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Processing of oxide advanced ceramics as inert electrodes

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Tin dioxide based ceramics, for their excellent corrosion resistance and heat resistant properties, are considered to be promising good materials for manufacturing non-consumable electrodes, in order to replace the carbon anodes in industrial aluminum electrolysis. Our studies in this latter field were focused on the SnO_2-based ceramics doped with Sb_2O_3 and CuO. Different samples of this material were obtained by ceramic method as cylindrical pellets. By X-ray diffraction, and Scanning Electron Microscopy the phase composition and microstructure of the studied materials were investigated. Electrical conductivity was performed in the 293-1273K temperature range into the especial laboratory cell. The electrochemical behavior of tin dioxide – based ceramic as inert anodes was examined in a laboratory scale aluminum electrolysis cell by anodic polarization and preliminary cyclic-voltammetry measurements. The obtained results allow to select the ceramic material to be used as inert electrode in aluminium electrolysis.

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1. Introduction

In recent years, aluminium smelters have made great progress in reducing emissions of various gaseous and particulate compounds that may have a negative impact on the global, regional and local environment [1-2]. The selection of a suitable anode material has proved to be very difficult task. The principal requirements for inert anodes are good electronic conductivity and chemical stability versus the electrolyte and the oxygen gas. The only materials that meet these requirements are a number of oxides. Over the years, many materials have been tested on a laboratory scale with mixed success [3]. One such material is tin oxide (SnO_2) doped with different additives. It is considered to be a promising material for manufacturing electrodes for melts electrolysis due to their excellent corrosion resistance and heat resistant properties. Our studies in this field were centred on the ceramics based on Sb_2O_3 and CuO doped SnO_2 in the compositional range of over 90wt% SnO_2 content [4-11]. 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 in order to diminish or remove them we considered necessary to study the chemical processes between the three oxides (SnO_2, Sb_2O_3, and CuO) that take place during the thermal treatment of their mixture. The studies performed in the all composition range of the initial SnO_2-Sb_2O_3-CuO ternary system underlined the complexity of the processes that took place in this system [12-14]. Thus, tin dioxide and antimony oxide give a limited solid solution with rutile type structure and of the $Sn_{1-x}Sb_xO_2$ form. Copper (II) oxide does not chemically react with SnO_2, but it forms a eutectic melt that significantly improves the sintering ability of the samples. It was found out that when Sb_2O_3 and CuO coexist with SnO_2 the chemical reaction of CuO and Sb_2O_3 takes place preferentially, forming $CuSb_2O_6$ and/or $Cu_4SbO_{4.5}$ binary compound. In an O_2 atmosphere or at high pressure, for molar ratio CuO: Sb_2O_3 >4 the $Cu_9Sb_4O_{19}$ compound can be formed, too [15]. The $CuSb_2O_6$ compound with trirutile type structure dissolves up to 25mol% 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 have mentioned that $Cu_4SbO_{4.5}$ compound does not dissolve in the SnO_2 matrix, but, probably, its presence determines the formation of an eutectic melt that improves densification properties [12].

The present work proposes the study of processing the SnO_2–based anode materials with a view to the enhancing of the electrochemical measurements accuracy in a laboratory cell.

2. Experimental

The oxide mixtures were prepared from SnO_2, Sb_2O_3 and CuO all of reagent grade (Merck). The powders having grain sizes below 60 μm were wet homogenized. Cylindrical samples with ∅ = 10 mm and variable heights obtained by pressing at 30 MPa were thermally treated at 1200 ^oC, for 4 hours. The heating rate of 10^0C/min and cooling rate of 20 ^oC/min was used.

After the thermal treatment they were analysed by X-ray diffraction and Scanning Electron Microscopy.X-ray diffraction was realized using a Scintag Automated Diffractometer (CuK_α radiation - $\lambda_{K\alpha 1}$=1.5406 Å), over the range of 10 to 80^o 2θ. X-ray step scans (0.01^o step size, 2.5 s counting time) were performed to measure the unit cell parameters.The Scanning Electron Microscopy was realized using a SEM Jeol 32 type equipment.

The ceramic properties as density (d), porosity (P_a) and linear shrinkage (Δl/l) by means of conventional procedures were determined.

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 293 to 1273 K. Seebeck effect was determined by means of a special device built up in NIPM laboratory [17].

The cyclic voltammetry was performed with Tacusessel/10-20X potentiostat in a laboratory electrolysis cell at the 1243K temperature and at current density of 0.8 Acm^{-2}. An electrolyte of composition: 83wt% Na_3AlF_6 + 7wt% AlF_3 +5wt% CaF_2 +5wt% Al_2O_3 was used as the electrolysis bath. The Cu/Pt connection was realized according to the method presented previously in the paper [18].

The flow chart of the experimental procedure is presented in the Fig. 1.

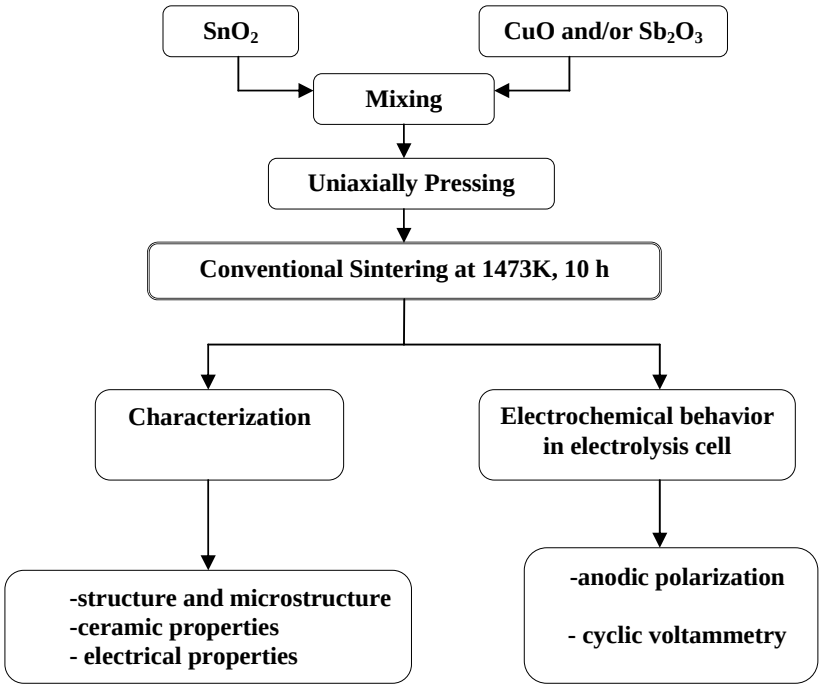

Fig.1. Flow Chart of experimental procedure.

2. Results and discussion

The initial nominal composition of the studied samples labeled SSO, SCO, SS_2CO, SSC_2O and SS_2C_4O is presented in the Table 1.

After thermal treatment X-ray diffraction data indicate the formation of the rutile type solid solution ($SnO_{2(ss)}$) as unique phase (Table 1) although Cu/Sb ratio of the samples SSC_2O and SS_2C_4O is higher than ½ and the $Cu_4SbO_{4.5}$ formation may occur [19]. A slight contraction of the elementary cell volume of the solid solution comparatively with SnO_2 (see Table 1) was evidenced.

Table 1. Initial composition, phase composition and lattice parameters of the samples.

Sample	Initial nominal composition	Phase composition	Lattice parameters		
			$a_0=b_0$ (Å)	c_0 (Å)	V(Å^3)
SnO_2*	SnO_2	SnO_2	4.7382(4)	3.1871(1)	71.55(1)
SSO	$Sn_{0.98}Sb_{0.02}O_{1.99}$	$SnO_{2(ss)}$	4.7343(4)	3.1847(2)	71.38(2)
SCO	$Sn_{0.96}Cu_{0.04}O_{1.96}$	$SnO_{2(ss)}$	4.7373(9)	3.1860(7)	71.50(4)
SS_2CO	$Sn_{0.97}Sb_{0.02}Cu_{0.01}O_{1.98}$	$SnO_{2(ss)}$	4.7263(8)	3.1813(6)	71.06(4)
SSC_2O	$Sn_{0.97}Sb_{0.01}Cu_{0.02}O_{1.975}$	$SnO_{2(ss)}$	4.7344(7)	3.1840(5)	71.37(3)
SS_2C_4O	$Sn_{0.94}Sb_{0.02}Cu_{0.04}O_{1.95}$	$SnO_{2(ss)}$	4.7344(7)	3.1840(5)	71.37(3)

*Literature data – 41- 1445 JCPDS file

The measured lattice parameters were well used for the calculation the bulk density of the substitutional solid solutions by Equation 1:

$$d_c = \{2xA_B + 2yA_C + 2[1-(x+y)]A_{Sn} + 4A_O\} / N_A \cdot V_{SnO2(ss)} \quad (1)$$

where:

- A_B, A_C, A_{Sn} and A_O are the atomic weights of antimony, copper, tin and oxygen
- N_A is the Avogadro's number
- $V_{SnO2(ss)}$ is the unit cell volume of the substitutional solid solution

The relative density was calculated by formula: $d_r = (d_{exp}/d_c)\%$ where d_{exp} is the experimental density measured by Archimede's method and d_c the bulk calculated density from X-ray diffraction data.

In the Fig. 2 the values of the apparent porosity, linear shrinkage and relative density of the ceramics are presented. It can be observed that the samples SSO and SS_2CO present low sintering ability. The high porosity of these samples indicates the presence of the open pores.

By DTA and TG analysis it was established that by thermal treatment over 1473K, the solid solution become unstable and starts to decompose [20]. Following reactions take place:

$$SSO: \quad Sn_{0..98}Sb_{0..02}O_2 \rightarrow Sn_{0.98+x}Sb_{0.02-x}O_2 + x/2Sb_2O_4 \quad (2)$$

$$x/2Sb_2O_4 \rightarrow x/2Sb_2O_3 + x/4O_2 \quad (3)$$

$$SS_2CO: \quad Sn_{0.97}Cu_{0.01}Sb_{0.02}O_2 \rightarrow Sn_{0.97+x}Cu_{0.01-x/3}Sb_{0.02-2x/3}O_2 + xCuSb_2O_6 \quad (4)$$

$$xCuSb_2O_6 \rightarrow x/4Cu_4SbO_{4.5} + 7x/8Sb_2O_3 + 9x/8O_2 \quad (5)$$

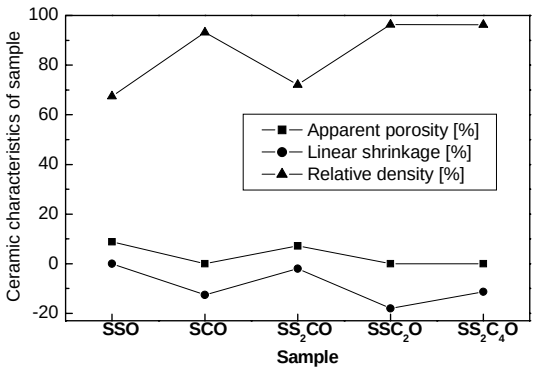

Fig. 2. Ceramic characteristics of the studied samples.

Fig. 3 shows the SEM image of a similar sample with the Cu/Sb ratio=1/2 (SS_2CO). Beside the primary phase composed of the relative uniform grains of about 3 μ, the presence of a secondary phase with grains of smaller size and of pores is evidenced. The secondary phase formation could be explained as a result of the decomposition of the solid solution as mentioned above (reaction 4).

The samples SCO, SSC_2O and SS_2C_4O have the relative density over 90% as it is recommended for anode materials. It is well known that the presence of the liquid phase improves sintering ability of the CuO doped SnO_2 (the case of the sample SC) [21].

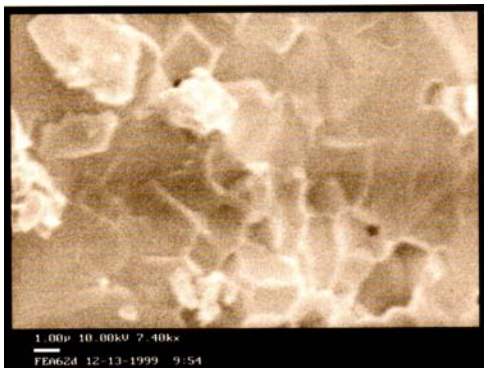

Fig. 3. SEM image of the sample (SS_2CO) with the Cu/Sb ratio=1/2, thermally treated at 1473 K.

For the samples SSC_2O and SS_2C_4O the presence of $Cu_4SbO_{4.5}$ compound and a small quantity of the liquid phase (between SnO_2 and CuO) improve the properties of the sintering.

In this case the $Cu_4SbO_{4.5}$ compound forms at temperature <1273K due to the fact that the Cu/Sb ratio>1/2 (see Table 1) according to the following reaction [13]:

$$CuSb_2O_6 + 7CuO \rightarrow 2\,Cu_4SbO_{4.5} + 2O_2\uparrow \quad (6)$$

During the thermal treatment over 1473K the diffusion of the antimony and copper ions to the surface takes place. This fact was visualized by electron microscopy in the Fig. 4(a-d).

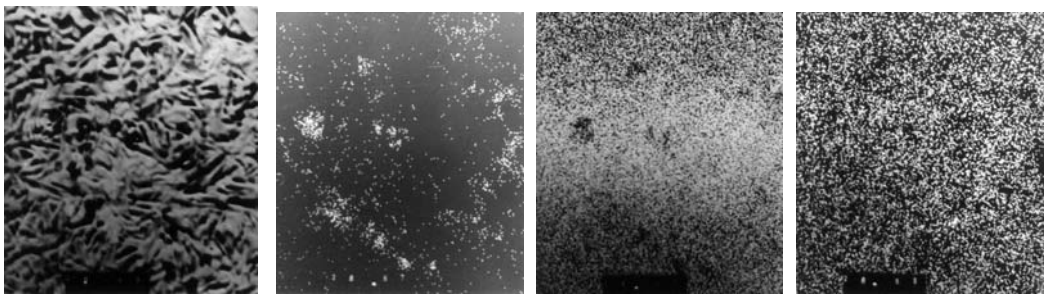

Fig. 4.Microscopy image of the sample with Cu/Sb atomic ratio >1/2. a.) The image of composition; b.) X-ray repartition of tin; c.) X-ray repartition of copper; d.) X-ray repartition of antimony.

The surface of the sample is practically covered with a layer of the $Cu_4SbO_{4.5}$ compound.

The values of the electrical resistivity (ρ) at 1243K, activation energy (ΔE_d) (determinated with an Arrhenius type relation in the 473-873K temperature range) and Seebeck coefficient (C_S) are given in the Table 3. These data indicate a good electronic type conduction for all studied samples.

Table 2. Electrical characteristics of the investigated samples.

Samples	ρ_{1243K}(ohm·cm)	$\Delta E_{d,\ 473\text{-}873K}$ (eV)	C_s (μV/K)
SSO	3.984	0.01	-12.3
SCO	1.859	-	-
SS_2CO	2.008	0.25	-25.8
SSC_2O	1.695	0.3	-1.8
SS_2C_4O	1.397	0.25	-1.7

Those samples were tested as anodes in the electrolysis laboratory bath. The measurements of the anodic polarization performed in a laboratory cell were correlated with the microstructure of the samples [22].

Voltages similar to those on Pt were obtained on the SSC_2 O and SS_2C_4O samples (the composition of electrolyte and conditions presented at Experimental part).

It was noticed that the lowest potential was obtained for the SS_2C_4O sample, which also have the highest electrical conductivity and porosity zero (Fig. 5).

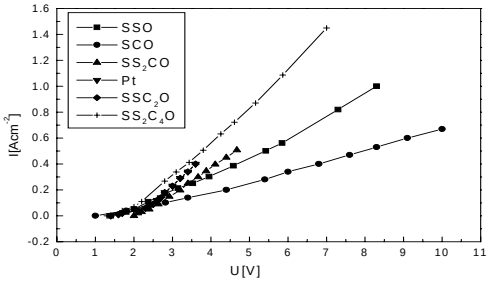

Fig. 5. Polarisation curves for the studied samples compared with Pt anode.

A typical cyclic voltammogram obtained in the experimental presented conditions is shown in Fig.6 and make complete this electrochemical study of the SnO_2-based inert anodes (sample SS_2C_4O).

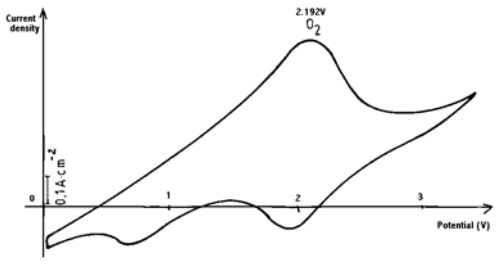

Fig. 6. Cyclic voltammogram recorded with the SS_2C_4O sample anode at 0.4V/s.

Taking in account the voltammograms at different scan rates polarization and the corresponding calculated scanning parameters (presented in Table 4) one can conclude that the oxygen discharge on the SnO_2-based ceramic anodes take place by one step mechanism.

The value of peak potential lies at about a medium value of 2.176V which is very closely to the theoretical reversible potential of the decomposition reaction of alumina:

$$Al_2O_3 \rightarrow 2Al + 3/2O_2 \qquad E_{rev}=2.196V \qquad (5)$$

Two electrons are exchanged without other secondary reactions and the process is reversible as the linearity equation between peak current and scanning rate have shown.

Table 3. Scanning parameters from different cyclic voltammograms obtained with SnO_2- based anode in a cryolite-alumina melt with 5%Al_2O_3 and at 1243 K.

v [V/s]	E_p [V]	$E_{p/2}$ [V]	ΔE	n
0.086	2.162	1.851	0.311	1.89
0.250	2.179	1.876	0.303	1.94
0.400	2.192	1.905	0.287	2.05

where: v = scan rate polarization ; E_p = peak potential ; $E_{p/2}$ = half peak potential ; $\Delta E_p = E_p - E_{p/2}$; n = number of electrons involved in the charge transfer reaction ($n=2.3(RT/\Delta E_p F)$.

It should be noted that the electrochemical behaviour of the samples in the electrolysis laboratory cell might depend on the connective pattern of the cell, so that the obtained results should be specific only to presently employed cell arrangement.

3. Conclusions

Consolidated cylindrical pellets of the CuO and/or Sb_2O_3 doped SnO_2 were obtained by ceramic method and annealing at 1200 ^oC, for 10 hours.

The structure, microstructure and electrochemical behaviour of obtained samples have been investigated. All the studied samples have a rutile type structure.

The microstructure depends of the initial chemical composition. The values of relative density over 90% were obtained only for the samples which contain copper ions.

The electrical resistivity (1.4 - 4.0 ohm·cm) of the samples at working temperature is almost the same. The electrochemical results obtained in a laboratory cell were correlated with the microstructure of the samples.

The obtained results in the present study allow to select the ceramic material to be used as inert electrode in aluminium electrolysis.

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