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SnO_2 - BASED INERT ANODES FOR ALUMINIUM ELECTROLYSIS. THE INFLUENCE OF CeO_2 ADDITION ON THE ELECTRICAL RESISTIVITY.

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ABSTRACT

Five recipes of SnO_2 - based ceramics masses were prepared. The influence of CeO_2 additions on the properties of ceramic masses was studied. It was found that the CeO_2 additions increase the electrical resistivity of these ceramic masses, but the electrical resistivity decreases with the CeO_2 content. The CeO_2 additions have the same influence on the activation energy for conductivity.

RESUMO

Foram preparadas cinco massas cerâmicas baseadas em SnO_2. Foi estudada a influência de CeO_2 sobre as propriedades destas massas. A adição de CeO_2 aumenta a resistividade elétrica, porém esta diminui em função do teor de óxido de cério. As adições de CeO_2 tem a mesma influência sobre a energia de ativação para condutividade.

KEYWORDS: **Inert anodes; aluminium electrolysis.**

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1. Introduction

It is very well known that the one of most crucial problems for the use of inert anodes for aluminium production is the slight corrosion resistance of these anodes during the electrolysis in cryolite - alumina melts.

In several papers and patents[1-6] MOLTECH and ELTECH proposed a method to increase the corrosion resistance of these ceramic anodes. This method was used both in the case of the anodes prepared from SnO_2 - based ceramics and in the case of anodes made from cermets. The method consists in introducing a Ce(III) salt in the molten electrolyte. During electrolysis, in the neighbourhood of the anode, the cerium is oxidised and precipitated as an oxifluoride compound deposited like a crust on the anode surface. In this way, a compact layer, adherent to the anode and with a good electronic conductivity is obtained. This layer is protective against the corrosion of molten cryolite.

The ELTECH company tested both in the laboratory and in a pilot plant[5,6] the corrosion resistance of some inert ceramic anodes covered with a protective layer of CeO_2. It was found that the corrosion was reduced about 10 times.

At the cathode in the presence of molten aluminium, the following reaction can occur:

$$CeF_3 + Al = AlF_3 + Ce$$

For this reaction $\Delta G^0 = 259$ kJ/mol, therefore the equilibrium of reaction is removed to the left.

In the present paper are shown results of the electrical resistivity measurements of some ceramic masses: SnO_2 - Sb_2O_3 - CuO - CeO_2 which can be formed on the anode surface during electrolysis.

2. Experimental

The following compositions of SnO_2 - based ceramics masses were prepared:

1. 98% SnO_2 + 2% CeO_2
2. 96% SnO_2 + 2% CuO_2 + 2% CeO_2
3. 95% SnO_2 + 2% SbO_3 + 2% CuO + 1% CeO_2
4. 94% SnO_2 + 2% SbO_3 + 2% CuO + 2% CeO_2
5. 92% SnO_2 + 2% SbO_3 + 2% CuO + 4% CeO_2

These were prepared by mixing the powders in water for 15 hours and then, after drying, by mixing them again with 2 - 3 % polyvinilic alcohol solution, as a binding agent. Pellets having 10 mm in diameter and 3 - 4 mm in height were pressed in a cylindrical mould at 150 atm. The pellets were sintered for 4 hours at 1300^{0}C in an electric furnace. For measuring the electrical resistance of the pellets, they were silver-coated on both sides with silver conducting paste that was then sintered at 700^{0}C. The electrical resistivity of these pellets in direct current was measured. We found that, due to the current passed through it, the pellet gets warmer. For reaching reproducible results, the pellet was thermostated in water at different temperatures.

3. Results and Discussion

The apparent density of the five ceramic masses were measured and the following values were found (Table 1).

The literature[7-10] show that these ceramics have good properties if their apparent density is at least 6.0 g cm^{-3} after sintering. It is noticed from Table 1 that recipe 1, with the composition: 98% SnO_2 + 2% CeO_2 has a very low density, therefore these ceramics are not sintered. The other recipes have good densities, but there is no correlation between the density and the CeO_2 content.

Table 1. Apparent densities of the ceramic masses: SnO_2 - Sb_2O_3 - CuO - CeO_2; t = 20^0C.

Recipe	Apparent density (g/cm^3)
1.	4.36
2.	6.12
3.	6.24
4.	6.37
5.	6.34

As shown in our previous paper[11-12] the electrical resistivity of the SnO_2 - based ceramic masses decreases exponentially with increasing current intensity. The same situation was found for the compositions studied in the present paper, as it is seen in Fig. 1 for recipe no. 5. Likewise, Fig. 1 shows that the electrical resistivity decreases with increasing temperature and this fact proves that these ceramics are semiconductors of n type, hence they have an electronic conduction.

The variation of electrical resistivity of the five ceramic masses, studied as a function of the current intensity is given in Fig. 2. The measured surfaces of the pellets were 0.5 - 0.55 cm^2, therefore the current intensities are twice higher. It is noticed that recipe no. 1 has the highest electrical resistivity, but this composition has the lowest density and is not well sintered.

Recipe no. 2, with CuO and CeO_2 as dopant has a lower electrical resistivity. As shown in our previous paper[11-12], the best SnO_2 - based ceramic mass is that which contains 2% SbO_3 and 2% CuO and has the electrical resistivity about 3-10 Ωcm in function of the quality of the raw materials and the sinterization temperature. If to this recipe, 1%, 2% or 4% CeO_2 is added, the ceramic masses no. 3 - 4 - 5 are obtained and their electrical resistivity are shown in figure 2. The CeO_2 addition in any proportion in the ceramic mass 96% SnO_2 + 2% SbO_3 + 2% CuO will increase its electrical resistivity. As seen in Fig. 2, the semiconductor resistivity decreases by CeO_2 concentration increasing.

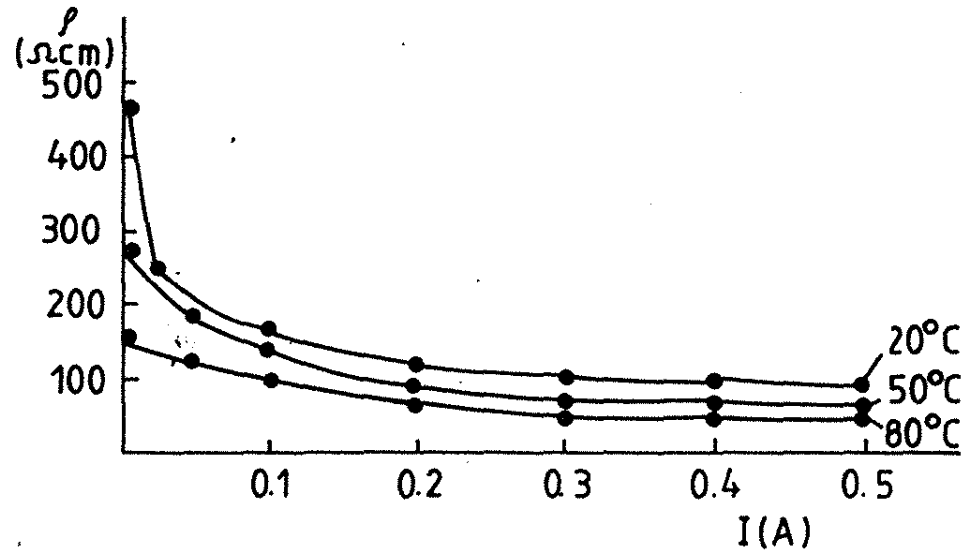

Fig. 1. Variation of the electrical resistivity of the ceramic mass: 92% SnO_2 + 2% SbO_3 + 2% CuO + 4% CeO_2 as a function of the current intensity and temperature.

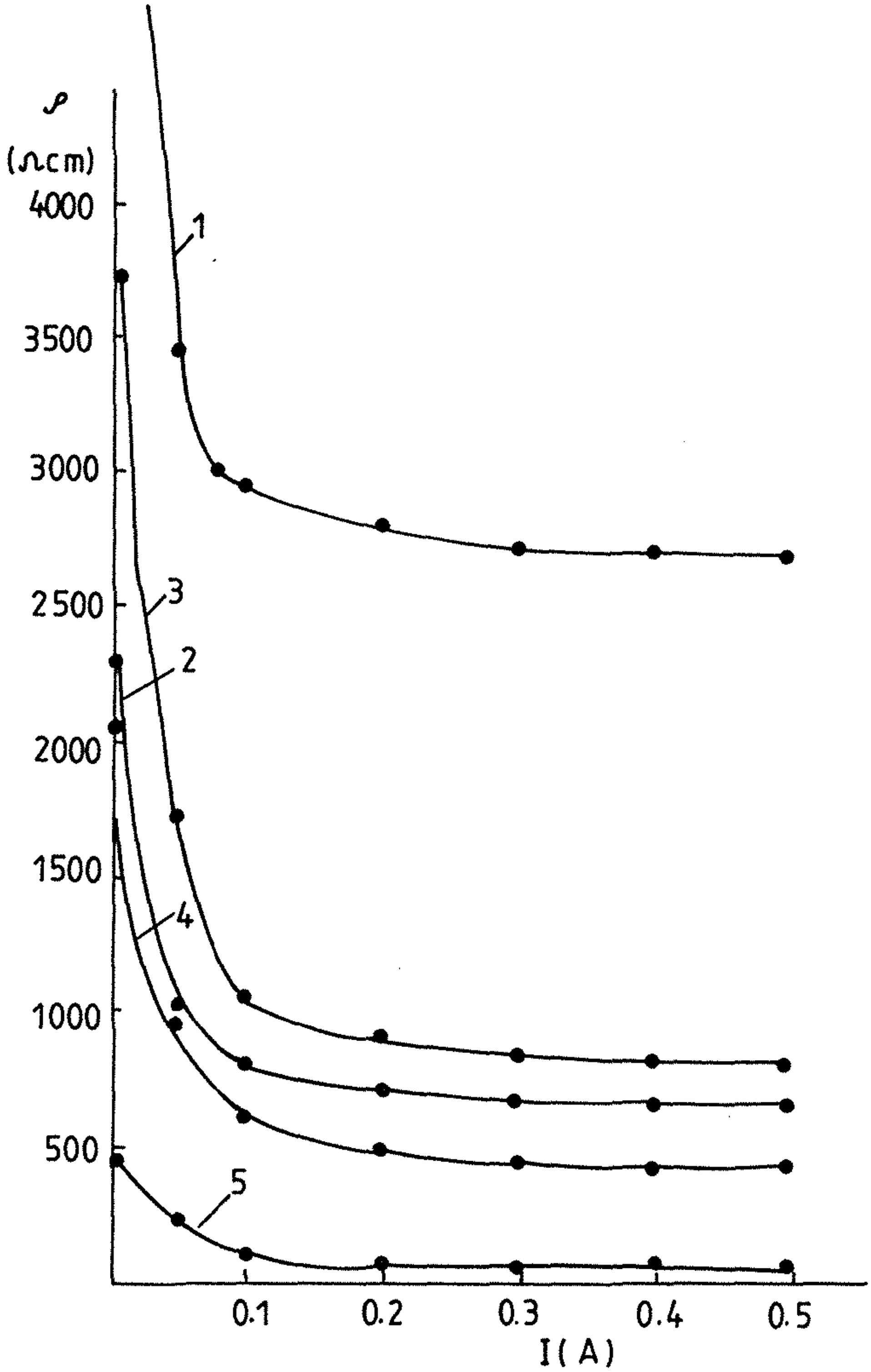

Fig. 2. Variation of the electrical resistivity as a function of the current intensity at $t = 20^0$ C of the ceramic masses with the following composition:

1. 98% SnO_2 + 2% CeO_2
2. 96% SnO_2 + 2% CuO_2 + 2% CeO_2
3. 95% SnO_2 + 2% SbO_3 + 2% CuO + 1% CeO_2
4. 94% SnO_2 + 2% SbO_3 + 2% CuO + 2% CeO_2
5. 92% SnO_2 + 2% SbO_3 + 2% CuO + 4% CeO_2

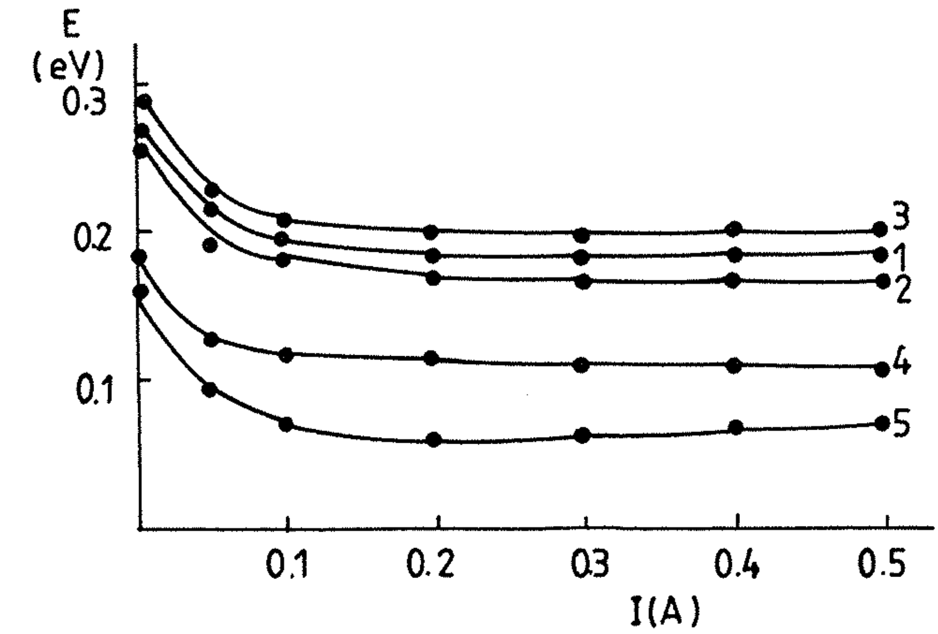

Fig. 3. Variation of the activation energy for electrical conductivity as a function of the current intensity at t = 20^0 C for ceramic masses with the following compositions:

1. 98% SnO_2 + 2% CeO_2
2. 96% SnO_2 + 2% CuO_2 + 2% CeO_2
3. 95% SnO_2 + 2% SbO_3 + 2% CuO + 1% CeO_2
4. 94% SnO_2 + 2% SbO_3 + 2% CuO + 2% CeO_2
5. 92% SnO_2 + 2% SbO_3 + 2% CuO + 4% CeO_2

Based on the electrical resistivity values, the electrical conductivities were calculated, and from the variation with temperature, the activation energies for conductivity were also derived as shown in Fig. 3. A similar variation as with the electrical resistivity was noticed .

If, for the basis recipe: 96% SnO_2 + 2% SbO_3 + 2% CuO, one adds 1%, 2% or 4% CeO_2 ceramic masses were obtained for which the activation energy for conductivity decreases with increasing CeO_2 content. For recipe no. 5, which contains 4% CeO_2, the activation energies are of the same order of magnitude as in the case of the basis recipe: 96% SnO_2 + 2% SbO_3 + 2% CuO[11]. Recipes no. 1 and 2, which contain other compositions, have intermediate values of the activation energy.

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