THE EFFECTS OF ADDITIVES ON THE ALUMINA SOLUBILITY IN CRYOLITE MELTS AT 1300K

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Because of its industrial importance in primary aluminum production by the Hall-Heroult process the alumina solubility in cryolite melts has been determined experimentally and modeled thermodynamically in terms of oxyfluoride solute complexes. In our previous work, a model including three oxyfluoride solutes $Na_2Al_2OF_6$ (acidic solute, called A), $Na_2Al_2O_2F_4$ (neutral solute, called N) and $Na_4Al_2O_2F_6$ (basic solute, called B) was proposed and the equilibrium constants for the formation of these three solutes were also derived. This model describes perfectly the melt structure of NaF-AlF_3 system with dissolved alumina.

Small amounts of LiF, CaF_2 and MgF_2 are common additives added to Hall-Heroult cells to improve physicochemical properties of the electrolyte and, in turn, to lower the liquidus temperature of the cryolite electrolyte and increase current efficiency. The effects of these additives on the alumina solubility in cryolite melts are of practical significance in the production of primary aluminum. The experimentally determined dependencies of alumina solubility upon the additions of these fluorides are available in the literature.

On the thermodynamic front, from experimental vapor pressures, emf's and/or Raman spectra, some authors have estimated changes in thermodynamic activities of NaF and AlF_3 in the pure, "stoichiometric" cryolite melt (cryolite ratio r = 3) with the small additions of LiF, CaF_2 and MgF_2: $\frac{\partial \ln a_{NaF}}{\partial x_{add}}$ and $\frac{\partial \ln a_{AlF_3}}{\partial x_{add}}$ (interaction derivatives).

An extension of our previous solution modeling in the NaF-AlF_3-Al_2O_3 system is presented here to understand the effects of these additives on the alumina solubility in a "stoichiometric" cryolite melt at 1300K. The interaction derivatives from the literature were used to calculate the activities of NaF and AlF_3 in the Al_2O_3-saturated pure cryolite melt (r = 3) in dependence upon the amount of fluoride added to the melt. The concentrations of the three oxyfluoride solutes A, N and B in the Al_2O_3-saturated melt were then calculated using the derived activity data, along with the equilibrium constants for the formation reactions of the solutes obtained from the previous work. The alumina solubility values were calculated for small additions from the equation:

$$[Al_2O_3] = \frac{([A] + 2[N] + 2[B])n_t}{3}$$

where n_t is the total moles of all the solutes in the melt, which is assumed to be unchanged by these small additions.

A comparison of these calculated alumina solubility values with those determined experimentally is shown in Table I, with 1 to 5 wt % of fluorides added to the NaF-AlF_3 melt. Table I indicates very good agreement between the calculated data and the experimentally determined data.

The present study will be extended to include the effects of additives on alumina solubility in other compositions of cryolite melts (r < 3) at 1300K.

Table I Comparison of alumina solubility values calculated from interaction derivatives with those determined experimentally with additions of fluorides

Addition wt %	Alumina solubility, molar fraction	
	From calculation	From experiments
0	0.075	0.074
LiF addition		
1	0.071	0.071
2	0.067	0.068
3	0.064	0.064
4	0.061	0.061
5	0.058	0.058
CaF_2 addition		
1	0.074	0.073
2	0.072	0.072
3	0.071	0.071
4	0.070	0.070
5	0.069	0.069
MgF_2 addition		
1	0.073	0.073
2	0.071	0.071
3	0.070	0.069
4	0.068	0.067
5	0.066	0.065