A Study of the Alumina Distribution in the Lab-Scale Cell during Aluminum Electrolysis

Olga Tkacheva, Pavel Arkhipov, Alexey Rudenko, Yurii Zaikov

Abstract—The aluminum electrolysis process in the conventional cryolite-alumina electrolyte with cryolite ratio of 2.7 was carried out at an initial temperature of 970 °C and the anode current density of 0.5 A/cm^2 in a 15A lab-scale cell in order to study the formation of the side ledge during electrolysis and the alumina distribution between electrolyte and side ledge. The alumina contained 35.97% α-phase and 64.03% γ-phase with the particles size in the range of 10-120 μm. The cryolite ratio and the alumina concentration were determined in molten electrolyte during electrolysis and in frozen bath after electrolysis. The side ledge in the electrolysis cell was formed only by the 13th hour of electrolysis. With a slight temperature decrease a significant increase in the side ledge thickness was observed. The basic components of the side ledge obtained by the XRD phase analysis were Na_3AlF_6, $Na_5Al_3F_{14}$, Al_2O_3, and $NaF\cdot5CaF_2\cdot AlF_3$. As in the industrial cell, the increased alumina concentration in the side ledge formed on the cell walls and at the ledge-electrolyte-aluminum three-phase boundary during aluminum electrolysis in the lab cell was found (FTP No 05.604.21.0239, IN RFMEFI60419X0239).

Keywords—Alumina, alumina distribution, aluminum electrolyzer, cryolite-alumina electrolyte, side ledge.

I. INTRODUCTION

GLOBAL trends in development of the aluminum industry in the direction of creating powerful high-ampere electrolytic cells, the advantages of which are undeniable, require novel solutions for organizing more energy-efficient and resource-saving technology [1]. It is possible to improve the aluminum production technology by means of organizing the fastest possible implementation of the electrolysis cell with minimal loss of resources, reducing the anode-cathode distance, decreasing the ohmic resistance in the current-carrying parts of the electrolyzer as well as the resistance of the electrolyte [2].

An increase in the power of the electrolyzer and, as a consequence, the anode area leads to a decrease in the interpolar space, reduction in the electrolyte volume in the electrolyzers, and creates the problem of an uneven distribution of alumina in the working space [3]-[5]. The uneven distribution of alumina in the electrolyte leads to a violation of technological process: fluctuations in current density and temperature, an increase in the frequency of anode effects.

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The anode effect in aluminum electrolyzers occurs when the space near the anode is the alumina depleted; it is accompanied by a sharp increase in voltage from 4 to 40 V, an increase in the anode current density, and an additional increase in overvoltage. Thus, the anode effect leads to significant energy costs, to the electrolyte overheating, to the loss of aluminum and a decrease in the current efficiency. Moreover, the perfluorocarbons, which are greenhouse gases, form and release into the atmosphere during the anode effect. The main strategy of the modern aluminum smelters is to conduct the electrolysis process without technological failure, which reduces the technical and economic indicators of production.

In order to eliminate the negative influence of the anode effect, it is necessary to study the processes of distribution and more complete dissolution of alumina in the working space of electrolyzers. Industrial alumina contains several crystalline modifications of α-Al_2O_3, β-Al_2O_3 and γ-Al_2O_3, of which only γ-Al_2O_3 is actively soluble in the cryolite melt. The alumina obtained by the Bayer method can contain as high as 15-60% α-Al_2O_3, which settles on the cathode and on the sides of telectrolyzer, changing the composition of the side and bottom ledge and forming crusts, which disrupts the technological process.

The precipitation formation brings the destruction of the cell bottom, the local electrolyte overheating and the change in resistance, which causes significant fluctuations in the voltage and significantly complicates the control of automatic alumina feed of the bath.

It is impossible to directly investigate the distribution of undissolved alumina over the space of an industrial electrolyzer. In order to do this, it is necessary to use conditions simulating real electrolyzer (density and viscosity of the medium, location of electrodes, bath feeders, ratio of geometric proportions, etc.) [6], [7].

The purpose of this work was to determine the alumina distribution in the electrolyte and side ledge formed during electrolysis in the conventional cryolite-alumina electrolyte in the lab-scale cell.

II. EXPERIMENTAL

A. Chemicals

The electrolysis was carried out in the cryolite electrolyte of conventional composition, consisting of NaF (57 wt.%), AlF_3 (49 wt.%) and CaF_2 (5 wt.%) with cryolite ratio (CR) 2.7. The electrolyte was prepared from the individual components NaF, AlF_3 (reagent-grade, Vekton).

The alumina (98.2% Al_2O_3) was supplied by LLC

Granchim. The alumina was added in an amount ensuring its concentration in the electrolyte of 4 wt.%, based on the assumption that the current efficiency in the lab cell was 70%.

The phase and granulometric composition of the alumina used was studied.

The XRD pattern of the alumina was obtained using a Diffractometer Mini Flex 600 (Rigaku). It was determined that the amount of the α phase $q\alpha = 35.97\%$, and the amount of the γ phase $q\gamma = 64.03\%$.

The Al_2O_3 particle size was determined in the range of 0.02-2000 μm using a Mastersizer 2000 (Hydro 2000S) instrument. Water was used as a dispersant. The particles distribution is given in Fig. 1. The Al_2O_3 particles size distribution is in the range from 10 to 120 μm.
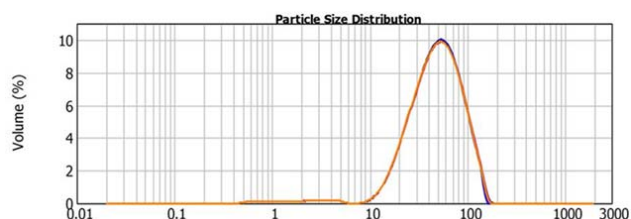

Fig. 1 Alumina particles size distribution

B. Procedure

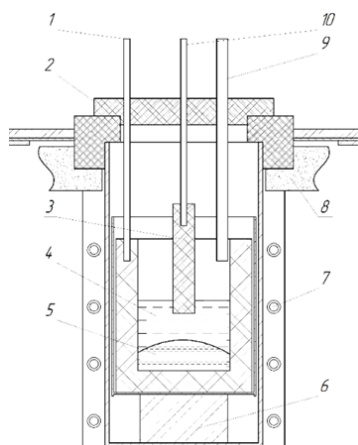The electrolysis was carried out in a lab setup, schematically depicted in Fig. 2.

Fig. 2 Electrolysis cell schematic: 1 - current lead to a graphite crucible-cathode, 2 - cover with mounted holes for current leads to electrodes and tube for additions and sampling, 3 – graphite anode, 4 – electrolyte, 5 – liquid aluminum, 6 – fire-clay brick, 7 – furnace, 8 – lining

Each experiment was carried out with a new graphite anode, which, if necessary, was replaced directly during the experiment. The anode cross section was 40x40 mm and the height was 140 mm. A hole with a diameter of 10 mm was drilled in the anodes for a copper current lead. Before testing, the anodes were dried at a temperature of 120 °C for 1 hour.

A graphite crucible filled with electrolyte and aluminum metal at the bottom was placed in a protective steel cup. The

cell was installed using the lifting mechanism in the furnace. The furnace shaft was closed with a lid with a heat insulator.

The operating parameters of aluminum electrolysis:
- current – 15 A;
- electrolyte temperature – 970 °C
- the anode current density – $0.5/cm^2$
- aluminum level – about 12 см;
- electrolyte level - 15 см;
- interpolar distance - 50 мм,
- elapsed time – about 70 h.

During electrolysis, the electrolyte samples were withdrawn to determine the alumina content and CR.

Measurements of the thickness of the side ledge, formed during the solidification of the electrolyte for the period and after electrolysis, were conducted by the measuring mechanism. After the experiment, dry sampling was carried out at various points of the frozen bath. The Al_2O_3 content was determined in the area of the electrolyte, the side and bottom ledge formation. The oxygen analysis was performed using an ONH836 Oxygen Analyzer instrument manufactured by LECO (USA).

III. RESULTS AND DISCUSSION

The experimental parameters are summarized in Table I. The elapsed time was 70.25 h. The initial test temperature was 980 °C. The electrolyte liquidus temperature was 962 °C; apparently, it decreased with alumina addions. The alumina concentration in the electrolyte remained at about 4 wt.% for the first 30 hours. However, subsequently it decreased to about 3 wt.%.

TABLE I
EXPERIMENTAL PARAMETERS

Time, h	Current, A	Voltage, V	$T_{electrolite}$, °C	Al_2O_3, mas.%	CR
2:40	15.0	1.7	980		2.68
8:30	14.8	1.57	973	4.62	
13:20	16.0	2.0	969	4.16	
20:35	16.2	2.05	967		2.45
23:00	16.1	2.17	965	4.16	2.45
37:00	16.1	2.23	965		2.37
47:00	16.1	2.28	964	3.48	
57:00	16.1	2.29	965	3.5	2.32
70:25	16.0	2.38	965	2.71	2.36

The dynamics of the solid layer's formation on the cell walls was obtained by measuring the profiles over time. The profile of the solid layers at the boundary of the electrolyte-cell wall, electrolyte-aluminum-cell wall, aluminum-cell wall is presented in Fig. 3. As can be seen, the side ledge in the electrolysis cell was formed only by the 13th hour of electrolysis.

The chemical analysis of the electrolyte samples (Table I) revealed that the CR value is close to the planned one and was 2.68 at the electrolysis beginning. Nevertheless, the CR decreased over the time, this is likely due to the formation of the solid side and bottom ledge. So, after 20 hours of electrolysis, the CR decreased to 2.45 and remained near this

value until the end of the experiment. As follows from Fig. 3, the first signs of the ledge formation (thickness of about 2 mm) appear by about 13th hour, and by 23d hour the ledge thickness reaches already 8-10 mm.
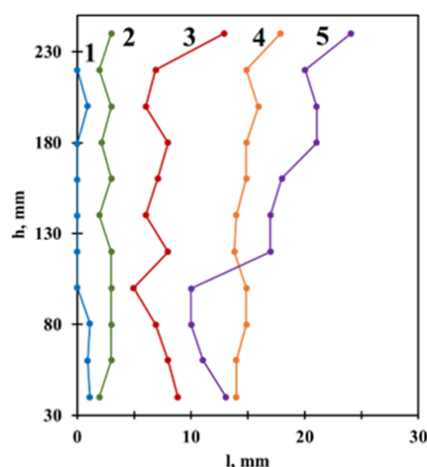

Fig. 3 Profile of the ledge formed on the cell walls by time (h): 1 – 8:30, 2 – 13:20, 3 – 23:00, 4 – 37:00, 5 – 70:25

With a slight decrease in the electrolyte temperature, a significant increase in solid precipitation occurs over the entire profile of the ledge (curve 3 in Fig. 3). However, the profile shape changes by the end of the experiment: the ledge thickness in the region of the three-phase boundary has decreased, possibly because the concentration of alumina in the electrolyte has fallen. However, a crust formed in the upper part of the cell. The electrolysis cell after cooling is shown in Fig. 4.

Fig. 4 Cell after cooling: A is a top view; B - cross section

The electrolyte and side ledge samples were taken in order to determine CR and alumina content. Sampling points are shown in Fig. 5. Description of the samples is given in Table II.

The XRD phase analysis of samples No. 4-11 revealed that the basic components were cryolite Na_3AlF_6 and $Na_5Al_3F_{14}$, Al_2O_3, a component containing calcium fluoride $NaF \cdot 5CaF_2 \cdot AlF_3$.

An increase in the alumina concentration in the frozen electrolyte from the top to the bottom is observed. The average concentration of alumina is 2.89 wt.%, which satisfactorily correlates with the result of the chemical analysis of the electrolyte sample taken by the 70th hour of electrolysis (Table I).

TABLE II
DESCRIPTION OF WITHDRAWN SAMPLES

| Sampling point (Fig. 5)	Description	CR	Al_2O_3, wt.%
1	Electrolyte, top	2.38	2.04
2	Electrolyte, middle	2.41	2.88
3	Electrolyte, over aluminum	2.50	3.75
4	Left wall, ledge-electrolyte, top	2.46	3.73
5	Left wall, ledge-electrolyte, middle	2.34	3.52
6	Left wall, ledge-electrolyte, over aluminum	2.38	3.79
7	Left wall, ledge-electrolyte-aluminum	2.51	3.75
8	Right wall, ledge-electrolyte, top	2.18	3.48
9	Right wall, ledge-electrolyte, middle	2.32	3.98
10	Right wall, ledge-electrolyte, over aluminum	2.39	4.35
11	Right wall, ledge-electrolyte-aluminum	2.43	3.96
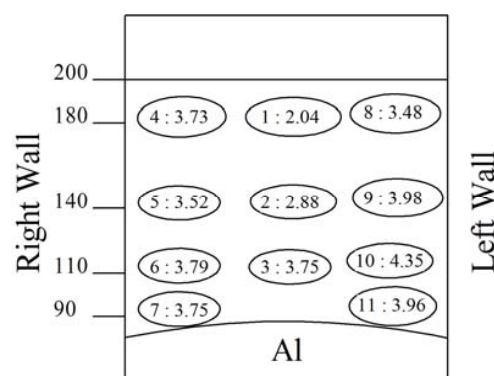
Fig. 5 Sampling points with indication of alumina content

The elevated alumina concentration in the solids formed on the cell walls and at the three-phase boundary of the ledge-electrolyte-aluminum, in comparison with the molten electrolyte, was found during aluminum electrolysis in the lab cell that is similar to the alumina distribution in the industrial cell. An increase in the alumina content was observed along the line from the cell center to the walls and top down along the cell wall.

A regular change in the CR at various points of the bath can be noted: it is higher in the electrolyte region directly above the aluminum and lower in the ledge-electrolyte-aluminum zone.

IV. CONCLUSION

The formation of the side ledge occurred by the 13th hour of electrolysis under given conditions: the anode current density of 0.5 A/cm2, initial temperature 970 °C, the alumina contained 35.97% α- Al_2O_3 and 64.03% γ- Al_2O_3 with the particles size in the range of 10-120 μm. According to the experimental results, it can be concluded that the chemical composition of the side ledge is different from the electrolyte composition, including the elevated alumina content.

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