Cathodic Behaviour of Carbon in Cryolite-Alumina Melts

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Carbon is used as cathode material during industrial electrowinning of aluminium from cryolite-alumina melts. The lifetime of industrial cells is often limited by cathode carbon failure. Due to poor wetting of carbon, cathode blocks are covered by a layer of liquid aluminium. However, variable amounts of so-called sludge containing molten and solid electrolyte may also be present on top of the cathode carbon. Wear of carbon is due to physical abrasion caused by solid alumina particles and the formation of aluminium carbide, which is soluble in aluminium and to a larger extent in cryolitic melts [1]. Sodium, which is present (~100 ppm) in the produced aluminium, may penetrate the carbon structure and cause swelling and eventually cracking and failure. A change from using anthrasitic carbon to graphitized materials has reduced the tendency for sodium intercalation in industrial cells. It has been shown that carbon can dissolve cathodically in cryolite melts [2]. The rate of the dissolution process was found to be determined by diffusion of dissolved aluminium carbide species $(Al_3CF_8^{3-})$ away from the cathode.

Experimental studies were carried out by long time (24 h) electrolysis at constant current density in molten Na₃AlF₆-AlF₃(10 wt% excess)-CaF₂(5 wt%)-Al₂O₃(sat) at 955 °C. Various carbon qualities were tested. The wear of the carbon cathode specimen was determined by measuring changes in weight, volume, density and porosity as well as geometrical dimension changes. The weight loss was found to increase by increasing current density; typical results showed a weight loss of ~3% at 0.05 A cm⁻² and ~12% at 0.30 A cm⁻². New experiments are under way to study wear of carbon cathodes by using an improved cell design involving a rotating cathode.

References

1. R. Ødegård, Å. Sterten, and J. Thonstad, J. Electrochem. Soc., 134, 1088 (1987).

2. H. Gudbrandsen, Å. Sterten, and R. Ødegård, Light Metals 1992, The Minerals, Metals & Materials Society, p. 521.