enriched up to 4% and 3%, respectively after three years. Thus the liquidus temperature of the electrolyte may be lowered by 40 to 45°C just by the enrichment of LiF and KF.

Accordingly, it is necessary to lower the operation temperatures by 40 to 45°C in order to maintain the same superheat of the electrolytes. However, since most operators don't know how much reduction of freezing temperatures has happened, many difficulties are met in forming electrolyte ledge due at a higher superheat. Therefore, it is important to realize the influences of KF and LiF on the reduction of liquidus temperatures and on the cell operation. It's suggested that the contents of KF and LiF be controlled below 3% by adding alumina materials without  $\text{Li}_2\text{O}$  or  $\text{K}_2\text{O}$ .

#### 4. Conclusions

In this study, the liquidus temperatures were studied experimentally for  $\text{Na}_3\text{AlF}_6$ - $\text{AlF}_3$ - $\text{CaF}_2$ -KF-LiF- $\text{Al}_2\text{O}_3$  melts, with up to 7% of  $\text{CaF}_2$ , KF and LiF, and 2% to 4% of  $\text{Al}_2\text{O}_3$  at CR from 2.2 to 3.0. An equation based on the experimental data was derived and can be used to calculate both normal industrial

electrolytes and electrolytes containing LiF and KF through feeding alumina materials. The reduction of the liquidus temperatures of the electrolyte is 2.8°C to 4.0°C by 1% KF and 8°C to 9°C by 1% LiF, respectively, dependent on other components.

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