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# THE EFFECT OF CALCIUM FLUORIDE ON ALUMINA SOLUBILITY IN LOW TEMPERATURE CRYOLITE MELTS

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## Abstract

The alumina solubility in the KF-NaF-$CaF_2$-$AlF_3$ molten salt system depending on the [NaF]/([NaF]+[KF]) ratio and calcium fluoride concentration was measured in the temperature range from 850 °C to temperature of primary crystallization. The cryolite ratio (CR), calculated as ([KF]+[NaF])/[$AlF_3$], was maintained at 1.3 and 1.5. The calcium fluoride impact on alumina solubility is more significant in electrolytes rich in potassium fluoride.

## Introduction

The effect of the calcium fluoride addition to the conventional electrolyte of the Hall-Heroult process for the aluminum production is well known [1]. The $CaF_2$ is added to the sodium cryolite mainly to reduce liquidus temperature. The presence of the $CaF_2$ beneficially impacts some other physical-chemical properties of sodium electrolyte including lower solubility of aluminum metal that results in increased current efficiency. However, the calcium fluoride reduces the alumina solubility in cryolite [2, 3]. This phenomenon is probably not so important for the Hall-Heroult process because typically the operating alumina concentration in the electrolysis bath is about 2-4 wt% that is at least two times less than the solubility of $Al_2O_3$ in sodium cryolite-based electrolytes at 950 °C.

The $CaF_2$ effect on alumina solubility becomes more substantial in conditions of low-temperature aluminum electrolysis as the operating alumina concentration of this process is close to saturation. Reduction of the liquidus temperature of electrolytes used for low temperature electrolysis is due to change of their composition. First of all, the significant decrease of liquidus can be achieved by adding an excess of aluminum fluoride in cryolite. The low cryolite ratio (CR) allows electrolysis at temperatures much lower than in traditional practice, but at the same time it negatively impacts the alumina solubility. For example, it was found [4] that the alumina solubility in the NaF-$AlF_3$ melt with CR=1.3 did not exceed 1.25 wt% at 800 °C. The substitution of sodium cryolite by potassium cryolite results in increase of alumina solubility. For example, in the KF-$AlF_3$ melt with CR=1.3 the alumina solubility is 5.5 wt% [5] at 750 °C that is suitable for aluminum electrolysis.

Nevertheless, the calcium fluoride is always present in industrial cells due to the presence of CaO in the alumina. According to [6] the $CaF_2$ addition of 5 wt% to the NaF-$AlF_3$ with CR = 1.3 slightly decreases the $Al_2O_3$ solubility from 3.2 to 3.0 wt% at 750 °C. However, it was found [7] that the alumina solubility decreases considerably, from 4.38 to 0.69 wt%, in the mixed NaF-$AlF_3$ and KF-$AlF_3$ system, containing 20 wt% of NaF, with the same CR (1.3), $CaCl_2$ content (5 wt%) and temperature (750 °C).

In our previous work [8] the liquidus of the potassium and sodium cryolite mixtures with cryolite ratio 1.3, 1.5 and 1.7 was determined. Based on this data the KF-NaF-$AlF_3$ electrolyte compositions for performing aluminum electrolysis in temperature range 750-850 °C were recommended. The objective of the present work is to study the effect of $CaF_2$ additions to the KF-NaF-$AlF_3$ molten system with CR 1.3 and 1.5 on the alumina solubility.

## Experimental

The electrolytes being studied were prepared from individual salts $AlF_3$, NaF, $CaF_2$ and KF·HF supplied by VEKTON (Russia). A salt preparation technique is described elsewhere [8]. For the first series of experiments three basic salt mixtures with CR=1.3 (CR=[KF]+[NaF])/[$AlF_3$]) were prepared: one NaF-$AlF_3$ mixture and two KF-NaF-$AlF_3$ mixtures with the [NaF]/([NaF]+[KF]) ratio 0.79 and 0.54. The second series of experiments was performed with the KF-NaF-$AlF_3$ mixtures (CR=1.5) with the [NaF]/([NaF]+[KF]) ratio 0.50 and 0.73.

The alumina solubility in the KF-NaF-$AlF_3$-$CaF_2$ melt was determined from the measurements of liquidus temperature during the cooling process. A glassy carbon crucible filled with a salt mixture was placed into the quartz cell tightly sealed with a cap having holes for the Pt-Pt/Rh thermocouple and gas in/outlet tubes. A device for alumina additions was attached to the gas inlet tube allowing alumina additions of about 0.5 wt% to the melt under argon gas flow. The temperature control and the data processing were performed using computerized measuring device APPA-109N.

A visual observation of the alumina dissolution process was also used as an ancillary method to confirm the obtained solubility data.

## Results and discussion

The liquidus temperatures obtained in the KF-NaF-$AlF_3$-$CaF_2$-$Al_2O_3$ melts are shown in Figure 1 for mixtures with CR=1.3 and in Figure 2 for mixtures with CR=1.5. The alumina solubility in the KF-NaF-$AlF_3$-$CaF_2$ molten mixtures in the temperature range from 850 °C to temperature of primary crystallization is presented in Table I. The lowest alumina solubility was found in NaF-$AlF_3$ electrolyte with CR=1.3 at 750 °C, as expected. It is below 1 mol% and is in agreement with the «FTHall database» [9] and data obtained by Skybakmoen et al. [10]. The calcium fluoride additions of 1.5 and 3.12 mol% decrease the $Al_2O_3$ solubility with 0.05 and 0.25 mol%, respectively (Figure 1a).

The $Al_2O_3$ solubility in the KF-NaF-$AlF_3$ electrolyte at 750 °C increases from 1.9 to 2.2 mol% when the ratio of [NaF]/([NaF]+[KF]) is reduced from 0.79 to 0.54 (Figure 1 b, c).

However the $CaF_2$ effect on the alumina solubility increases noticeably. The higher the $CaF_2$ concentration in the melt is, the more the alumina solubility decreases. In the electrolyte with [NaF]/([NaF]+[KF]=0.79 at 750 °C the $CaF_2$ addition of 1.6 mol% decreases the alumina solubility by 0.2 mol%, whereas a further increase in the calcium fluoride concentration to 3.21 and 4.02 mol% decreases the $Al_2O_3$ solubility to 0.8 and 0.35 mol, respectively.

In the electrolyte with [NaF]/([NaF]+[KF])=0.54 the $CaF_2$ effect on the alumina solubility is more noticeable. The calcium fluoride addition of 1.66 mol% decreases the alumina solubility from 3.3 to 2.8 mol% at 850 °C. The $Al_2O_3$ solubility decreases to 0.55 mol% when the $CaF_2$ concentration is increased to 2.49 mol%.

The data obtained for the NaF-KF-$AlF_3$ melt with CR=1.5 and [NaF]/([NaF]+[KF])=0.50 was used to evaluate the mutual impact of the CR and calcium fluoride concentration on the alumina solubility (Figure 2). The $CaF_2$ addition of 1.63 mol% decreases the alumina solubility to 3.72 mol% at 800 °C. According to the Figures 1 and 2 the lower the CR is the more the calcium fluoride content influences the alumina solubility.

Table I. Alumina solubility (mol%) in KF-NaF-$AlF_3$-$CaF_2$ melts

| CR | [NaF]/([NaF]+[KF]) | t, °C | [$CaF_2$], wt% | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 0 | 2 | 0 | 2 | 3 | 4 | 5 |
| | | | Visual observation | | Cooling curves data | | | | |
| 1.3 | 1.00 | 750 | - | - | 0.77 | 0.74 | - | 0.67 | - |
| | | 800 | - | - | 1.18 | 1.04 | - | 0.99 | - |
| | 0.79 | 700 | - | - | 1.62 | 1.42 | - | - | - |
| | | 750 | - | - | 1.86 | 1.68 | - | 0.82 | - |
| | | 800 | 2.10 | 1.83 | 2.30 | 1.93 | - | 1.02 | 0.21 |
| | | 850 | 2.42 | 2.29 | 2.42 | 2.26 | - | 1.40 | 0.29 |
| | 0.54 | 750 | - | - | 2.28 | - | - | - | - |
| | | 800 | 2.70 | 2.19 | 2.76 | 2.32 | - | - | - |
| | | 850 | 3.48 | 3.11 | 3.30 | 2.84 | 0.58 | - | - |
| 1.5 | 0.50 | 750 | - | - | 1.89 | | - | - | - |
| | | 800 | 2.58 | 2.09 | | 2.58 | - | - | - |
| | | 850 | 3.32 | 2.97 | | 3.32 | - | - | - |

The data obtained in the present work are in satisfactory agreement with reference [7] (Figure 3). However, there is a disagreement between the results for the electrolytes with [NaF]/([NaF]+[KF])=0.54 and 5 wt% $CaF_2$ (Figure 4). This can be explained by the fact that the addition of 5 wt% $CaF_2$ to this melt rises liquidus temperature almost 100 degrees [8]. It may be assumed that some measurements [7] at this composition were performed in a solid-liquid system. In case, the composition of the liquid phase could be different from the weighed out composition. Hence, the temperature dependence of the alumina solubility could differ from other compositions because the equilibrium between the solid and liquid phases will change the electrolyte composition with temperature. The change in the slope of the temperature dependence could indicate that this is the case. The similar trend of the temperature dependences obtained in the KF-NaF-$AlF_3$-$Al_2O_3$ and KF-$AlF_3$-$Al_2O_3$ electrolytes by different authors is given in Figure 5.

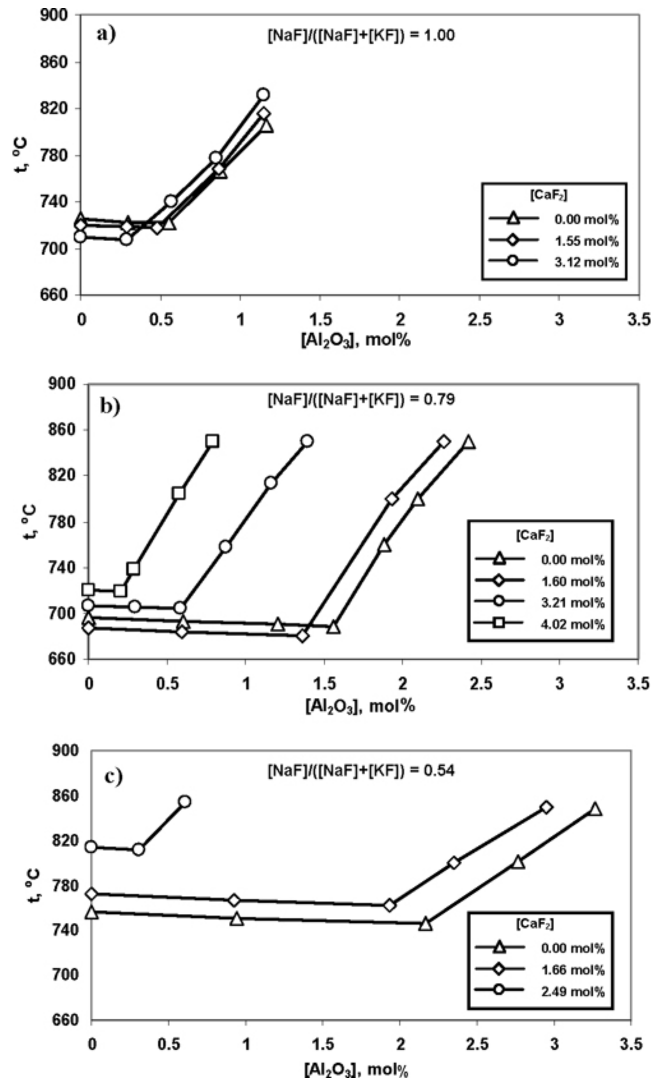


Figure 1. Liquidus temperatures in the KF-NaF-$AlF_3$-$CaF_2$ mixtures (CR=1.3) depending on $CaF_2$ and $Al_2O_3$ concentrations

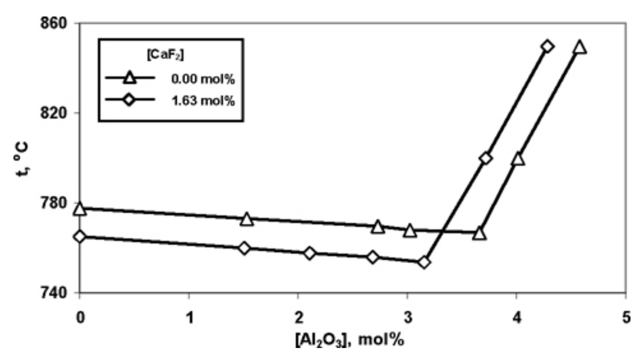


Figure 2. Liquidus temperatures in the KF-NaF-$AlF_3$-$CaF_2$ mixtures (CR=1.5) depending on $CaF_2$ and $Al_2O_3$ concentrations. [NaF]/([NaF]+[KF])=0.50

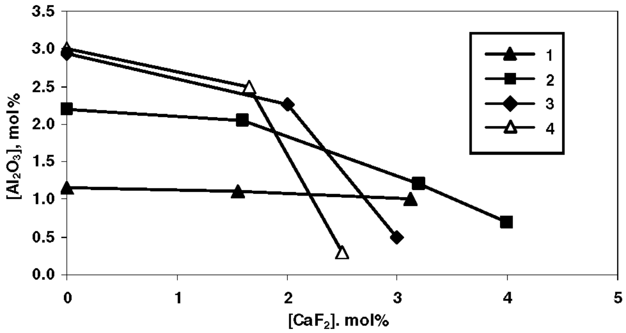


Figure 3. Mutual effect of NaF and $CaF_2$ content on alumina solubility at 850 °C in:
1 - $NaF-AlF_3$, CR=1.3 [this work];
2 - $KF-NaF-AlF_3$, CR=1.3, [NaF]/([NaF]+[KF])=0.79 [this work];
3 - $KF-NaF-AlF_3$, CR=1.3, [NaF]/([NaF]+[KF])=0.54 [this work];
4 - $KF-NaF-AlF_3$, CR=1.3, [NaF]/([NaF]+[KF])=0.54 [7]

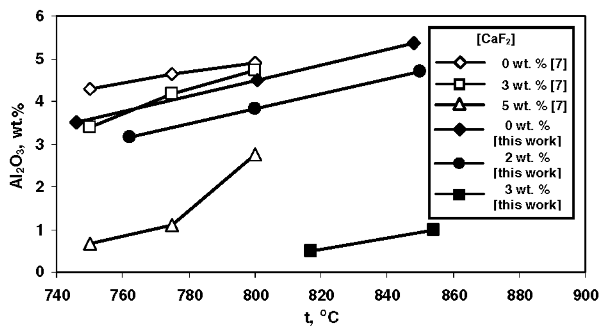


Figure 4. Alumina solubility in the $KF-NaF-AlF_3$ mixture with CR=1.3 and [NaF]/([NaF]+[KF])=0.54

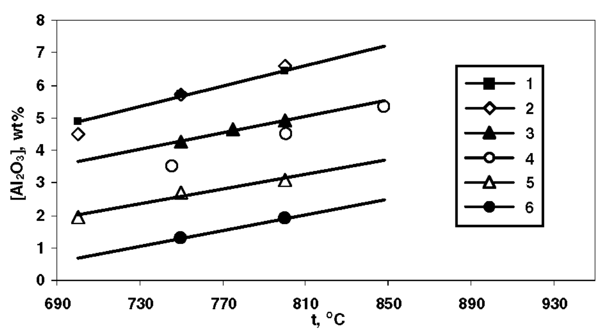


Figure 5. Temperature dependence of alumina solubility in:
1 - $KF-AlF_3$, CR=1.3 [12];
2 - $KF-AlF_3$, CR=1.3 [13];
3 - $KF-NaF-AlF_3$, CR=1.3, [NaF]/([NaF]+[KF])=0.54 [12];
4 - $KF-NaF-AlF_3$, CR=1.3, [NaF]/([NaF]+[KF])=0.54 [this work];
5 - $KF-NaF-AlF_3$, CR=1.3, [NaF]/([NaF]+[KF])=0.79 [this work];
6 - $NaF-AlF_3$, CR=1.3 [this work]

## Conclusions

The investigation of calcium fluoride effect on the alumina solubility in the $KF-NaF-AlF_3-CaF_2$ molten mixtures allows making the following conclusions:

- $CaF_2$ additions decrease the alumina solubility in all electrolytes being studied
- The more portion of the KF in the $KF-NaF-AlF_3-CaF_2$ melt the more impact of the calcium fluoride on the alumina solubility.
- The lower CR the more the calcium fluoride affects the alumina solubility at constant temperature.


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