Electrolysis of Cryolite-Alumina Melts on Solid Cathodes

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Abstract

Attempts of the electrochemical synthesis of titanium diboride (TiB2) coatings on a carbon cathode in a cryolite melt and the subsequent study of the surface by electron microscopy made it possible to establish the cause of the unsatisfactory quality of cathode precipitation and instability of the electrolysis process. The cause is the chemical and physical inhomogeneity of the surface of polycrystalline cathodes. Point depressions, closed and open porosity, microcracks, fractures and surface folds initiate the phenomenon of "pseudo-wettability" by the mechanism of capillary phenomena, for which the conditions of occurrence and features were investigated by numerical methods. These surface defects initiate the current concentration at the micro defect sites and lead to an increase in the rate of cathodic processes with the development of concentration polarization and an increase in voltage to the decomposition potentials of cryolite, sodium fluoride and aluminum. The consequences of these negative processes are the interaction of intrinsic and impurity-aggressive elements with the surface material, the progressive development of physical micro-defects and the passivation of the cathode with refractory sediments and electrolyte components. To solve these problems, it was proposed to use the technology developed in the laboratory for boronization of composite cathodes and low-temperature synthesis of titanium diboride.

Keywords: solid electrode, chemical inhomogeneity, physical micro-defectiveness, limiting diffusion current density, surface wettability, cathode passivation.

1. Introduction

The new generation cell technology with drained cathodes and vertical arrangement of electrodes involves the use of large-sized pressed or cast electrode products made of materials that are inert or less consumed in an aggressive environment. Since Belyaev and Studentsov in the 1930s [1-3] and Ransley in the 1950s [4, 5] published their reports and patents about the advantages of using oxides, carbides and borides of refractory metals for electrodes of aluminum cells, two "aluminum revolutions" were announced. The first of these that began in 2000s from Credit Suisse First Boston Corporation [6] did not occur, but in the continuation received the appearance of a new innovative company. In May 2018, the aluminum giants Alcoa Corporation and Rio Tinto Aluminum announced the creation of the Elysis joint venture in Montreal (https://elysis.com), which plans to introduce a revolutionary electrolysis technology using inert electrodes in Canada in 2024, calling it "low carbon" [7].

Taking into account the next "aluminum revolution", which Alcoa has been developing for about 35 years and UC Rusal has been at the threshold of introducing inert anodes for about 15 years [8], reducing its implementation time and overcoming existing problems require the support of scientific and practical potential from academic institutions. Apparently, the challenge is not only in the high cost of products from titanium diboride, but also in the features of the cathode processes on solid polycrystalline cathodes for the electrolysis of cryolite-alumina melts.

2. Electrochemical Deposition on the Cathode of Boron, Titanium and Aluminum

Theoretically, there are no formal restrictions on the reduction of titanium and boron on an inert or reactive cathode:

$$B_2O_3 + 3/2C = 2B + 3/2\ CO_2 \qquad E^0_{B3+/B} = -0.626\ V \qquad (1)$$
$$TiO_2 + C = Ti + CO_2 \qquad E^0_{Ti4+/Ti} = -0.807\ V \qquad (2)$$

The sequential reduction of titanium and boron suggests their subsequent interaction with the formation of an aluminum-wettable layer of titanium diboride:

$$Ti+2B = TiB_2 \qquad \Delta G^0_{1300} = -320\ kJ/mol \qquad (3)$$

After the formation of a TiB_2 layer on the carbon surface, one can proceed to the electrolysis of cryolite-alumina melts according to standard technology, with a drained cathode or vertical electrodes. Attempts to implement this technology [8] in the laboratory ended with visual wetting of the carbon cathode by a layer of electrolytically deposited aluminum. However, upon a closer examination (X-ray and SEM-EDS analyses), the observed wettability is qualified as "pseudo-wettability" since the contact of aluminum with the cathode surface was occurred through an electrolyte layer of discrete thickness. It was suggested that the cause of the effect of "pseudo-wetting" is the heterogeneous surface of polycrystalline materials with numerous micro and macro irregularities, cracks and pores. For a better understanding and the solution of the problem, an investigation based on experimental work and numerical methods was carried out, and the following was determined:

- Features of electrochemical deposition and synthesis of wettable coatings and aluminum on the carbon cathode;
- Numerical study of wetting conditions for polycrystalline cathode products;
- Restrictions on the use of solid cathodes for electrolytic aluminum production;
- Perspective directions for creating aluminum-wettable coatings for the cathode design of cells.

3. Experimental Work and Discussion of Results

Electrochemical deposition of titanium, boron and aluminum was carried out for 24 hours at a calculated geometric current density of 0.82 A/cm^2 and a temperature of ~ 970 °C. A graphite crucible was used as an anode; and carbon cathodes that were milled to a diameter of 30 mm and a height of 50 mm were divided into two groups:

- Samples after milling with visually observed surface microdefects from the tool in the form of furrows, open porosity, scoring, and surges, and
- Samples with a visually smooth surface which is further carefully polished and washed in distilled water.

In the melt, on the basis of technical cryolite, borax, titanium oxide and in the final stage for 2 hours – aluminum oxide, were added. Under galvanostatic conditions, the voltage dynamics during the experiment was recorded continuously. The presence or absence of aluminum on the cathode at the end of the experiment was a visual indicator of the degree of wettability of the surface

Figure 1 shows the voltage dynamics of two of the numerous attempts to synthesize titanium diboride at the carbon cathode, followed by electrolysis of cryolite – alumina melts. In both cases,

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