High Temperature NMR Study Of Aluminium Dissolution In Cryolitic Melts

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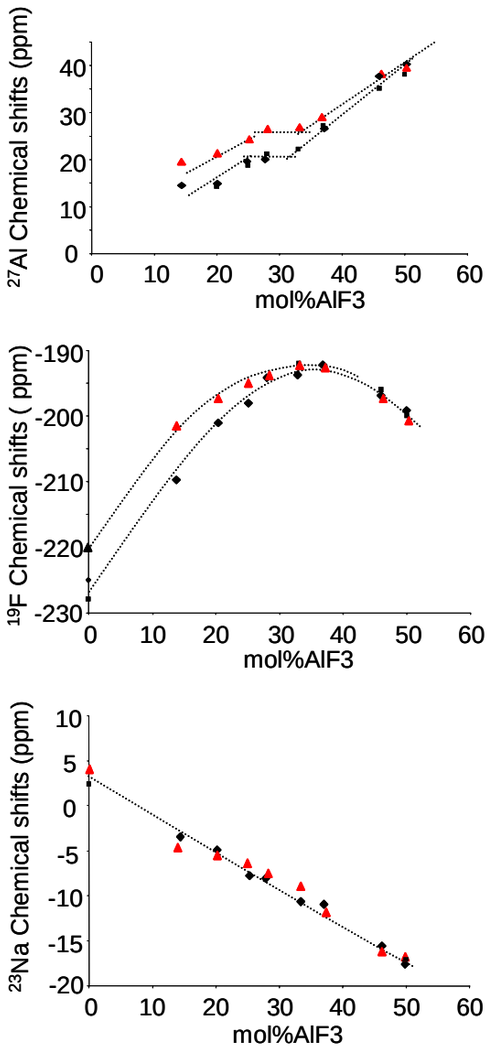
In the Hall-Heroult electrolytic process used for the production of aluminium, the electrolyte consists of a complex mixture of AlF_3, Al_2O_3, LiF, NaF and CaF_2. In the industrial cells, the metal produced has a higher density than the bath and falls down on the bottom of the cell. The metal is then in contact with the electrolyte and the graphite container. It can induce secondary reactions such as aluminium dissolution in the bath that will influence strongly the electrical rate of the process. Solubility of aluminium is low (≈ 0.1 wt% Al) and depends on different factors, such as the acidity of the melt, the temperature and the nature of additives. Compared to the other metals-molten salts systems, the system Al-NaF-AlF3 is considerably more complex. In addition of the Al dissolution in the salt, one must take into account exchange reactions such as Al + 3NaF ⇅ AlF3 + Na, and the appearance of new species. The sodium metal arising from the reduction of Al becomes the major component of the vapour phase over the melt and induces also a number of secondary reactions. Fog formation and Al droplets dispersed in the melt contributes also to the concentration of dissolved metal. Visual observations, analysis of the metal in the quenched sample, weight loss and vapour pressure measurement are reported in the literature and give some idea of the complexity characterizing that system.

These liquids are corrosive, hygroscopic and difficult to study experimentally. Using the laser-heated device, associated with a tightly closed crucible, we have studied different compositions of the NaF-AlF_3-Al system by ^{27}Al, ^{23}Na and ^{19}F in situ NMR at 1030°C. The samples were also characterized after rapid cooling at room temperature by MAS NMR, X-rays diffraction and microscopy in order to describe the structure of solidified phases. We have observed a systematic shift towards higher chemical shifts values for ^{27}Al and ^{19}F signals, attributed to the creation of new “AlFx” species with lower average coordination while the ^{23}Na signals are just slightly modified.

The results were confirmed by DSC experiments up to the liquid, in the same mixtures. The combination of different experimental techniques shows the enrichment of the solidified samples by chiolite and tends to confirm the exchange reaction 3NaF+Al↔AlF3+3Na.



High temerature ^{27}Al, ^{19}F and ^{23}Na NMR chemical shifts evolution with composition in NaF-AlF3-Al melts : Comparison between the values measured with ▲ and without Al ◆