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Current Efficiency, Corrosion and Structural Changes in SnO$_2$-Sb$_2$O$_3$-CuO Inert Anodes for Aluminium Electrolysis

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(Dated: Received on December 20, 2013; Accepted on March 17, 2014)

A systematic study was conducted on current efficiency (CE), corrosion and structural changes in SnO$_2$-based inert anodes (made of 96wt%SnO$_2$+2wt%Sb$_2$O$_3$+2wt%CuO) on a laboratory Hall-Heroult aluminium cell. The influence of operating parameters and electrolyte composition on the CE and corrosion process were evaluated. The CE was found to be more than 90% and catastrophic corrosion took place at low percent of Al$_2$O$_3$, high percent of LiF, low cryolite ratio and high current densities. From all the structural changes that took place in the SnO$_2$-based inert anodes, we assumed that the most important contribution was due to the migration of CuO towards the outer limits of the constituent grains of SnO$_2$ based ceramic. The complex process occurred during the formation of various phases and their sintering ability both directly depended on Cu/Sb molar ratio.

Key words: Inert anode, Aluminium electrowinning, Current efficiency

I. INTRODUCTION

Since the inception of the Hall-Heroult Process, many attempts have been made to develop inert anodes to replace the consumable carbon ones for aluminum electrowinning [1–3]. Inert anodes offer potential savings in operating costs by eliminating carbon anodes replacement, greenhouse gases and carcinogenic polyaromatic compounds. These anodes can also provide higher control of the anode-cathode distance (ACD). Electrowinning of alumina with inert anodes liberates only pure oxygen at anode, after the overall reaction:

$$2\text{Al}_2\text{O}_3 \xrightarrow{980 \, ^\circ \text{C}} 4\text{Al} + 3\text{O}_2$$ (1)

oxygen, which is environmentally very friendly, can be collected as a valuable byproduct.

Among several materials studied, tin oxide (SnO$_2$) has been proven the most promising candidate for manufacturing of inert anodes. Different doping materials have been used for preparing SnO$_2$ semiconductor ceramics. From a large variety of compositions of SnO$_2$-based ceramic materials, the 96wt%SnO$_2$+2wt%Sb$_2$O$_3$+2wt%CuO mixtures gave the best results from the point of view of physico-chemical properties and microstructure [4–9].

Most of the work on SnO$_2$-inert anodes has concentrated on material selection and test of performance according to some specific criteria such as physico-chemical properties and corrosion resistance of the anodes. A significant problem for application of inert anodes is the attainable current efficiency with respect to aluminium. In a discussion about which parameters govern the current efficiency of inert anodes (oxygen evolving anodes), one should bear in mind the fact that the solubility of oxygen in cryolite-alumina melts is by far lower than that of CO$_2$ [10]; the solubility of CO$_2$ at 960 °C is 4.6 mmol/L-atm, while that of oxygen at 950 °C is 3.0 µmol/L-atm.

The current efficiency (CE) in a 10 A laboratory aluminium cell is determined with an inert anode (97wt%SnO$_2$+2wt%Sb$_2$O$_3$+1wt%CuO), as well as carbon anodes [11, 12]. The average value of the current efficiency is close to 89% on inert anode, while it is 85%–87.2% for carbon and graphite anodes.

It is generally accepted that the current efficiency of any electrolysis is determined by the operating parameters and bath composition of the electrolysis cell. However there are still scarce data in literature about this subject [13–16]. That is why we performed this systematic study on the current efficiency, corrosion and structural changes on the 96wt%SnO$_2$+2wt%Sb$_2$O$_3$+2wt%CuO anode in a laboratory aluminium electrolysis cell.

II. EXPERIMENTS

In the present work, the CE was determined by measuring the total amount of oxygen evolved at the anode. The electrolysis cell and accuracy of the method were previously described in detail [14, 16]. The influence
of operating parameters including temperature, current density (c.d.), ACD, electrolyte composition, NaF/AlF₃ molar ratio (cryolite ratio, CR) and concentration of Al₂O₃, LiF, NaCl and MgCl₂, were evaluated.

In the same time as the anode corrosion appeared to be the main obstacle for the use of inert anodes in commercial cells [17], the corrosion rate of SnO₂-based inert anodes was studied by the weight method as a function of c.d. and ACD and concentration of Al₂O₃ and LiF. The weight of anode was determined before each experiment. After the experiment any adhering electrolyte on the anode was removed by washing in a 30%AlCl₃·6H₂O solution at 80 °C for 4 h and subsequently in water. The weight of the anode was determined again after being dried and the corrosion rate was obtained from the weight loss, using the following equation:

\[ r = \frac{\Delta W}{\tau S} \]  

(2)

where \( r \) is anode corrosion rate, \( \Delta W \) is weight loss of the anode after the experiment, \( \tau \) is duration of the experiments, \( S \) is anode surface area immersed in the electrolyte. The weight loss method was very reliable because the shape of the anode was somewhat irregular when corrosion took place.

III. RESULTS AND DISCUSSION

A. Effect of operating parameters on the current efficiency and corrosion

A plot of CE versus c.d. and ACD at different temperatures is shown in Fig. 1. The CE increases monotonously with increasing c.d. in the range of 0.5–2.0 A/cm² and does not change significantly when the ACD increases above a certain limit, here about 2 cm. The CE decreases with the increasing temperature of the electrolyte. The experimental data show that there is a systematic decrease of CE with increasing temperature from 900 °C to 980 °C. The CE decrease of about 0.5% is noted for each 10 °C temperature increase. Those data indicate that there is a significant potential for achieving very high current efficiencies with the use of low-melting bath and low ACD in the Hall-Heroult cells with inert anodes. Figure 2 shows the effect of ACD and c.d. on the corrosion rate of SnO₂-based inert anodes.

The results indicate that CE does not change appreciably when the ACD increases above a certain limit, here about 2 cm. It is essential that inert anodes can operate at low ACD to save energy. It has been suggested [13–15, 17, 18] that direct reduction of anode material by the dissolved metal in the electrolyte could be one important cause of inert anode corrosion. This effect might be expected to become more important if ACD is reduced. According to reported data [11, 12, 17, 19], the corrosion rate of SnO₂-based oxygen inert anodes show only a slight increase (2.0–2.7 mg/cm²·h) when the ACD decreases from 5 cm to 2 cm. Our measurements on corrosion of the studied anodes demonstrate that lowering ACD may not result in corrosion of anode, which is in good agreement with other SnO₂ anode compositions.

Fitting the curves from Fig.1, a polynomial equation can be derived:

\[ y = a + bx + cx^2 + dx^3 + ex^4 \]  

(3)

where \( y=\text{CE}, x=\text{c.d. and ACD results, the parameters} a-e \) are shown in Table I.

However it should be noted that the effect of the interpolar distance may depend on the connective pattern of the cell, so that the results in Fig.1 and Fig.2 could be specific only to the presently employed cell arrangement. The CE increases monotonously with increasing...
especially at low Al concentrations. The alumina concentration on aluminum solubility, e.g.,
\[ \text{SnO}_2(s) + \frac{4}{3} \text{Al}_{\text{diss}} = \text{Sn} + \frac{2}{3} \text{Al}_2\text{O}_3 \] (4)
The reaction takes place if dissolved metal reaches the anode surface. It may occur when anodic current density is zero or close to zero. However, above a certain current density, it is not likely that dissolved metal can attack the anodically polarized anode surface which is surrounded by oxygen bubbles. The lower CE values obtained over current density range below 0.3 A/cm² could be correlated with similar process. To avoid any corrosion, the current density range of 0.5–0.8 A/cm² (usually industrial current densities) is recommended. Over the range, no apparent disintegration of the anode occurs provided that the bath is saturated with alumina.

B. Effect of bath composition on the current efficiency and corrosion

Many attempts have been made to improve the current efficiency of the Hall-Heroult process through changes in bath chemistry. In Fig. 3 we present the effect of the bath composition on the CE. One can see that it is a rather slow CE increase with increasing alumina content at high and medium alumina concentration, while there is a drastic decrease at low concentration (<2wt%Al₂O₃). The effect of the alumina concentration on the CE is disputable since a change in alumina concentration influences the size of the gas bubbles as well. It is also known that the solubility of aluminum in melted NaF-AlF₃-Al₂O₃, which is one of the main causes of CE decrease, gets lower at addition of Al₂O₃. However, the effect of gas bubbles on the size of bubbles may be more important than the influence of the alumina concentration on aluminum solubility, especially at low Al₂O₃ concentrations. This effect should be assigned to O₂ bubbles formed at the anode which influences the anodic overvoltage. When their size is small, the gas retention time is short, and the anodic overvoltage is lower than that in the case of larger gas bubbles. The drastic decrease observed on the CE at low Al₂O₃ concentration (<2wt%) could be assigned to the SnO₂-based anode which is subjected to a serious corrosion process. Taking into account the considerations above and those in Fig. 3, optimal additions are obtained at Al₂O₃ concentration higher than 3wt%, that is 5wt%–6wt%Al₂O₃ from a practical point of view.

Over the years many attempts have been made to improve the CE of the Hall-Heroult process through changing the chemical and physical properties of the bath which would exert a positive effect on the CEs in bath chemistry. The improvement has often been attributed to the decrease of bath temperature that has been caused by these additives, especially of LiF, MgF₂, and NaCl.

The main advantage of low-melting baths is a lower aluminum solubility in the bath due to the reduced temperature and further the heat loss from the cell is reduced which may increase the cell life and enhance potential use of inert anodes. The main disadvantage comes from lower alumina solubility and lower electrical conductivity of the bath. As we have mentioned in an earlier work [15], the CE on SnO₂-based inert anodes increases when temperature decreases. As an additive, LiF can improve the physico-chemical properties of the electrolyte, beneficially decrease density, viscosity and liquidus temperature, and drastically increase electrical conductivity, being the most recommended additive. Note also that CE increases with increasing LiF concentration up to ~5wt%. This behavior may be correlated with the increase of electrical conductivity. Above 5wt%LiF concentration a sudden decrease in the CE is observed and one can correlate the increase of CE with the increase of corrosion and penetration of LiF in the structure of SnO₂-based inert anodes. One must also take into account the fact that addition of LiF improves separation of the deposited liquid metal from the electrolyte during aluminum electrolysis, but at concentration higher than 5wt%LiF an important increase in electrolyte volatility takes place and also the co-deposition of metallic lithium at the cathode becomes possible; although these phenomena are not noted when one measures the anodic gas. A compromise has to be made and that is why we consider that an addition of 3wt%–4wt%LiF is optimal.

The influence of NaCl and MgF₂ is also shown in Fig. 3 and one can see that NaCl has a negative effect on the CE and MgF₂ effect appears to be less than that of LiF. We can conclude that LiF is superior to all other additives from both chemical and CE points of view.
As shown in Fig. 4, the corrosion rate increases rather slowly with decreasing Al$_2$O$_3$ concentrations, but a drastic increase takes place at low alumina concentrations (<1wt%Al$_2$O$_3$). In the same time above certain concentration of LiF a strong increase appears in the corrosion rate, but at high current density (>1.5 A/cm$^2$). As have been demonstrated in the CE effect, above 6wt%LiF the anode is corroded in a few minutes. This behavior could be explained by the solubility of SnO$_2$ which increases markedly with decreasing Al$_2$O$_3$ concentration [20].

As the composition of the melted fluoride exerts a great influence on the CE, CR is the most important. Particular interest is attached to the CR range from 2.4 to 3.0 which represents the range used in industrial cells. The temperature and Al$_2$O$_3$ concentration are maintained constant to allow the monitoring of influence CR exerted upon CE over 1.5–3.0 CR range. The experimental data are shown in Fig. 5.

Note that CE constant decreases monotonously with increasing CR. The decrease of CE is in good agreement with the destruction of the surface of SnO$_2$-based anode. Likewise other studies have also shown that corrosion of SnO$_2$-based inert anode decreases with CR even if Al$_2$O$_3$ concentration is constant [19].

C. Structural study of SnO$_2$-based inert anodes

It is well established that the corrosion resistance of an electrode is influenced by its microstructure, i.e. the composition of the grain, grain size, and presence of different phases in the grain boundary. A single-phase material is desirable to ensure uniform corrosion of an electrode. Figure 6 shows micrographs obtained by electron microscopy of the studied sample, thermally treated at 1300 °C, 6 h plateau. The presence of a copper rich second phase through the SnO$_2$ is noticed. This can be due either to an inability to attain a good dispersion for small additions wherein mixing is conventionally done by wet homogenization, or formation of some compounds which cannot be incorporated into SnO$_2$ lattice. The hypothesis is sustained by the studies over the whole concentration range of composition on the SnO$_2$-Sb$_2$O$_3$-CuO ternary system [21, 22].

It is known that the formation of CuSb$_2$O$_6$ binary compound (from CuO and Sb$_2$O$_3$ equimolecular mixture) is a basic stage of the further solid-state inter-

action in this system [23]. By thermal treatment at 1100 °C CuSb$_2$O$_6$ compound is solved into SnO$_2$ matrix up to 25mol% when a solid solution with SnO$_2$ crystal structure (rutile) is formed. For the samples having CuO in excess, the reduction of CuO to Cu$_2$O and formation of the Cu$_3$SbO$_4$$_{5}$ compound occur simultaneously, in air. In some special conditions...
(i.e. high pressure or oxygen pressure) another binary compound, Cu₄Sb₂O₁₉, having a higher copper content, has been identified [24, 25]. We must notify that neither Cu₄SbO₂₅ nor Cu₅Sb₄O₁₉ (cubic structure) dissolves into SnO₂ lattice (tetragonal structure). The studied anode material with the initial composition 96wt%SnO₂, 2wt%Sb₂O₃, and 2wt%CuO has a CuO:Sb₂O₃ molar ratio=1:4 and the formation of Cu₄SbO₂₅ is possible. On the other hand, oxygen evolved at the anode during the electrolysis process could lead to the formation of the Cu₅Sb₄O₁₉ compound. These compounds may be responsible for corrosion process.

IV. CONCLUSION

The high CE values (92%) and good corrosion rates for usual industrial conditions prove that the utilization of SnO₂-based inert anodes still represents a convenient alternative to the present technology of obtaining aluminium with carbon anodes. However industrial application of these anodes requires tests of behavior at long term electrolysis in a bath with lower temperature (<950 °C). In the same time we assume that the most important contribution in the structural changes of those anodes is due to the migration of CuO toward the limits of the constituent grains of SnO₂-based ceramic and that formation of various phases is directly dependent on Cu:Sb molar ratio. When CuO:Sb₂O₃≥1 complex compounds are formed and they are responsible for the corrosion process.

(b) K. Billehaug and H. A. Oye, Aluminium 57, 228 (1981).