Study on Electrochemical Performance of Alloy Inert Anodes in Low-Temperature Aluminium Electrolytes

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https://doi.org/10.71659/icsoba2025-al071

Abstract

During electrolysis in low temperature aluminium electrolyte systems at 1073 K, with bath ratios of 1.15, 1.25 and 1.35, respectively, the anode potential and self-corrosion potentials of the alloy inert anode tend to decrease with increasing bath ratios. The decomposition voltage of alumina increases with increasing bath ratios. When electrolysis is carried out in low-temperature electrolytes with higher bath ratio (1.35), the degree of electrochemical reaction on the surface of the alloy anode is stronger, and the self-corrosion potential of the alloy anode is smaller (0.25 V), with a larger trend of self-corrosion. Pre-melting the low-temperature aluminium electrolyte before electrolysis not only enhances the uniformity of electrolyte composition but also inhibits the hydrolysis reaction between AlF_3 and adsorbed water, thereby suppressing HF gas generation. This reduces anode corrosion, extends anode service life, and stabilizes long-term electrolysis processes.

Keywords: Alloy inert anodes, Low temperature aluminium electrolysis, Electrochemical properties, Bath ratio, Anode potential.

1. Introduction

The traditional aluminium industry uses carbon as anode material, and there are many problems: (1) large consumption of materials, requiring a huge processing anode plant, with high investment and production costs; (2) carbon anodes need to be replaced, causing high labour intensity; (3) due to the continuous consumption of the carbon anodes, the interpolar distance is unstable; (4) the electrolysis reaction produces a large amount of greenhouse gases, including PFC (perfluorocarbon) gases and asphalt fumes emission, which causes pollution of the environment. Alternatively, the use of inert anodes in the process of aluminium electrolysis has the following advantages: (1) electrodes are not consumed, which reduces the production cost; (2) the interpolar distance is stable and easy to control; (3) the anode is replaced less often, which reduces the intensity of labour; (4) a higher anode current density can be used, which increases the capacity of electrolysis cells; (5) the anode product is oxygen, which avoids environmental pollution [1, 2].

The theoretical decomposition voltage for aluminum electrolysis of alumina with inert anodes is about 1 V higher than that of carbon anodes. But for an inert anode with a wettable cathode, the interpolar distance can be reduced, maybe down to 1 cm. In addition, the inert anode oxygen precipitation overpotential is lower than the carbon anode overpotential. Thus, it may be possible that the inert anode cell technology can give energy consumptions close to the values for the best traditional cells.

Inert anodes is now the focus of attention and research of the international aluminium industry and materials community. The research on inert anodes mainly focuses on the selection of anode materials. Since metal anodes possess better electrical and thermal conductivity and mechanical processing properties than ceramic anodes and cermet anodes, they have been the focus of attention of the aluminium industry and the materials science community. The inert anodes are considered to be one of the most promising anode materials for aluminium electrolysis [3–12]. In this paper, the electrochemical performance of a copper-iron aluminium-based alloy inert anode in low temperature aluminium electrolyte at 1073 K (≈ 800 °C) is investigated to provide technical support for the use of alloy inert anodes in a low temperature aluminium electrolyte.

2. Experimental

Before the test, the working electrode and reference electrode need to be prepared. The inert anode of copper-iron-aluminium base alloy to be tested was machined into a working electrode in the shape of a cylinder, which was connected to the guide rod of a copper rod and then covered with a corundum protective tube to expose its working area. A certain mass of crushed 5N (99.999 %) high-purity aluminium was loaded into a corundum blind tube with a diameter of 1 mm hole 10 mm from the bottom. Then a tungsten wire guide rod with a diameter of 1 mm and a length of 100 mm longer than that of the blind tube was put into the corundum blind tube. Finally, the corundum blind tube was placed into a high-temperature pit-type furnace protected by argon, and then taken out after 10 min at 1023 K. The high-purity aluminium reference electrode was prepared. The prepared working electrode and reference electrode were fixed together on a BN base.

A certain mass of electrolyte of the NaF-KF-AlF_3-6 wt.% Al_2O_3 system (Bath ratio CR = ([NaF] + [KF]) / [AlF_3]) was weighed and loaded into a high-purity graphite crucible and vibrated. Then the working electrode and reference electrode fixed on the BN base were placed on top of the electrolyte, and the graphite crucible was covered. The graphite crucible was placed in the high-temperature pit-type furnace, then covered with the furnace lid, the protective gas conduit was connected, and the thermocouple put in. Finally, the argon protective gas was turned on, and the heating started according to the procedure up to the test temperature, this last being maintained constant for a certain period of time.

Before the start of the electrochemical test, the three-electrode system was connected: working electrode, reference electrode and counter electrode (the counter electrode for this test was a high-purity graphite crucible, and the guide rod was a stainless-steel rod connected to it). The electrochemical workstation used for the test was an IM6 electrochemical workstation from Zahner, Germany. The schematic diagram of the test setup and the three electrodes are shown in Figures 1 and 2.

e. Low-temperature pre-melting of the electrolyte prior to electrolysis trials effectively will remove or significantly reduce adsorbed water, thereby inhibiting the hydrolysis reaction between aluminum fluoride (AlF_3) and adsorbed water. This suppression minimizes anode corrosion during electrolysis and may lower the electrode potential of the anode. Additionally, electrolyte pre-melting enhances compositional homogeneity. Combined with the electrochemical reaction intensity of alloy anodes and energy efficiency considerations, pre-melted electrolyte potentially extends anode service life and stabilizes long-term electrolysis processes.

5. References

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