

INITIAL 1000A ALUMINUM ELECTROLYSIS TESTING IN POTASSIUM CRYOLITE-BASED ELECTROLYTE

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Abstract

Aluminum electrolysis testing in a 1000A cell at 750°C is described. The cell was fitted with 3 vertically oriented aluminum-bronze anodes and 3 wetted cathodes, maintaining an anode-to-cathode distance of 2.2 cm. The electrodes were immersed in a KF-AlF₃ electrolyte with a cryolite ratio of 1.3. Alumina was automatically fed to the cell to maintain a dissolved alumina concentration of 5 wt%, confirmed by analysis. Boron nitride was used as the cell liner material. During electrolysis, the voltage was stable near 4.0 volts at a current density of 0.5 A/cm². Oxygen gas evolved from the cell was measured with an oxygen sensor. During the 24-hour initial electrolysis test, the anodes were protected by a dense oxide layer.

Introduction

Presently, aluminum metal is produced by the 120-year-old Hall-Heroult electrolysis process. Electrolysis in a molten sodium-cryolite-based electrolyte (NaF-AlF₃), serving as a solvent for alumina (Al₂O₃), requires high temperature operation (970°C). The problem with the current practice of high-temperature molten-salt electrolysis in the Hall-Heroult process is the consumable carbon anode, which leads to process inefficiencies, excessive GHG emissions, and added cost. To improve energy efficiency of the conventional Hall-Heroult aluminum technology the main challenge is to replace consumable carbon anodes with non-consumable inert anodes. As of the present, there is no information concerning the successful implementation of inert anodes in conventional aluminum electrolysis. High operating temperature in current practice is a significant factor affecting anode and materials stability.

New approach to energy-efficient aluminum production was conceived and investigated by the Argonne – Kingston Process Metallurgy – Noranda Aluminum team [1-4]. This approach to a step-change aluminum production technology was developed in the following pathways:

- Change electrolyte chemistry. That allows for lower operating temperature.
- Change the anode and cathode materials. The low operating temperature provides more materials options.
- Change the configuration to a vertical cell. Inert anodes enable new energy-efficient cell designs.

It was proposed to use potassium cryolite as an electrolyte for aluminum electrolysis. A KF-AlF₃ molten system with CR=1.3 and concentration of dissolved alumina 5 wt% allows for carrying out electrolysis at as low as 700°C. The values of alumina solubility for this electrolyte in the temperature range of 700-800°C are comparable with the operational alumina concentration

in a conventional sodium-cryolite-based bath. Several commercially available alloys were evaluated as inert anodes in electrolysis tests in KF-AlF₃ melts at 700°C. It was found that aluminum bronze consistently performed better than the other alloys.

The numerous electrolysis tests performed in 20 and 100 A cells fitted with vertical aluminum bronze anodes and wetted cathodes in potassium cryolite-based electrolyte confirmed the feasibility of the new low-temperature aluminum electrolysis process in the temperature range 700-770°C. The operating window for sustaining low-temperature electrolysis during long-term tests was determined. The stable voltage indicates the smooth and steady electrolysis. The voltage deviations during aluminum electrolysis with an inert anode is mainly determined by the anode processes. Nevertheless, sometimes the voltage instability can be ascribed to the cathode processes. To avoid voltage fluctuation caused by the formation of the cathode incrustation the temperature of electrolysis cell should not be below 700°C. Moreover, the recommended temperature for the electrolyte prior to lowering electrodes and beginning electrolysis is 750-770°C. The NaF accumulated during long-term electrolysis in an electrolytic bath negatively impacts the cell performance. To take the NaF content in the electrolyte into account it is necessary to adjust the operating temperature. The electrolyte composition was continuously analyzed and it was recognized that neither cryolite ratio nor sodium content in electrolyte changed noticeably at least during 100 hours of 100A electrolysis. The aluminum metal product impurity level was tracked during electrolysis. The constant level of copper in produced aluminum during electrolysis in 20 and 100 A cells indicated the correlation between the rate of the aluminum bronze anode scale dissolution and the rate of aluminum production. This balance can be shifted by an increase in current efficiency of the process that will result in producing aluminum of better quality. It is recognized that even in 100A tests, the purity level in the aluminum can vary due to circumstances associated with cell operation that would not occur at higher amperages over longer times.

Based on the 20 and 100 A tests, the design criteria for a 1000A ultra-high efficiency aluminum production cell, utilizing metallic (aluminum bronze) vertical inert anodes and drained wetted cathodes in a low-temperature potassium-cryolite-based electrolyte was developed. A pilot high amperage electrolysis cell was constructed. Results of initial 1000A aluminum electrolysis testing are presented in this paper.

Materials compatibility tests

All 20 and 100 A lab-scale electrolysis tests previously performed were in alumina crucibles which cannot be used for the larger cell. The selection of an appropriate construction material for high amperage electrolysis cell remains a very important problem.

Compatibility tests were performed to determine suitable materials to be used for 1000A crucibles. Materials tested included tar bonded silicon carbide, nitride bonded silicon carbide, and grade AX05 boron nitride (Saint Gobain).

Electrolysis test in a tar bonded silicon carbide crucible

The electrolysis testing procedure is described elsewhere [3, 4]. Electrolysis test in $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ electrolyte (CR=1.3) in a 4000 cm^3 tar bonded silicon carbide crucible at current 25-50A (anode current density 0.25-0.5 A/cm^2), temperature 740°C, was performed during 47 hours. An automatic feeding system was developed to deliver desired amounts of alumina at specified intervals. Timing was adjusted so that alumina feeding rate would be the same as alumina consumption rate, otherwise undissolved alumina would collect on the bottom of the cell [4]. The oxygen content in the electrolyte samples was analyzed by a LECO RO600 Oxygen Determinator.

The cell was not sealed with a cap so oxygen evolved on the anode was not measured. The electrolysis cell was equipped with two molybdenum quasi-reference electrodes to help identify the origin and extent of voltage deviations. The current, voltage, and anode and cathode potentials were recorded. The operating parameters of electrolysis are presented in Figure 1. The electrolysis was stable. The voltage established itself near 3.5-3.6 V at a current of 45-50 A. The alumina concentration in the electrolyte was close to saturation. (The alumina solubility in KF-AlF_3 at CR=1.3 and $T=750^\circ\text{C}$ is 5.5 wt%). The elevated level of oxygen in the electrolyte during the early stage of electrolysis is due to all the oxygen containing impurities introduced to the electrolyte together with raw materials [3].

Observation of the crucible revealed that there was no damage after the electrolysis was completed but the bottom of the crucible became very flaky (Figure 2). A black sparkling substance covered the alumina sheaths of the electrodes' electrical leads, the wall crucible area above the melt and aluminum on the bottom. Produced aluminum metal was contaminated with a large amount of silicon.

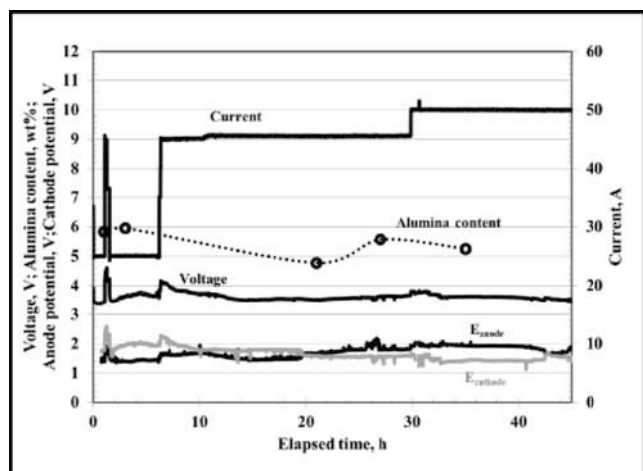


Figure 1. Operating parameters of aluminum electrolysis performed in a tar bonded silicon carbide crucible. (Electrolyte $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ with CR=1.3, temperature 740°C)

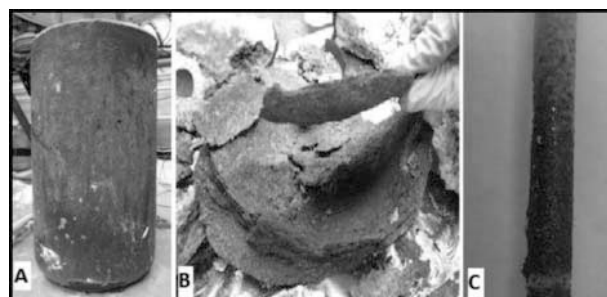


Figure 2. Tar bonded SiC crucible: A) after electrolysis in $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ electrolyte; B) flaky bottom; C) alumina casing suspended over the electrolyte was covered with black sparkling substance

Nitride bonded silicon carbide sample testing

Sample of nitride bonded silicon carbide (SiC) (15.0x7.5x3.8 cm) was tested for 380 hours in conditions of inert nitrogen atmosphere. Sample was half immersed into the KF-AlF_3 electrolyte (CR=1.3), alumina saturated, at temperature 750°C. A 1500 cm^3 graphite crucible was used. Weight and size of samples were measured periodically. Weight of the SiC (nitride bonded) sample increased 10% (from 1130.7 to 1233.0 g) by the first observation in 103 hours of exposure to the melt, but size did not change. Neither weight nor size changed during the next 273 hours. Nevertheless sample and walls of the graphite crucible, especially in the interface area, were covered with thin fragile metal-like layer. A nitride bonded SiC sample after 380 hours test is shown in Figure 3.

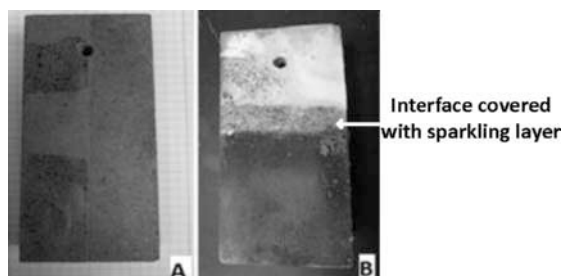


Figure 3. Nitride bonded SiC sample exposed to $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ melt in N_2 atmosphere at 750°C: A) before test; B) after 380 h

Boron nitride sample testing

Compatibility testing was also performed on boron nitride (BN) sample (15.0x7.5x2.5 cm). The procedure described above for SiC sample test was applied. Neither weight nor size of the BN sample changed during the test in the inert nitrogen atmosphere. Therefore it was tested in an open cell in air. A BN sample (19.0x2.5x2.5 cm) was exposed for 950 hours to the KF-AlF_3 electrolyte saturated with alumina and the molten aluminum metal, placed on the bottom of alumina crucible. The bottom half of the sample was immersed into the electrolyte and molten aluminum and the top half remained in air. Tested sample was removed and observed periodically. The weight and thickness at specified positions of the sample were recorded. The view of the BN sample is given in Figure 4. It was observed that solid electrolyte built up at the interface of the air and electrolyte. The portion of the sample that was immersed in the molten Al changed from white to grey. No significant deterioration was observed on the surface of the sample, even after 950 hours. The weight of the

sample increased 5% because it was difficult to remove all of the solid electrolyte crust. The difficulty in removing the electrolyte crust (near the interface) caused variations in the thickness of the sample. The portion of the sample that was immersed in the electrolyte and molten aluminum increased only 1 mm in thickness.

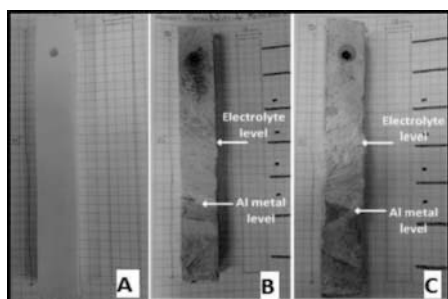


Figure 4. BN sample exposed to $\text{KF-AlF}_3\text{-Al}_2\text{O}_3\text{-Al}$ melt in air at 750°C : A) before test; B) after 410 h; C) after 950 h

Electrolysis test in a boron nitride crucible

Since the AX05 BN material exhibited very good resistivity to the molten potassium cryolite it was used to construct a 10A electrolysis cell, a prototype of a 1000A cell. A 1200 cm^3 boron nitride crucible was inserted into a matching stainless steel (SS) shell. To prevent the external walls of the SS shell from oxidation they were sprayed with BN.

A 10A electrolysis test with one plate aluminum bronze anode ($7.0 \times 2.8 \times 1.3\text{ cm}$) and one plate wetted cathode ($5.4 \times 2.8 \times 1.3\text{ cm}$) was performed in the constructed crucible. The anode current density was 0.5 A/cm^2 . The cathode current density was 0.65 A/cm^2 . The voltage and the anode and cathode potentials were stable throughout electrolysis (Figure 5).

To determine if the BN crucible in the SS shell can be used again the crucible, with molten electrolyte, was kept for 24 hours at 740°C . Three times, the electrolyte was poured out and crucible was set to cool. No signs of cracking were observed.

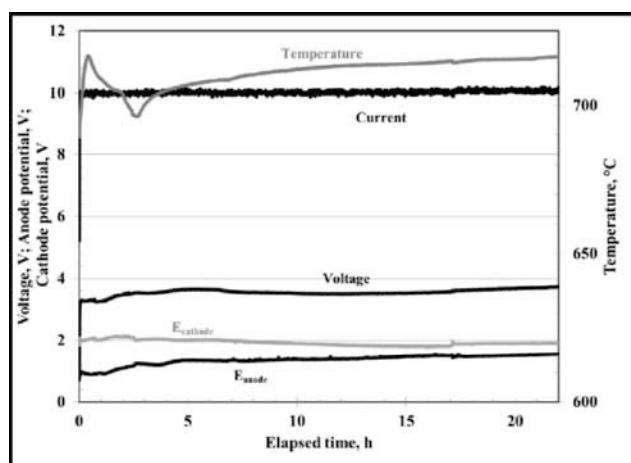


Figure 5. Operating parameters of electrolysis performed in a 10A BN crucible (Electrolyte $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ with $\text{CR}=1.3$ and alumina concentration $4.5\text{ wt}\%$)

It was assumed that grade AX05 BN can be used as a cell construction material exposed to potassium cryolite electrolytes during 1000A aluminum electrolysis.

1000A electrolysis test

Aluminum electrolysis in the $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ electrolyte (with $\text{CR}=1.3$ and alumina concentration $5\text{ wt}\%$) was performed at a current of 1000A, temperature of 750°C , and in a cell fitted with vertical orientated plate electrodes. The aluminum bronze anodes and wetted cathodes had the same dimensions: $28.0 \times 15.0 \times 2.5\text{ cm}$. The cell contained an anode and cathode system which included a total of six anodes and cathodes. The anode and cathode current density was 0.5 A/cm^2 . The anode-cathode distance was 2.2 cm .

An electrolysis crucible was fabricated from a stainless steel (SS) container, in the shape of a rectangle. The SS container was sprayed with BN. Inside this container a 50 L BN crucible was placed (Figure 6). The entire assembly was covered with a steel cap that gave access to electrical leads, thermocouple, feeding tube, as well as outlet and inlet gas. This cap was insulated with fiber-ceramic on the side exposed to the electrolyte. The bus bar was constructed in such a way that the distance between anodes and cathodes can be adjusted. The bus bar for the anodes was made of aluminum bronze while the bus bar for the cathodes was made of SS. Alumina was delivered to the cell automatically through two feeding tubes positioned in two different locations on the cap. Nitrogen gas flow was kept at 10 L/m .

A scrubber purification system was specially developed for 1000A testing. It was composed of three columns, the first of which was filled with glass wool to collect solid particles in the outlet gas. The second column was filled with dried alumina to absorb HF and traces of moisture. The final column was empty to allow any solids to settle out and prevent possible contamination of the oxygen sensor. The outlet gas rate was slightly higher than the input and was drawn from the cell using a pump and controlled by a valve. This created a slightly negative pressure within the chamber.

The potassium electrolyte with $\text{CR}=1.3$ was prepared in advance. A mixture of the KF (Aldrich) and the AlF_3 (supplied by Noranda Aluminum smelter) was melted in an alumina crucible and cooled in an ingot to obtain 2-3 kg blocks. These blocks were kept in a nitrogen filled container.

After the prepared electrolyte (71 kg) was added to the cell, a shroud was mounted on the furnace and used to support the cap with the electrode and bus bar system (Figure 7). The furnace was heated in a nitrogen atmosphere at a rate of 50 degree/h . When the temperature of the furnace reached 750°C , the shroud was removed and the electrodes were lowered into the electrolyte. The electrodes were held in the molten electrolyte for 30 minutes without being electrically energized. This time was necessary for the electrodes to be heated to 750°C and for the electrodes to be connected to the power supply. The cell voltage and operating temperature were monitored by a National Instruments data acquisition unit and recorded once every second by the Labview computer program. The outlet gas oxygen content was recorded every 30 seconds using the Rapidox software. View of the set-up when electrolysis is in progress is shown in Figure 8.

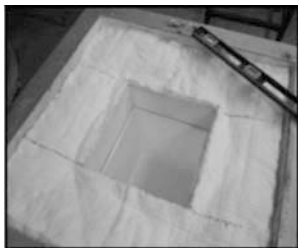


Figure 6. BN crucible inside the SS shell placed in the furnace



Figure 7. Shroud mounted on furnace supporting system of electrodes and bus bars



Figure 8. View of furnace when electrolysis is in progress

The plot of operating parameters of the 1000A electrolysis in the $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ electrolyte (CR=1.3) is given in Figures 9 and 10. At the beginning of the electrolysis the current was increased in steps (250, 500, 750, 1000 A) with each step taking approximately 25 minutes. The voltage stabilized near 4 V. There was voltage oscillation of about 150 mV during the electrolysis (Figure 10). The electrolysis was sustained and no voltage fluctuation was observed. The temperature set point was difficult to determine due to the slow response time of the furnace. During the first three hours, the temperature was manually adjusted to the desired 750°C . After setting the temperature, no spontaneous temperature change was observed.

Oxygen in the outlet gas was detected by an oxygen sensor. Since the outlet gas was pumped from the cell the air from outside was drawn into the cell impacting the oxygen reading. To obtain the actual oxygen values the cell should be calibrated considering all gas flows. Nevertheless, in the initial 1000A test the stable oxygen level in the outlet gas indicated the stable course of the electrolysis. With any change in current, there was an instant change in oxygen concentration, proving the consistency of the electrolysis. After the third hour, there was a sharp decrease in oxygen content followed by a temperature decrease. Between 7 and 8 hours of the electrolysis there was a noticeable increase in oxygen content which is difficult to explain at the moment. However, the oxygen concentration stabilized at this new level. After the 13th hour of electrolysis the oxygen reading was interrupted due to the blockage of the outlet tube made of SS. It was clogged with the SS corrosion products. However the very steady voltage readings indicated the smooth course of electrolysis throughout entire test.

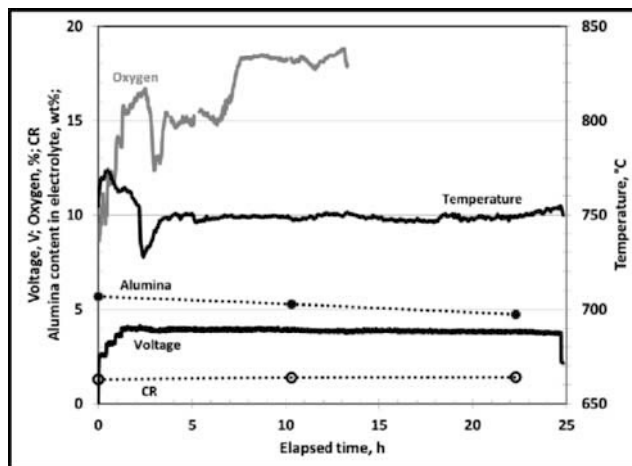


Figure 9. Operating parameters of 1000A aluminum electrolysis in the $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ electrolyte

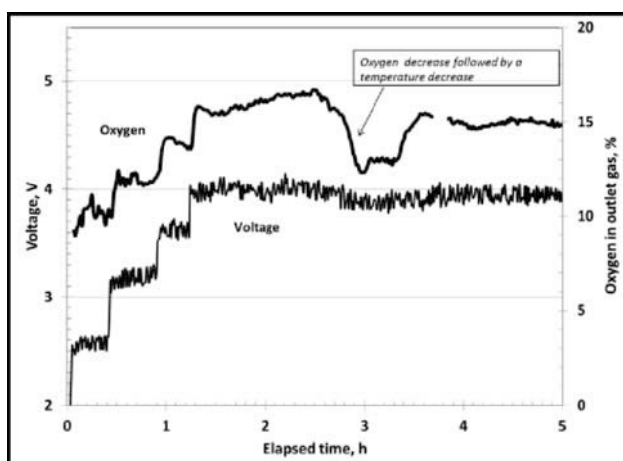


Figure 10. Enhanced plot of voltage and oxygen concentration in the outlet gas during first 5 hours of 1000A aluminum electrolysis in the $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ electrolyte

Samples of electrolyte were withdrawn during electrolysis and analyzed for the elements: oxygen (by LECO RO600 Oxygen Determinator), potassium, sodium, aluminum, and copper (by ICP-OES). At the beginning the alumina concentration in the electrolyte was close to its solubility in potassium cryolite (CR=1.3) at 750°C (Figure 9) but it slowly decreased during electrolysis because of frequent feeding disruptions. The alumina powder often jammed in the Teflon tubing. The CR remained constant throughout the entire test. The content of sodium in electrolyte was 0.16 ± 0.02 wt%. Copper was not found in the electrolyte.

The picture of the electrodes suspended over the melt, just after electrolysis was stopped, is presented in Figure 11. It was discovered that the alumina sheaths covering the current leads were dissolved in the electrolyte due to inadequate feeding. The SS bus bar was significantly corroded while the aluminum bronze bus bar was covered with a black protective layer.

The anodes were covered with an oxide scale (Figure 12A). No destruction of the anodes due to corrosion was observed. During cooling, the anode scale cracked and fell away from the anodes (Figures 12B and 12C). The scale on the anode surfaces which

face a cathode had nearly identical thicknesses (0.5 mm on average). However, the scale on the anode surface facing away from the cathode was thinner (0.35 mm). All of the anodes looked identical, no matter their individual position in the electrode system (inside or outside). The anode scale detached from the anode surface after electrolysis was analyzed by a Bruker D8 Advance XRD. XRD spectra are given in Figure 13. The side of the scale facing the electrolyte contained Cu_2O (with the traces of CuO) and K_3AlF_6 . The composition of the side facing aluminum bronze – Cu , Cu_2O and KAlF_4 – indicated electrolyte penetration through the anode scale. SEM-EDS elemental analysis of the rust anode flake determined that F , O , K , Al , and Cu were the dominant elements. Traces of Ni , Fe , and Mn were also present.

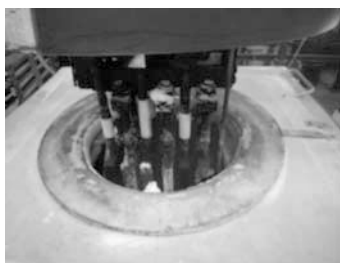


Figure 11. After electrolysis, electrodes suspended above melt

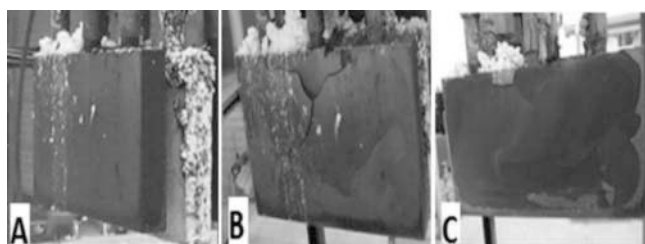


Figure 12. Anode after 1000A electrolysis:
A) 1st minute after electrodes were withdrawn out of the melt;
B) cooling anode; C) cold anode

Cathodes located between anodes had a smooth surface covered with a thin layer of aluminum. The outside surface of one cathode and the top edge of cathodes (facing towards bus bar) had some solid incrustation. One cathode with solid incrustation on the top edge can be seen in Figure 12A. It was observed that the cathode incrustation was composed of two layers. An internal layer, closer to the cathode's surface, was black and could be easily crushed. An external layer situated over the internal layer was grey, firm and difficult to crush. XRD analysis of the milled cathode incrustation (mixture of both layers) indicated the material to be KAlF_4 and K_3AlF_6 . No Al_2O_3 was found. XRD analysis of the internal black layer (detached from the grey layer) detected only KAlF_4 .

After electrolysis was completed the electrolyte was ladled out of the cell. Only a portion of the aluminum metal produced could be taken out of the cell because of the size of the ladle. As a result, the current efficiency (CE) could not be measured using the mass of aluminum produced. In order to estimate the CE of the 1000A electrolysis test the resistivity of the cell contents (molten electrolyte and aluminum) was measured using two molybdenum wires fixed inside an alumina tube. This device was immersed into the cell in a position 5 cm from the crucible wall. The mass of aluminum on the bottom of the crucible is believed to have a curved surface which is convex along the walls and flatter in the

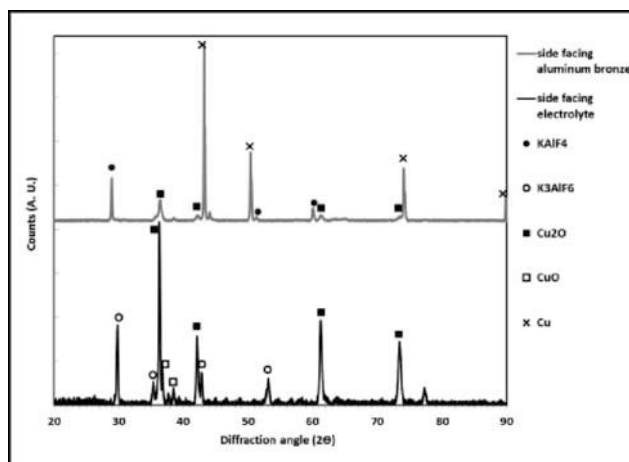


Figure 13. XRD spectra obtained on the anode scale from the sides facing electrolyte and aluminum bronze

middle. The value of the resistivity changed one order of magnitude at the distance of 1.5 cm from the bottom. It was assumed that the aluminum metal pool on the bottom of the crucible was 1.5 cm high, that is about 5700 g of Al . Thus, according to these measurements the CE of the electrolysis test was about 70%.

First of all, the low CE of the initial 1000A aluminum electrolysis test was explained by a technical issue - an inadequate alumina feeding during electrolysis. Actually, the low CE can be a result of many factors. The back reactions such as reoxidation of dissolved or dispersed aluminum metal by oxygen in potassium cryolite at temperatures below 800°C are not well studied yet. It is obvious that the aluminum metal solubility in the melt decreases with decreasing temperature and does not significantly affect the CE as it occurs in conventional electrolysis. A dispersion of Al droplets in a cell with vertical electrodes seems to be the more important issue which could be due to the cathode material. The good wetting properties of the cathode material prevent Al droplets from spreading into the bulk by allowing the molten aluminum to move smoothly down on an electrode surface and drip to the bottom of the cell. Oxygen gas generated on the inert anode also appears to behave differently. So, Cassyre [5] studied the process of oxygen generation on metal inert anodes on the lab scale. Oxygen bubbles are generated compactly and uniformly over the anode surface, but they do not coalesce. The bubble diameter on inert anodes is 10-30 times less than that on graphite anodes. Oxygen bubbles likely do not significantly induce electrolyte flow in the interelectrode gap and enhance the back reactions. In addition, the bubbles do not efficiently stimulate the process of alumina dissolution. It was assumed, based on our previous study of low-temperature electrolysis in potassium cryolite-based electrolyte in 20 and 100A cells utilizing aluminum bronze anodes and wetted cathodes, that the CE of the large-scale process can be significantly improved by adjusting operating parameters.

Copper was not found in the electrolyte samples whereas it was determined to be present in the aluminum metal at about 2.8 wt%. The elevated content of Cu in the aluminum produced is explained by the fact that the electrodes were immersed into the molten electrolyte without being electrically energized for 30 minutes prior to electrolysis. This allows the surface of the anodes to be dissolved in the electrolyte. The initial Cu contamination of the

aluminum was not considerably reduced by the relatively small increase of aluminum mass during 24 hours of electrolysis. Another reason why the aluminum metal contained significant amount of copper could be the constantly decreasing alumina concentration in the electrolyte due to feeding interruptions. A decrease of O^{2-} in the melt leads to shifting of the $Cu_2O \rightarrow 2Cu^+ + O^{2-}$ equilibrium to the right and to dissolution of the anode oxide scale.

Conclusions

Based on the initial 1000A electrolysis test some fundamental and technical conclusions were drawn. They included the following:

- The aluminum electrolysis in a 1000A cell equipped with the system of the vertically oriented inert aluminum bronze anodes and wetted cathodes in the potassium cryolite electrolyte at 750°C was steady and sustained for 24 hours.
- Boron nitride exhibited good compatibility as a liner material for electrolysis cell.
- Automatic feeding system providing the continued delivery of alumina to the cell has to be improved.

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