Microstructure and Electrochemical Behaviour of some SnO$_2$-based Inert Electrodes in Aluminium Electrolysis

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Z. Naturforsch. 57 a, 71–75 (2002); received August 20, 2001

Presented at the NATO Advanced Study Institute, Kas, Turkey, May 4 - 14, 2001.

Some types of anodes that could replace the usual carbon anodes in aluminium production by the Hall-Heroult process are based on SnO$_2$. The present investigation deals with SnO$_2$-Sb$_2$O$_3$-CuO ceramics having an SnO$_2$ content of $\geq$96%), Sb$_2$O$_3$ and CuO being dopants. The ceramic pellets, thermally treated at 1400 °C for 4 hours, were analysed by X-ray diffraction and IR spectroscopy. The structural analysis of the samples evidenced an SnO$_2$ (ss) type solid solution. All samples were electronically conductive (small negative values of the Seebeck coefficients), having an activation energy ranging within 0.02 - 0.3 eV.

The anodic polarisation curves obtained with those anodes in an electrolyte of 88% Na$_3$AlF$_6$, 7% Al$_2$O$_3$ and 5% CaF$_2$ were studied. The results were correlated with the microstructure of the investigated samples.

Key words: SnO$_2$ Ceramics; Inert Anodes; Anode Polarisation; Molten Salts.

1. Introduction

Replacement of the consumable electroconductive carbon anodes of the Hall-Heroult cell by inert SnO$_2$-based anodes has interested many researchers for a long time [1 - 4]. Our studies in this field were centred on ceramics based on Sb$_2$O$_3$ and CuO doped SnO$_2$ [5, 6].

Dense electronconductive ceramics containing more than 90wt% SnO$_2$ were used. The optimum composition (from the viewpoint of the densification and electrical conductivities) was found to be 96wt% SnO$_2$, 2wt% Sb$_2$O$_3$, and 2wt% CuO. In the papers [7 - 9] the electrochemical behaviour of this anode material in a cryolite-alumina bath was studied, and the current efficiency (CE) was evaluated to be $\approx$92%, compared to 87% of carbon anodes.

The optimum working parameters of the electrolysis cell, i.e. temperature, current density, interelectrode distance and electrolyte composition were determined. Due to the fact that anode corrosion appears to be the main obstacle for the use of inert anodes in commercial cells [10], the corrosion rate of SnO$_2$-based inert anodes was studied as a function of the interelectrode distance (ACD), current density (CD) and concentration of Al$_2$O$_3$ and LiF [11].

During the electrochemical investigations some irregularities were found (it seemed that a small amount of oxygen was consumed on the anode).

To understand the causes of these phenomena to diminish or remove them, we studied the chemical processes between the three oxides (SnO$_2$, Sb$_2$O$_3$, CuO) taking place during the thermal treatment.

The studies performed in the SnO$_2$-Sb$_2$O$_3$-CuO ternary system underlined the complex phase relationship [12 - 14].

Thus, tin dioxide and antimony oxide give a limited solid solution with rutile type structure of the Sn$_{1-x}$Sb$_x$O$_2$ form. Copper (II) oxide does not react chemically with SnO$_2$, but it forms a eutectic melt that improves significantly the sintering.

When Sb$_2$O$_3$ and CuO coexist with SnO$_2$, the chemical reaction of CuO and Sb$_2$O$_3$ takes place preferentially, forming CuSb$_2$O$_6$ and/or Cu$_4$SbO$_4$, binary compounds.

In an O$_2$ atmosphere or at high pressure, for a molar ratio CuO/Sb$_2$O$_3$ $>$ 4 the Cu$_4$Sb$_2$O$_{10}$ compound can also be formed [15]. Up to 25mol% CuSb$_2$O$_6$ with
trirutile type structure dissolves in the SnO$_2$ lattice. A solid solution of the Sn$_{1-x}$Cu$_x$/;$_3$Sb$_{2x}$/;$_3$O$_2$ form is obtained. We mention that Cu$_4$SbO$_4$/;$_5$ does not dissolve in the SnO$_2$ matrix, but probably by forming a eutectic melt it will improve the densification properties [12].

The purpose of the present paper was to study the correlation structure-microstructure-electrical characteristics and the anode polarisation of the SnO$_2$-based ceramics.

2. Experimental

The oxide mixtures were prepared from reagent grade (Merck) SnO$_2$, Sb$_2$O$_3$ and CuO. The powders with grain sizes below 60 μm were homogenized wet. Cylindrical samples with ø = 10 mm and variable heights obtained by pressing at 30 MPa were heated to 1400 °C with a 4 hours plateau. A heating rate of 10 °C/min and cooling rate of 20 °C/min was used. After the thermal treatment the samples were analysed by X-ray diffraction, IR spectroscopy and electron microscopy. The ceramic properties density ($d$), porosity ($P_a$) and linear shrinkage ($\Delta l/l$) were determined. To ensure a good electrical contact during the run of experiments, the pellets were polished and gold plated by a special treatment [16].

The resistivity measurements were carried out with a B-641/Wyne Kerr autobalance bridge, in low impedance scheme, connected to an especially designed conductivity cell [16] over a temperature range from 20 to 1000 °C.

Seebeck effect measurements were performed with a special device built up in the NIPM laboratory [17].

The anodic polarization curves were obtained by current-voltage measurements under galvanostatic conditions. Speeds of 3 - 5 steps/min at 10 - 30 mA were applied at increasing and decreasing current [8].

Table 1. Starting composition, phase composition and ceramic properties of the samples thermally treated 4 hours at 1400 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SnO$_2$</th>
<th>Sb$_2$O$_3$</th>
<th>CuO</th>
<th>CuO/Sb$_2$O$_3$ molar ratio</th>
<th>Phase composition</th>
<th>Ceramic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>V (Å$^3$)</td>
</tr>
<tr>
<td>S$_1$</td>
<td>98</td>
<td>2</td>
<td>–</td>
<td>–</td>
<td>SnO$_2$(ss)</td>
<td>71.4</td>
</tr>
<tr>
<td>S$_2$</td>
<td>98</td>
<td>–</td>
<td>2</td>
<td>–</td>
<td>SnO$_2$(ss)</td>
<td>71.4</td>
</tr>
<tr>
<td>S$_3$</td>
<td>97.5</td>
<td>2</td>
<td>0.5</td>
<td>0.91</td>
<td>SnO$_2$(ss)</td>
<td>71.4</td>
</tr>
<tr>
<td>S$_4$</td>
<td>98</td>
<td>1</td>
<td>1</td>
<td>3.71</td>
<td>SnO$_2$(ss)</td>
<td>71.2</td>
</tr>
<tr>
<td>S$_5$</td>
<td>96</td>
<td>2</td>
<td>2</td>
<td>3.70</td>
<td>SnO$_2$(ss)</td>
<td>71.2</td>
</tr>
</tbody>
</table>

* $\Delta V = \frac{V_{\text{sample}} - V_{\text{SnO$_2$}}}{V_{\text{SnO$_2$}}} \times 100\%$, $V_{\text{SnO$_2$}} = 71.5 \text{Å}^3$.

3. Results and Discussions

3.1. Structural, Ceramic, and Electrical Characteristics

The studied samples were labelled with symbols from S$_1$ to S$_5$. Their initial compositions are listed in the Table 1.

According to the initial composition and CuO/Sb$_2$O$_3$ molar ratio (Table 1) the terms of the paragenesis of the samples have been considered belonging to the following systems:

- S$_1$: SnO$_2$-Sb$_2$O$_3$ binary system,
- S$_2$: SnO$_2$-CuO-Cu$_2$O ternary system,
- S$_3$: SnO$_2$-CuSb$_2$O$_6$-Sb$_2$O$_4$ pseudoternary system.

After thermal treatment, the X-ray diffraction data indicate the formation of a rutile type solid solution (SnO$_2$(ss)) as unique phase (Table 1).

A slight contraction of the elementary cell volume of the solid solution compared with SnO$_2$ was evidenced (Table 1).

The ceramic properties, namely apparent porosity ($P_a$), linear shrinkage ($\Delta l/l$) and density ($d$), also presented in Table 1, pointed out an inadequate sintering of the S$_1$ and S$_3$ samples.

In Table 2 the microstructure and electrical characteristics (conductivity, activation energy, and
Seebeck coefficient) of the samples are presented. The presence of liquid phase (sample $S_2$), pores (samples $S_1$ and $S_2$) and $Cu_4SbO_{4.5}$ traces (samples $S_4$ and $S_5$) is mentioned in column 2 of Table 2.

It is well known that the presence of the liquid phase improves the sintering ability of CuO doped SnO$_2$ (the case of the sample $S_2$). The high porosity (Table 1) of the $S_1$, $S_2$ samples indicate the presence of the open pores. Figure 1 shows the porous surface of the $S_2$ sample.

Thermal treatment over 1200 °C makes SnO$_2$($\alpha$) unstable [18]. The following reactions take place:

\[
S_1: \text{SnO}_2(\alpha) \xrightarrow{\beta>1200^\circ\text{C}} (1-x)\text{SnO}_2(\alpha) + x\text{SnO}_2 + y\text{Sb}_2\text{O}_3
\]

\[
S_1: \text{SnO}_2(\alpha) \xrightarrow{\beta>1200^\circ\text{C}} (1-x)\text{SnO}_2(\alpha) + x\text{SnO}_2 + y\text{CuSb}_2\text{O}_6 + z\text{Sb}_2\text{O}_3
\]

and can increase the pore volume.

The samples $S_4$ and $S_5$ belong to the SnO$_2$-CuSbO$_6$-Cu$_4$SbO$_{4.5}$ pseudoternary system containing very small amounts of Cu$_4$SbO$_{4.5}$ which does not dissolve in the SnO$_2$ matrix.

The X-ray diffraction spectrum at the surface of the sample $S_2$, presented in Fig. 2, confirms the presence of this compound, preferentially oriented.

The electrical conductivity $\chi = 1/\rho$ at 970 °C, calculated from experimental resistivity data ($\rho = R S / I$, where $R$ and $S$ stand for the resistance and area of the sample section, respectively, and $I$ is the distance of the voltage contact), is listed in Table 2. The electrical conductivity is quite high in all samples at this temperature, and in agreement with the microstructure of the samples. The highest value of the conductivity was found for the sample $S_4$ according to its high density and large charge carrier number.

The activation energy ($\Delta E_A$), determined from the linear dependency of the $\ln \chi$ vs. $1/T$ with an Arrhenius type relation

\[
\chi = \chi_0 e^{\Delta E_A / RT}
\]

is also given in Table 2. The values range from 0.01 to
Fig. 3. The evolution of anodic overvoltage vs. current density on different anodes. 1: vitrous carbon; 2: graphite; 3: pretreated carbon; 4: SnO₂-based Inert; 5: Pt.

0.3 eV, suggesting electronic type conduction for all investigated samples. The values of the Seebeck coefficient (Table 2) obtained in this investigation support this viewpoint.

3.2. Electrochemical Behaviour in the Cryolite-Alumina Melts

It is well known that the Hall-Heroult process for aluminium production uses consumable carbon anodes. The cell reaction is the following:

\[ \frac{1}{2} \text{Al}_2\text{O}_3 + \frac{3}{4} \text{C} = \text{Al} + \frac{3}{4} \text{CO}_2, \quad E_{\text{rev}} = 1.169 \text{ V}. \]

The anode product, when inert anodes are used, is oxygen, and the cell reaction is

\[ \frac{1}{2} \text{Al}_2\text{O}_3 - \text{Al} + \frac{3}{4} \text{O}_2, \quad E_{\text{rev}} = 2.196 \text{ V}. \]

This large difference in emf between these two processes is partly offset by higher overvoltage on carbon (0.4 - 0.6 V) than on SnO₂-based inert anodes, see Figure 3.

The overvoltage increases with the current density at 970 °C and an obvious difference between the overvoltage of carbon, Pt and SnO₂-based anodes is noted. The anodic process of SnO₂-based anodes occurs with 3 - 4 times lower overvoltage than of carbon anodes, and similar to Pt inert anodes.

In Fig. 4 we present anodic polarization curves of the studied samples, comparatively with those of Pt anodes, obtained in an electrolyte of composition 83wt% Na₃AlF₆ + 7wt% AlF₃ + 5wt% CaF₂ at 970 °C.

Fig. 4. Anodic polarization curves, obtained in an electrolyte of composition 83% Na₃AlF₆ + 7% Al₂O₃ + 5% CaF₂ at 970 °C. ○ (gray): SnO₂ + 2% Sb₂O₃; ●: SnO₂ + 2% CuO; □: SnO₂ + 2% Sb₂O₃ + 0.5% CuO; ■: Pt; △: SnO₂ + 1% Sb₂O₃ + 1% CuO; ○: (dark) SnO₂ + 2% Sb₂O₃ + 2% CuO.

At the current density of 0.8 A cm⁻² (which is used in industry) the highest voltage was found on the S₂ sample. This sample contains a small amount of SnO₂-CuO-Cu₂O ternary eutectic melts, which can act as a potential barrier.

The samples S₁ and S₃, that present the higher apparent porosity (open pores), also exhibit a high voltage.

Voltages similar to those on Pt were obtained on the samples S₄ and S₅. It was noticed that the lowest potential was obtained for the sample S₅, which also has the highest electrical conductivity and the porosity zero.

The presence of the microphase Cu₄SbO₄.₅ at the working temperature (970°C) did not distort the electrical behaviour. Indeed Shinada and Mackenzie [19] identified in the 380 - 1000 °C temperature range, in air, the following chemical reaction:

\[ \text{Cu}_4\text{SbO}_4.5 \rightarrow \text{CuSb}_2\text{O}_6 \frac{380 - 1000 ^oC, in air}{\text{CuSb}_2\text{O}_6} \]

which could improve an additional incorporation of CuSb₂O₆ in the SnO₂ labilized lattice.

The ohmic drops (measured by the interruption current method and with an oscilloscope) on all those electrodes were very high, varying in the range 2.2 to 7 V at 0.8 A cm⁻². Those high ohmic drops exist because of the high resistance in the electrolysis circuit.
4. Conclusion

This study makes for the first time an exhaustive investigation of the structure and electrochemical behaviour of SnO$_2$-based inert anodes.

All the studied samples were presented as a rutile type solid solution, but with different microstructure. The electrical conductivity and the anodic polarization were closely associated with the microstructure of the samples.