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Laboratory-scale performance of a binary Cu–Al alloy as an anode for aluminium electrowinning

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Abstract

A binary Cu–Al alloy (9.4 wt.% Al) has been investigated as a potential inert anode for aluminium electrowinning. Anodes have been tested in a laboratory electrolysis cell both with and without preformed oxides. Electrolysis was conducted in cryolitic electrolytes with anode current densities of 0.5 A cm^{-2}. The anodes operated satisfactorily as measured by electrical parameters. However, substantial corrosion of the Cu-metal substrate was observed. The external oxide generated on pre-treated anodes was porous and allowed the electrolyte to penetrate through to the Cu-metal whereby corrosion was initiated. An untreated anode formed an in situ surface alumina film, but this did not prevent corrosion of the substrate.

Keywords: Inert anode; Copper alloys; Corrosion; SEM; XRD

1. Introduction

Aluminium is produced industrially by the electrolytic reduction of aluminium oxide dissolved in molten cryolite. This process has not changed fundamentally for over 100

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years and incorporates electrodes constructed from carbon. Oxygen formed at the anode surface reacts with the carbon and exits the process as CO_2. In this way the anode is consumed and must be regularly replaced. A long-term goal of the aluminium industry has been to develop a non-consumable anode, which would release O_2 instead of CO_2. The key drivers for non-consumable anodes are the elimination of greenhouse gas emissions, and the elimination of costs and process inefficiencies associated with anode changing.

No successful inert anode material has yet been discovered but a variety has been tested including metals, ceramics and cermets [1,2]. Metallic anodes have several potential advantages, notably low electrical resistance, good electrical connections, and ease of fabrication. The challenge for such a material is the prevention of metal corrosion in the high-temperature electrolyte, and subsequent contamination of the Al-metal product. A strategy for achieving this is the formation of an oxide layer at the electrolyte/anode interface, which will protect the metal from molten cryolite. Sadoway first suggested that alloys, which form protective oxide layers, could potentially be used as inert anodes [3]. It is expected that any oxide will eventually dissolve in molten cryolite, so the oxide must be self-repairing under electrolysis conditions. Formation of this surface oxide will most likely be via a reaction between an alloy constituent and the oxygen formed at the anode surface. The oxide layer must be thick enough to protect the metal, yet thin enough to allow the flow of electric current. For this reason the rate of oxide formation should be approximately equal to the rate of oxide dissolution in the electrolyte. Aluminium oxide is preferred as a protective barrier for the simple reason that its inevitable dissolution in the electrolyte will not lead to contamination of the aluminium product.

Hryn et al. have tested a number of binary alloys [4], leading to the proposal of a dynamic Cu–Al anode [5]. The anodes operated for periods up to 47 h, and the current density varied between 0.25 and 2.4 A cm^{-2}. This work showed that Cu–Al anodes could perform well, as measured by external electrical parameters, giving voltage traces that were indistinguishable from platinum. However, a significant degree of Cu contamination of the Al-product was reported. Cu-based alloys are favoured due to copper's useful bulk properties such as good electrical conductivity and fracture toughness. Under certain conditions Cu–Al alloys grow a self-limiting aluminium oxide film, making them a suitable candidate for an inert anode.

The minority element in a binary alloy may form an internal oxide array or preferentially oxidise on the metal surface, depending on its concentration. The critical concentration for preferential surface oxide formation is a function of temperature and oxygen pressure [6]. A number of authors have investigated preferential Al-oxidation in air. In the case of Cu–Al an Al content greater than approximately 3 wt.% is required [7,8]. Preferential formation of Al_2O_3 may be achieved in air at temperatures in excess of 900 °C, as well as in low-pressure environments ($<10^{-3}$ Pa) at temperatures as low as 600 °C [9]. However, these findings may not transfer directly to oxidation within a molten cryolite environment. Hyrn et al., who had studied Cu–Al anodes in cryolite, have not reported on the materials performance aspects.

As a result, many questions remain on the behaviour of Cu–Al as an anode in a cryolitic electrolyte. There has been no published work, which addresses the important issue of in situ anode oxidation mechanisms. This paper outlines a study focused on reaction scale characterisation of Cu–Al anodes.