Current Efficiency Obtained with SnO_2-based Inert Anodes in Laboratory Aluminium Cell

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A systematic study of the current efficiency (CE) in a laboratory aluminium cell with SnO_2-based inert anodes was carried out by measuring the overall amount of oxygen relieved at the anode, using two different methods.

Inert ceramic anodes of 96% SnO_2, 2% Sb_2O_3, 2% CuO in wt% composition were prepared and investigated. The influence of: temperature, current density, anode-cathode distance, cryolitic ratio, content of alumina and different additives was studied. At the same time the influence of the age of boron nitride (BN) sheath of the inert anode on the CE was evaluated.

Key words: Inert Anodes; Current Efficiency; Aluminium Electrolysis; Ceramic Anodes; Molten Salts Electrolysis.

1. Introduction

The only commercial process in use for making aluminium is the Hall-Heroult process, in which alumina (Al_2O_3) is dissolved in a bath consisting mainly of cryolite (Na_3AlF_6), at temperatures in the region of 950 - 980 °C with carbon anodes. Other common constituents of the bath are AlF_3, CaF_2, LiF and MgF_2. The overall cell reaction will generate Al and CO_2, and the carbon anode is consumed during the electrolysis.

Many attempts have been made to develop inert anodes to replace the carbon anodes, but the search for inert anode materials has proved to be one of the most difficult challenges for modern materials science.

Using inert anodes, the anode product is O_2 instead of CO_2.

Among several materials studied, tin oxide (SnO_2) with different doping materials has proved to be the most promising candidate for manufacturing inert anodes [1 - 3]. Of all the mixtures studied, 96 wt% SnO_2 + 2 wt% Sb_2O_3 + 2wt% CuO gave the best results [4 - 6].

High current efficiency is often used as an optimization criterion in aluminium electrolysis. For this purpose, current efficiency measurements in a small laboratory cell have given valuable information, and results of such experiments are often cited, but very few for SnO_2-based inert anodes [7 - 11].

In the present study, methods of determining the current efficiency (CE) of SnO_2-based inert anodes in aluminium electrolysis have been tested and the dependence of the CE on the electrolysis parameters (temperature, current density, anode-cathode distance) in an electrolyte of constant composition has been determined, studying at the same time the influence of the bath composition (cryolite ratio, alumina content and additives as LiF, MgF_2 and NaCl).

2. Experimental

The measurements of the CE have been done by collecting the total amount of the evolved anodic oxygen gas by two different methods: one with a calibrated manometer and theother with an elastic balloon and some burettes, the calculation method being the same. The electrolysis cell and the system for the quantitative capture and measurement of the anodic gas volume by the first method were described in [10, 11].

Sarting from the equation

$$Al_2O_{3(diss)} \rightarrow 2Al_{(l)} + {}^3/_2\, O_{2(g)},$$

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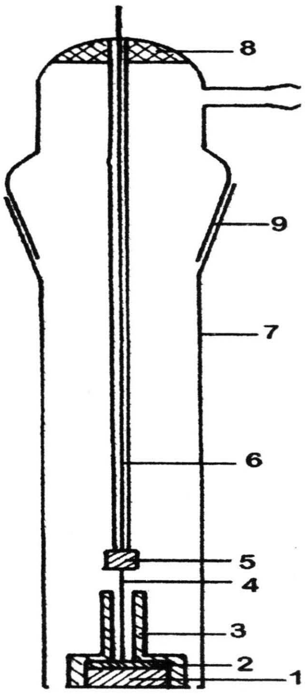

Fig. 1. System of collecting oxygen gas. 1. SnO_2-based inert anode; 2. Copper layer; 3. BN sheath; 4. Pt wire; 5. Mo bonding; 6. Mo wire; 7. Alumina tube; 8. tight closing; 9. ground glass.

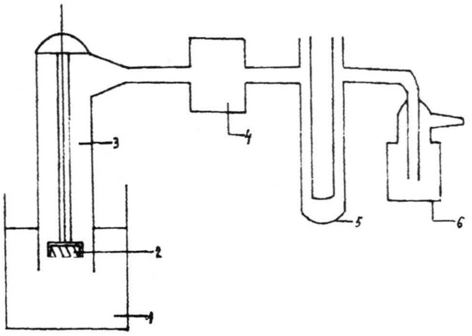

Fig. 2. Method 1 of collecting and measuring anodic oxygen gas 1. molten electrolyte; 2. SnO_2-based inert anode; 3. anodic gas collecting tube 4. control cock (needle valve); 5. calibrated manometer with liquid; 6. water bubbling evacuating vessel.

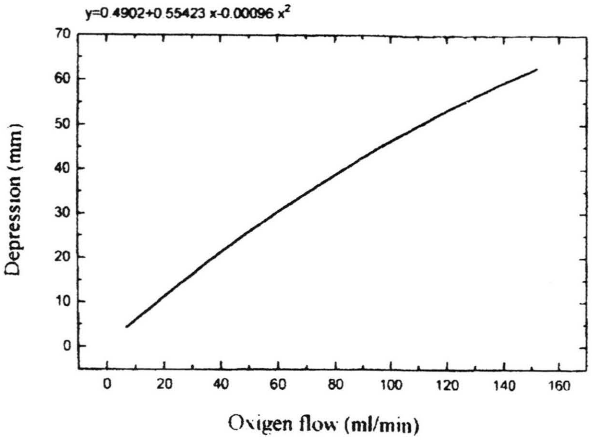

Fig. 3. Calibrated curve of the liquid manometer.

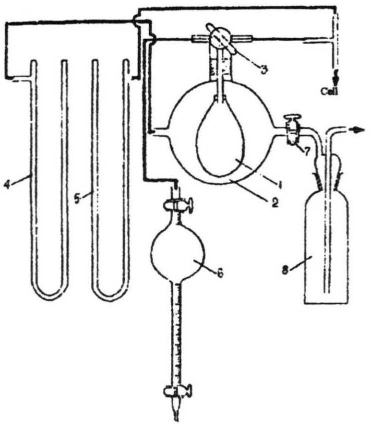

Fig. 4. Method 2 of collecting and measuring the anodic gas. 1. elastic baloon; 2. depressing baloon; 3. cock with 3 ways; 4., 5. liquid manometers for controling the depressing baloon and the level of the melt in the anodic tube; 6. burette; 7. cock for controling the applied vacuum; 8. buffer vessel.

the theoretical volume of oxygen evolved at the anode is

$$V_{\text{oxygen(t)}} = (133.532\, M/P_a)(1 + 0.003663\, t_a),$$

where P_a and t_a are the ambient pressure and temperature; M is for the amount of O_2 obtained in agreement with the current passing through the electrolyte and measured with a coulometer.

Finnaly the current efficiency is determined by the equation

$$\text{CE} = V_{\text{oxygen(exp)}}/V_{\text{oxygen(t)}} * 100,$$

The system of collecting the oxygen gas from the electrolysis cell is presented in Figure 1.

Figures 2 and 3 present the first method of collecting and measuring anodic oxygen gas and the calibrated curve of the liquid manometer.

The second method of collecting and measuring the oxygen anodicaly evolved is presented in Figure 4.

The reagents of p.a. purity employed in the preparation of the electrolyte were from Riedel de Haen and Merck. The electrolyte was contained in a graphite crucible with a sintered alumina lining, but this lining was not used when the effect of alumina concentration was studied. The cell (70 mm inner diameter, 100 mm height) was placed in the central uniform temperature zone of the electric furnace type Auto-Electro Melt-Kerr Manufacturing, USA.

The inert anodes, prepared by a ceramic method, had a composition of 96 wt% SnO_2 + 2 wt% Sb_2O_3 + 2 wt% CuO and were cylinders of 8 mm diameter and 4 mm height. In order to accurately delimit the anode surface area exposed to the cryolite-alumina melt, the anode was fastened in a boron nitrate (BN) sheath.

3. Results

Both methods for collecting and measuring the oxygen anodic gas gave good and similar results, but the first method was simpler.

The current efficiency was found to decrease systematically with increasing temperature and to increase monotonously with increasing current density in the range 0.5 - 2 Acm^{-2}. This evolution is shown in Figure 5. Below 0.2 Acm^{-2} it some oscillations of the electrolysis parameters were found, correlated with a slight corrosion of the anode [12, 13].

The anode-cathode distance (ACD) was defined with respect to the position where the contact with the metallic phase occurs when the anode is lowered, taking as reference the anode surface. Figure 6 shows the effect of the ACD on the CE. These results indicate that the CE does not change significantly when the anode-cathode distance increases above 2 cm, which is essential for saving energy. Those data are in good agreement with the corrosion studies [14, 15].

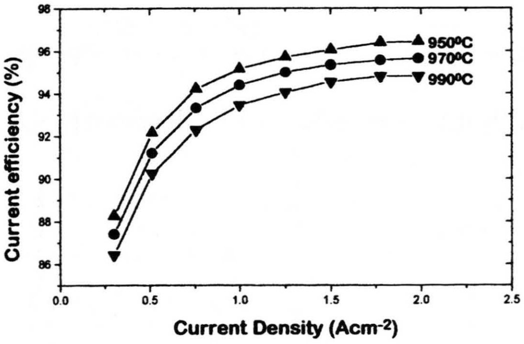

Fig. 5. The influence of the current density and temperature on the current efficiency for SnO_2-based inert anodes in an electrolyte of CR = mol NaF/AlF_3 = 2.48, 5% CaF_2, 5% Al_2O_3.

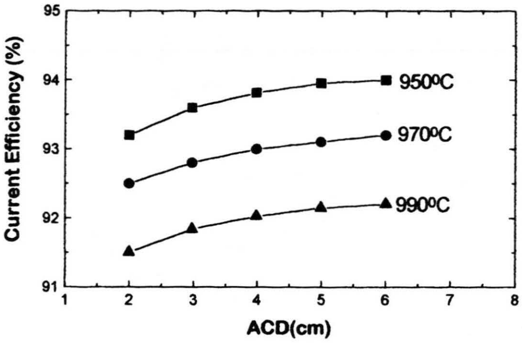

Fig. 6. The influence of anode-cathode distance and temperature on the current efficiency of the SnO_2-based inert anodes in an electrolyte of CR = 2.48, 5% CaF_2, 5% Al_2O_3.

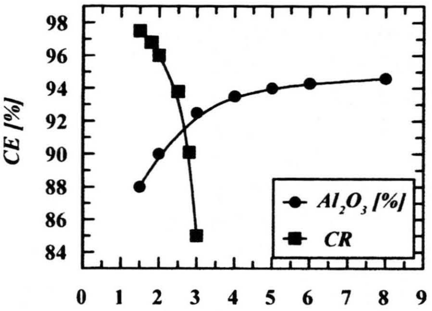

Fig. 7. Effect of the cryolitic ratio and the content of alumina on the current efficiency of SnO_2-based inert anodes in an electrolyte with 5% CaF_2, 4 cm ACD, 0.8 $A\,cm^{-2}$ and 970 °C.

Figure 7 shows the relationship between the CE, the cryolitic ratio (CR = $molNaF/molAlF_3$) and the alumina content. It was found that the current efficiency increases with increasing Al_2O_3 content at medium and high alumina content, while there is a drastic decrease below 2 wt% Al_2O_3, a behaviour which can be explained by drastic corrosion of the inert anode [13, 16]. In the range CR = 2.4 - 3.0, which represent the range used in industrial cells, the experimental data show that the CE decreases monotonously with increasing CR, in good agreement with the destruction of the surface of the SnO_2-based inert anode.

As one of the possibilities to improve the current efficiency is to change the bath composition, the influence of different additives was studied. Those additives were chosen which improve the chemical and physical-chemical properties of the aluminium electrolysis cell [7]. Figure 8 shows that LiF and MgF_2 in-

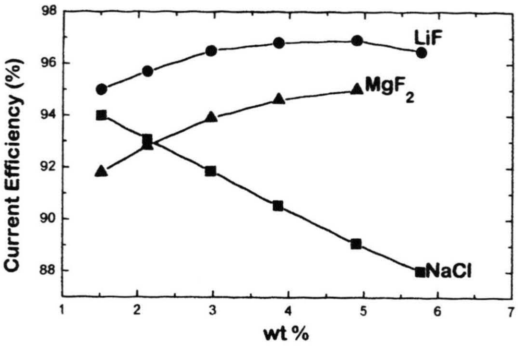

Fig. 8. The influence of various additives on the current efficiency of SnO_2-based inert anodes in an electrolyte of CR = 2.48, 5% CaF_2, 5% Al_2O_3, with 4 cm ACD, 0.8 Acm^{-2}.

crease the CE, while NaCl decreases it. The influence of LiF is greater that that of MgF_2 and this behaviour may be correlated with the increase in the electrical conductivity. However it is not recommended to use more than 3 - 4 wt% LiF, as after 5 wt% LiF a dramatic decrease of the CE is observed and at the same time a destroying of the anode material was seen. It is assumed that this is happening by the penetration of LiF into the structure of the SnO_2-based inert anode.

Because the SnO_2-based inert anode was fastened in a BN sheath it was observed that the current efficiency depends on the age of boron nitride sheath exposed at the oxygen anodic gas. When one uses the same BN sheath for more than three experiments under identical experimental conditions, the current efficiency drops by about 7%. This is shown in Figure 9. The explanation of this behaviour must lie in the properties of the boron material.

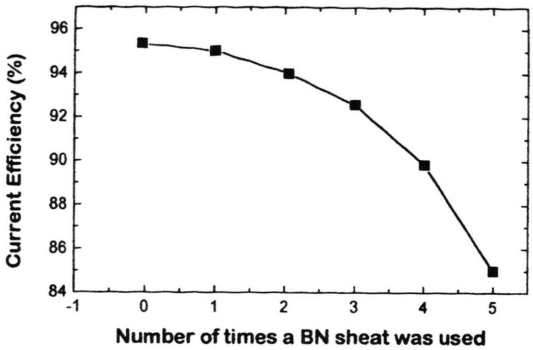

Fig. 9. Correlation between the observed current efficiency and the age of boron nitride sheath of the inert anode.

4. Conclusions

This study proves that the current efficiency determination by means of anodic gas measurements can be carried out successfully in a laboratory aluminium cell with SnO_2-based inert anodes.

The current efficiency obtained with inert anodes of 96% SnO_2, 2% Sb_2O_3, 2% CuO was greater than 91.5%, compared to 87% with carbon anodes, and was in good accordance with the corrosion process.

This proves that utilization of 96% SnO_2, 2% Sb_2O_3, 2% CuO inert anodes could represent an alternative to the present technology of obtaining aluminium with carbon anodes.

Also utilization of those anodes rather than conventional carbon ones allows operation at shorter anode-cathode distance. But industrial application requires tests of the behaviour on long term electrolysis.

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