

Sintering and Behaviour of Tin Dioxide-Based Electrodes

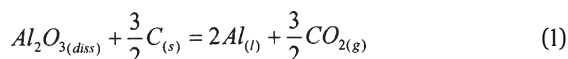
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In the present paper we studied the conditions of obtaining sintered ceramic anodes and we tested their behaviour in a laboratory aluminium electrolysis cell. The material chosen for this study consisted of SnO₂ doped of the optimum composition from the viewpoint of the densification and electrical conductivities was 96 wt% SnO₂ + 2 wt% Sb₂O₃ + 2 wt% CuO. Starting from the studies of granulometry and the pressability curves, cylindrical electrodes were obtained by isostatic pressing. In order to establish in which case the sintering process was complete, a structural analysis of two samples (S₁ and S₂) was made by SEM. The fine granulation of the powder for S₂ generates a higher grade of compactness by pressing and so a better qualitative sintering is achieved. In order to observe their behaviour the ceramic materials (S₁, S₂) were tested in aluminium electrolysis cell. Good results for current efficiency, corrosion, anodic polarization and overvoltage were obtained. Long term aluminium electrolysis has shown that the current and voltage varied in very close limits, which means that those anodes give good results from the point of view of the stability of electrolysis parameter.

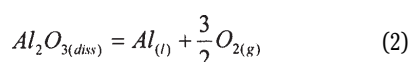
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Aluminium is the third most abundant element in the earth crust and its unique properties has made it the metal experiencing the highest annual growth in demand. The only commercial process in use for making aluminium is the Hall-Heroult process. Alumina, Al₂O₃, is dissolved in a bath consisting mainly of cryolite, Na₃AlF₆, at temperature in the region of 1223-1273K. The dissolved alumina is decomposed electrochemically using carbon anodes and a cathodically polarized metal pad at the bottom of the carbon cell is deposited. The oxygen reacts with the carbon anodes giving CO₂ as made product and the primary cell reaction is given by:



The carbon anode has some inherent disadvantage. The most obvious is directly related to the consumption of anode material. This aspect has led to an exhaustive search for a new technology involving inert anodes.

Inert anodes have been considered for years to be the future of aluminium metal production. An inert anode is characterized by not taking part in the process. In that situation the overall cell reaction of the Hall-Heroult process does not involve the anode material unlike reaction (1). With inert anodes, the total cell reaction can be described by eq. (2), where the dissolved alumina is depolarized at the electrode leading to formation of oxygen at the anode and of aluminium at the cathode:



This reaction has a higher standard emf at 1273K (E~2.19V) than reaction (1), (E=1.16V), but it is however believed that this can be offset by lowering the interpolar distances and by the lower overvoltages associated with inert anodes [1].

The search for inert anodes materials has proved to be one of the most difficult challenges for modern materials

sciences [2]. Great efforts have still not yet led to any fully acceptable material and the work may perhaps best be characterised as a long and mostly unfruitful struggle [3]. The development of inert anodes is, however, presently claimed to be one of the highest research priorities among primary aluminium producers [4].

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. Among several materials studied tin dioxide, SnO₂, has received much attention as a candidate for manufacturing of inert anode because of its very low solubility in cryolite. Two problems have been encountered i.e. the low conductivity of SnO₂ and the difficulties in obtaining a dense sintered structure.

That is why we decided to make this study over the pressing and sintering conditions for elaborating SnO₂-based ceramic anodes. The material chosen for this study consisted of SnO₂ doped with Sb₂O₃ to achieve electrical conductivity and with CuO added as sintered aid. Dense electro-conductive ceramics of rutile type were obtained in the compositional range over 90wt% SnO₂ content. Taking in account literature data on tin oxide inert anodes and former of our studies on those materials [4-15], we used in this study only one composition with two different conditions of elaboration (sample S₁ and S₂). Those samples were also tested from the point of view of chemical and electrochemical behaviour.

Experimental part

The study began with research for characterization the powder mixtures of metallic oxides (SnO₂-Sb₂O₃-CuO) which were then used for preparing ceramic non-consumable anodes.

The "granulometric analysis" of these powder mixtures was done using the Fisher method by determining the medium diameter and the specific surface of the grains. The specific surface was determined by calculating the specific surface of materials for the samples checked. The

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Table 1
GRANULOMETRY ANALYSIS FOR S_1 and S_2 .

Sample	$\phi_{\text{medium}}(\mu\text{m})$	Specific surface ($\text{cm}^2/\text{g}_{\text{material}}$)
S_1	1.32	45.45
S_2	1.26	47.61

mixing of powder oxides (SnO_2 , Sb_2O_3 , CuO) with grain size of 1.2-1.4 μm was mixed and pressed at 30MPa in a special matrix without any temperature. The obtained cylindrical pellets ($\phi=10\text{mm}$ and $h=5\text{mm}$) were then sintered for 6 h at 1673K in an electric laboratory furnace. After the thermal treatment the samples (S_1 , S_2) were subjected to a granulometry analysis by the Fisher method.

Physico-mechanical determinations were also made in order to characterize the pressing capacity of the samples. For this we used an isostatic press, an analytical balance (with precision $1 \cdot 10^{-4}\text{g}$) and a micrometer (with precision $1 \cdot 10^{-3}\text{mm}$). It is well known that the shape and size of a compact material can be modified during sintering as a result of the phase modification during this process.

Those samples were also tested from the point of view of electrochemical behaviour in a laboratory aluminium electrolysis cell presented in a former paper [1,2]. Measurements of current efficiency, corrosion, overvoltage and cyclic voltammetry were made in the same device as those presented in former papers [6, 9, 10]. The flow chart of the experimental procedure is presented in the figure 1.

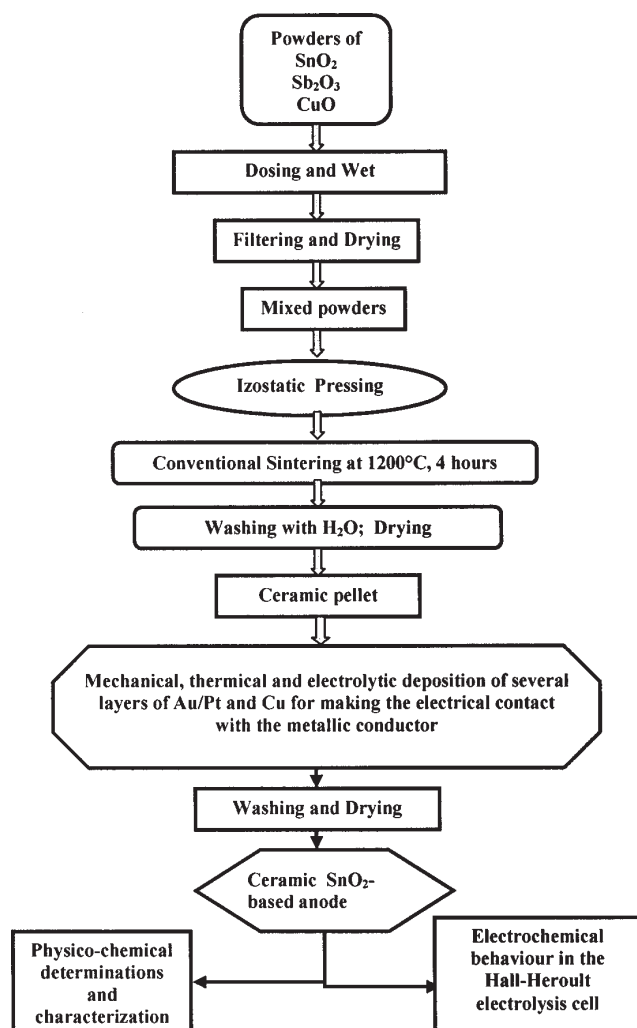


Fig.1 Flow chart of the experimental procedure.

Results and discussion

The ceramic of composition 96wt% SnO_2 -2wt% Sb_2O_3 -2wt% CuO was found optimal from the point of view of electrical conductivity, ceramic properties and densification [4]. Two samples (S_1 and S_2) with the upper composition and having the characteristics presented in table 1, was used in this study.

The results obtained by granulometry analysis on S_1 and S_2 are presented in table 1 and show a good granulometry homogeneity and big specific surface.

From the point of view of the powder metallurgy, the best behaviour has the powder mixtures with low grain size and high specific surface. Those mixtures realize an optimal degree of compactness by pressing and after sintering have good hardness and density. This means that the data from table 1 indicate that from the granulometric point of view both of the studied samples gave good parameters.

It is well known that the shape and size of the ceramic pressed is changing during the sintering process because of the phase changes in the process. The structural changes imply also changes over the size, which are technologically defined as "contraction". The industrial experience has shown that during the sintering process the lowering of the size (so the highering of the contraction) is of 10-20%. That is why has appeared the necessity to establish the contraction by calculation, in order to control

Table 2
CHARACTERISTICS OF THE CERAMIC MATERIAL S_2 .

Parameters	Values
Diameter (mm)	10
Height (mm)	5
Phase composition	$\text{SnO}_{2(\text{ss})}$
$\text{CuO}/\text{Sb}_2\text{O}_3$ molar ration	3.7
Lattice parameters (nm)	$a_0 = b_0 = 0.4732$; $c_0 = 0.3185$
Microstructure	Traces of $\text{Cu}_4\text{SbO}_{4.5}$
Porosity	0
Shrinkage [$\Delta l/l(\%)$]	-11.3
Seebeck coefficient [$C_s (\mu\text{V}\text{K}^{-1})$]	-1.7
Density (gcm^{-3})	6.55
Resistivity (Ωcm)/1243K	1.215
Conductivity ($\Omega^{-1}\text{cm}^{-1}$)/1243K	0.823
Activation energy [$\Delta E(\text{eV})$]	0.01

phenomena and size precision for the sintering sample. The experimental work took care of the bilateral pressing and conclusions were extrapolated to the isostatic pressing.

Any technological process begins with the dosage of the powder material. In order to calculate the "contraction" the powders must be well measured by gravimetric or volumetric analysis. Better results were obtained by the volumetric dosing. We are interested in identifying the mass of powder necessary for filling the cavity of the matrix with the mass of pressed ceramic.

Starting from the relation:

$$V_{fill} \rho_{fill} = V_{press} \rho_{press} \quad (1)$$

where:

V_{fill} = volume of the material to fill the press matrix (cm³)

V_{press} = volume of the pressed shape (cm³)

$\rho_{fill}, \rho_{press}$ = corresponding densities (gcm⁻³)

$V_{fill} = S_l * h_{fill}$ and $V_{press} = S_t * h_{press}$

S_l = cross section

h_{fill}, h_{press} = heights of the filling and pressed material the filling coefficient (C_{fill}) can be calculated:

$$C_{fill} = \frac{h_{press}}{h_{fill}} = \frac{\rho_p}{\rho_{fill}} \quad (2)$$

so that :

$$h_{fill} = h_{press} \frac{\rho_p}{\rho_{fill}} \quad (3)$$

Knowing the theoretical density of the powder material (ρ_p) can be calculated the "linear contraction" (C):

$$C = \left[1 - \frac{\rho_p}{\rho_s} \right]^{-1/3} * 100(\%) \quad (4)$$

where: ρ_s = density of the sintered material.

Taking in account the volumic anisotropy of the contraction it is necessary to determine the linear contraction (on the pressing direction) and the transversal contraction (perpendicularly on the pressing direction). For that we plotted the pressability curves [$\rho_s = f(p)$] by experimental determinations. This is very important especially as it was observed variation of granulometry not only from sample to sample, but also in the same sample of powder mixture. So by measuring the shape of the cylindrical samples (S_1 and S_2) before and after sintering for a well known pressing force we obtain:

-the contraction on the pressing direction as :

$$C_h = \left(1 - \frac{h_p}{h_s} \right) * 100 \quad (5)$$

-the contraction on the normal direction as:

$$C_p = \left(1 - \frac{\Phi_s}{\Phi_p} \right) * 100 \quad (6)$$

where:

C_h = contraction of the height of the pressed material

C_p = contraction of the diameter of the pressed material

h_p, Φ_p = height and diameter of the pressed material

h_s, Φ_s = height and diameter of the sintered material.

The size of C_h and C_p was determined for different pressing forces (p) and then pressability curves may be plotted. From the pressability curve te optimal pressing

conditions (wt of the pressing material and the heigh of the pressed ceramic obtained) can be established.

As we know the size of the sintered pellets, the C_p of the presses pellet can be easily determined with equation (6) by measuring the size and shape (with balance and micrometer). The value of C_h corresponding to the determined C_p is taken from the diagram $C_h C_p = f(p)$. For the samples S_1 and S_2 the pressability curves [$C_h(\%) = f(p)$] and the diagram [$\rho_p = f(p)$] were plotted (fig. 2,3 and 4).

From the figure 2 and 3 the optimal range of the pressing forces was established to be 900-100 daN for S_1 and 700-900 daN for S_2 .

The degree of compactness by pressing was found higher for S_2 as shows the figure 4 where S_1 exhibits a modulation in the range of the pressing force of 200-700daN.

In order to establish in which case the sintering process was complete and good for obtaining inert anodes a structural analysis of the samples was made by SEM.

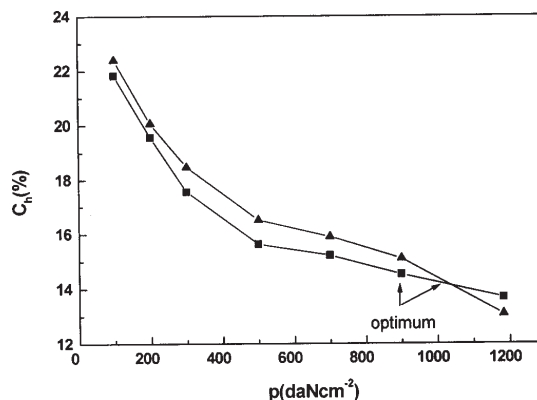


Fig.2. Pressability curve for S_1

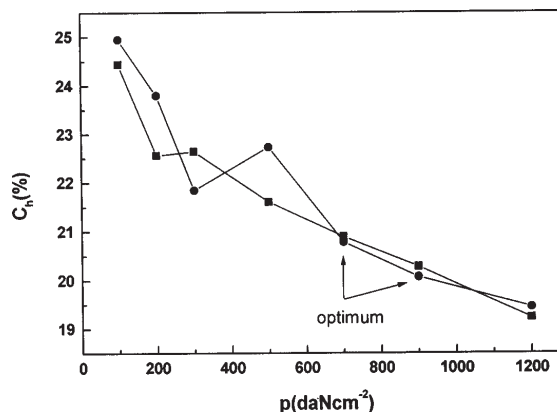


Fig.3. Pressability curve for S_2

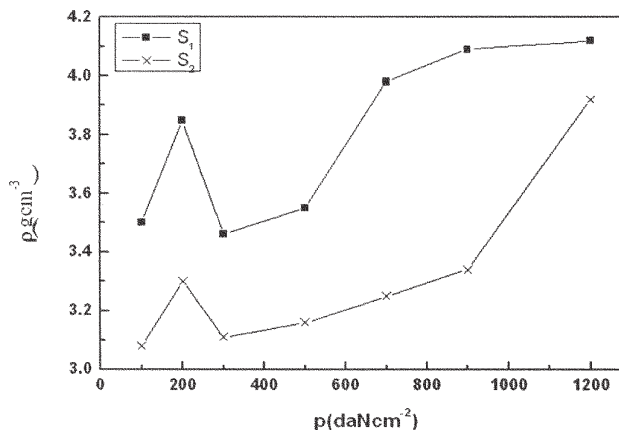


Fig.4. Variation of the powder density with the pressing pressure for S_1 and S_2

The structural analysis by SEM made on those two samples is presented in figure 5 and 6. The sample S_2 presents a more compact structure with crystals better evidenced and a higher homogeneity.

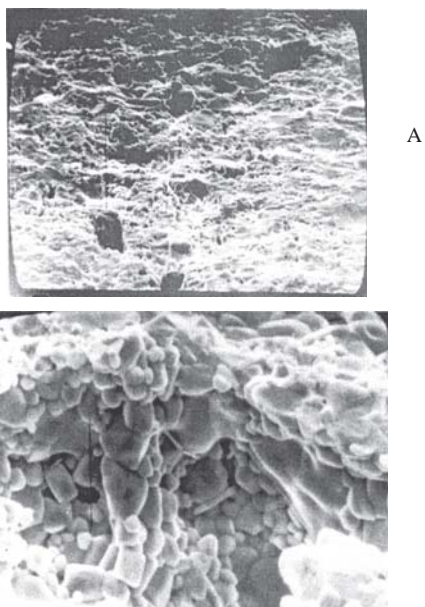


Fig.5 SEM analysis on sample S_1 : A= .1000 ; B= . 5000

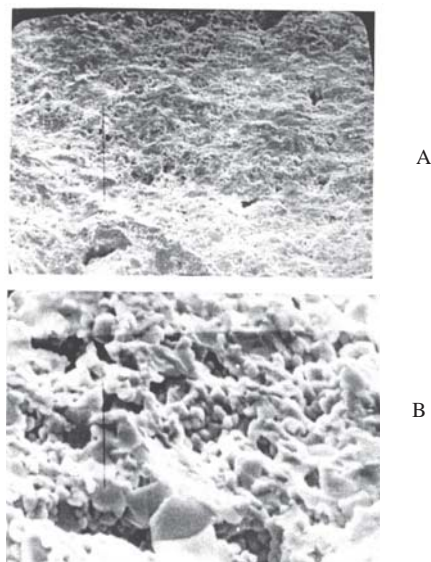


Fig.6. SEM analysis on sample S_2 : A= .1000 ; B= . 5000

In the SEM picture for S_1 , 1000 (fig. 5a) it is clearly noticed an inclusion. The sintering process is better for S_2 (fig. 5b). So we can appreciate that the better qualitative sintering of S_2 is done by the fine granulation of the powder which generates a higher degree of compactness by pressing.

In the same time as a result of the SEM analysis we suppose that the bind with the pressing material is not homogeny. This can produce (generate) agglomeration of the metallic oxide grains, which during sintering can form crystallite generating porosities. Also it is possible to make agglomeration of the binder which during the sintering process could generate little holes and crystallite porosities of cavity type and faults (as shown in fig. 5b).

However we assume that this degree of porosity is not disturbing for our purpose and will not produce breaking in the ceramic materials.

In conclusion it seems that the mechanical process of making those samples (S_1 and S_2) is not the better one from the point of view of homogenization and it is necessary to realize this process by better granulation on an atomizer or by a higher time of homogenization.

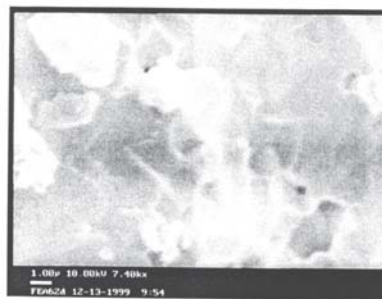


Fig.7 SEM analysis on new sample S_2

Table3
CORROSION RATE OF THE CERAMIC ANODE S_2 FUNCTION OF THE COMMON OPERATING PARAMETERS AND ADDITIVES USED IN THE HALL-HEROULT PROCESS.

Parameters	Corrosion Rate ($\text{gcm}^{-1}\text{h}^{-1}$)
c.d. = 0.7-0.9 A/cm^2	0.0209-0.0231
ACD = 2-4cm	0.0037
Al_2O_3 (5 wt%)	0.0312
LiF (3 wt%)	0.0650

c.d. = current density

ACD = anode-cathode distance

After making a new and better process of homogenization we obtain samples of S_2 composition with better properties (fig. 7).

Those pellets were tested as inert anodes in a laboratory aluminium cell. The current efficiency of an aluminium electrolysis cell with a S_2 anode was determined and results are presented in figure 8.

The current efficiency increases monotonously with increasing c.d. in the range 0.5-2 Acm^2 and does not change significantly when the ACD increases above certain limit, here about 2 cm. According to data from figure

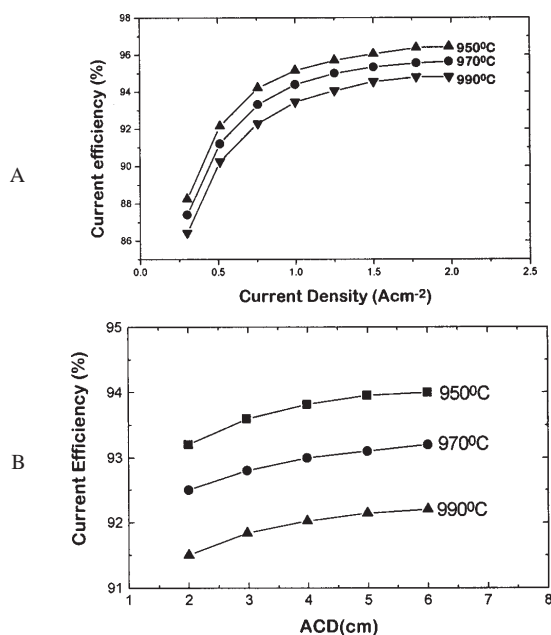


Fig.8 The influence of temperature and electrolysis parameters over the current efficiency of the aluminium electrolysis with an S_2 -anode: A. current density; B. anode-cathode distance.

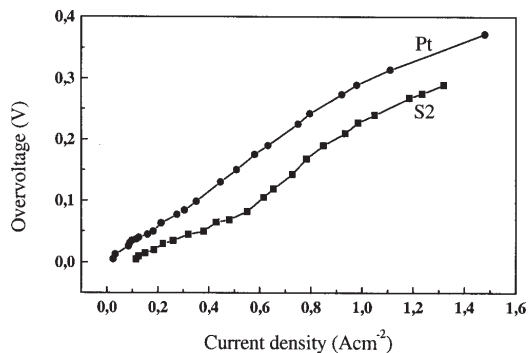


Fig. 9. Anodic overvoltage on S₂ and Pt anodes

8 the current efficiency decreases with increasing the temperature of the electrolyte. In the study of current efficiency low below the 0.2 A/cm² range oscillations of electrolysis parameters were noted. In this area a slight corrosion of anodes was also observed.

According to literature data [10, 15] the corrosion mechanism refers to direct reduction of the anode material by dissolved metal, reaction which takes place if dissolved metal reaches the anode surface and this may occur when anodic current density is zero or close to zero. The lower current efficiency over the current density below 0.3 A/cm² could be correlated with similar process. To avoid any corrosion the current density range 0.5-0.8 A/cm² are recommended.

The behaviour of the S₂ anode from the point of view of corrosion was studied by gravimetric measurements and the obtained data are presented in table 3.

In order to complete the electrochemical study some measurements were done on S₂ anode along with a Pt anode. From polarization curves we observed that S₂ anode has similar voltages as the classical Pt inert anode. We also found that overvoltage on those S₂ anodes is 4-6 times lower than on carbon anodes, behaviour that suggests an interdependence of the overvoltage with the porosity of the studied materials (fig. 9)

Finally a long term aluminium electrolysis (~60h) on those anodes (fig. 7) has shown that the current and voltage varied in very close limits (0.65±0.05 A and 4.25±0.25V), which means that those anodes give good results from the point of view of the stability of electrolysis parameters as shown in figure 10.

As the anodes showed no visible sign of wear or corrosion after removal from the cell, it was believed that the voltage rise experienced with the highest current density occurred at the cathode. Taking in account all our former systematic studies on those materials on phase composition and microstructure, we conclude that the formation of a complex compound during the sintering process make the initial solid solution unstable. These

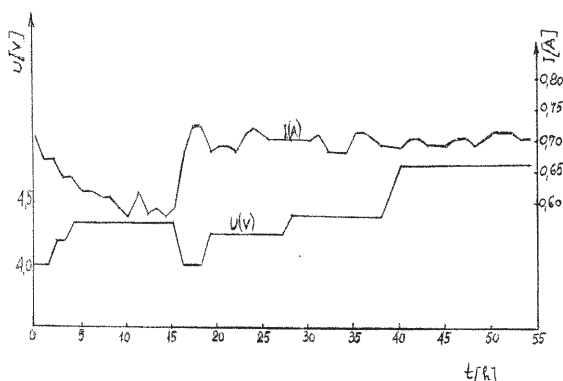


Fig.10. Variation of current and potential during the aluminium electrolysis with an 96%SnO₂-2%Sb₂O₃-2%CuO anode

complex compounds (Cu₈Sb₂O₉) which appear on the surface of the inert anodes represent grains for the corrosion process. The SEM investigations did on the anodes samples after electrolysis and it is obvious the direct action of the cryolite-alumina bath on the ceramic material. However literature showed that all oxide materials have a finite solubility in the tested electrolytes and consequently the anode materials will corrode slowly and corrosion products will be reduced into the aluminium produced and so unacceptable aluminium contamination may result.

Because those ceramic anodes have many good properties we propose that in future to study the possibility of using them in magnesium electrolysis where the electrolyte is not so aggressive.

A same subject was studied in [17].

Conclusions

An exhaustive study on the pressing condition of obtaining sintered ceramic SnO₂-based inert anodes was done and the optimum conditions were established correlated with the structure of the obtained material. Those anodes were tested in aluminium electrolysis cell and good results from the point of view of electrochemical behaviour were obtained. However a slight solubility takes place which contaminate the aluminium product. Taking in account the good properties of those inert anodes we propose to test them in the future in magnesium electrolysis.

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