On the Solubility of Aluminum in Cryolitic Melts

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The solubility of aluminum in NaF-AlF₃-Al₂O₃ melts with various additives was found to increase with increasing NaF/AlF₃ molar ratio (CR) and increasing temperature and to decrease with additions of Al₂O₃, CaF₂, MgF₂, and LiF to the melts. With the use of literature data for the activities of NaF and AlF₃ in cryolitic melts, three dissolution reaction models were found to give a good fit to the experimental solubility data. According to the most probable of these models the total concentration of dissolved aluminum (aluminum and sodium species) is given by

\[ \text{CaI} = \text{CNa}(\text{diss}) + \text{CAlF}_3^- + \text{CAlF}_4^- + \text{CAlF}_6^- \]

During the last years many efforts have been made to model the loss in current efficiency in the Hall-Héroult process caused by Eq. [1]. In these works the need for a reliable equation for the equilibrium concentration of dissolved aluminum as a function of the most common variables has been clearly demonstrated.

As can be seen from the data that will be discussed in the following, there have been a relatively large number of papers related to the solubility of aluminum in cryolitic melts. Today there seems to be some agreement about the level of aluminum solubility in alumina saturated cryolite melts. Today there seems to be some agreement about the level of aluminum solubility in alumina saturated cryolite melts. Today there seems to be some agreement about the level of aluminum solubility in alumina saturated cryolite melts. Today there seems to be some agreement about the level of aluminum solubility in alumina saturated cryolite melts. Today there seems to be some agreement about the level of aluminum solubility in alumina saturated cryolite melts. Today there seems to be some agreement about the level of aluminum solubility in alumina saturated cryolite melts. Today there seems to be some agreement about the level of aluminum solubility in alumina saturated cryolite melts. 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The major problem in these experiments was to ensure saturation of dissolved aluminum. The results showed that the analyzed concentration was far too low if the lid did not close the crucible tightly. This could in most cases be detected by inspecting the lid after the experiments. The results from such experiments are not reported. When no lid was used, the analyzed concentration of dissolved aluminum at \( CR = 3.00 \) and 1000 °C was roughly 60 pct of the concentration found with a tight-fitting lid under otherwise identical conditions. Under these conditions the observed concentrations of dissolved aluminum are very close to those reported by Yoshida and Dewing, who did not have a lid on the compartment where the melt was “titrated” with oxygen. This is probably the reason why their results were low in dissolved aluminum.

When several samples were taken in succession from the same melt at \( CR = 3.00 \), the concentration of dissolved aluminum was found to decrease as a function of time after removal of the lid. This is probably due to evaporation of sodium, since \( P_{Na} = 60 \) torr at \( CR = 3.00 \) and 1000 °C.

Similar to observations reported by Rolseth and Bjørn et al., some sort of passivation of the aluminum surface occurring in alumina-saturated melts was also encountered in the present work. This passivation problem was more or less overcome by stirring the melt and the aluminum after one hour at the experimental temperature, and by not adding any alumina when mixing the components. When the lid was tightly fitted and when precautions were taken to avoid passivation, the solubility experiments were fairly reproducible, as can be seen from Figure 1.

The variation of the concentration of dissolved aluminum as a function of the NaF/\( \text{AlF}_3 \) molar ratio shows the same trend as reported by Haupin, Thonstad, and Yoshida and Dewing, but it is opposite to that reported by Zhurin, Thonstad, and Yoshida and Dewing, who did not separate hydrogen and methane and a part of the reported value for dissolved aluminum in his work must therefore in fact be due to dissolved aluminum carbide. Haupin tried to separate the hydrogen and methane resulting from the reaction between HCl and the melt samples. However, the reported concentrations of dissolved aluminum carbide, based on the volume of methane, are low, and the concentration was reported not to vary with the cryolite ratio. Therefore, it is possible that the gas separation had not been complete and that a fraction of the dissolved metal in fact was due to dissolved aluminum carbide. Vetyukov and Vinokurov used crucibles of Russian-made boron carbonitride (BNC), for which the exact composition and stability is not known. However, in the presence of B\(_4\)C, formation of Al\(_4\)C\(_3\) is thermodynamically feasible according to the following reaction:

\[
4\text{Al}^{(l)} + 3\text{B}_3\text{C}_{(s)} = \text{Al}_4\text{C}_3(s) + 12\text{B}_{(s)} \quad [2]
\]

\[
\Delta G_{1200}^{\circ} = -7.72 \text{ kJ/mol}
\]

\[
\Delta G_{1300}^{\circ} = -0.51 \text{ kJ/mol} \quad [3]
\]

The discrepancy in the solubility data as a function of the NaF/\( \text{AlF}_3 \) ratio reported by Vetyukov and coworkers.