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Contribution to the study of SnO_2-based ceramics

Part II *Effect of various oxide additives on the sintering capacity and electrical conductivity of SnO_2*

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The SnO_2-based ceramic materials are interesting mainly as candidate materials for stable electrode construction for the aluminium electrolysis and other industrial applications. In all cases, a high density and electrical conductivity are imperative. It was found that the electrical conductivity is closely associated with the density of various oxide mixtures. The investigation into the influence of various oxide additives, namely Sb_2O_3, CuO, ZnO, La_2O_3, Cr_2O_3, Fe_2O_3, TiO_2, MnO_2 and MoO_3, showed that only CuO increases the density of the composites. The addition of Sb_2O_3, which is claimed in the literature to increase the electrical conductivity, was found to be effective only in the presence of CuO. Based on the experimental results, the composite containing 2 mass % Sb_2O_3 and CuO was found to be best suited for the industrial utilization.

1. Introduction

Natural SnO_2 crystals are typical insulators below $-269\,^{\circ}C$ while above room temperature they exhibit semiconductor properties, their electrical conductivity ranging from 10^{-6} to $10^{-1}\ S\,cm^{-1}$, depending on the temperature and the nature and purity of tin(IV)oxide [1–4]. Studies on the electrical conductivity of SnO_2-based ceramic materials revealed the major influence exerted by the nature of the dopants and the thermal treatment, i.e. the sintering conditions. The electrical resistance is claimed [5–9] to be decreased drastically (by 4 to 5 orders of magnitude) by the addition of Sb_2O_3 as, following its limited solubility in the SnO_2 lattice, the concentration of charge carriers increases. On the other hand, the sintering capacity was found to be greatly improved by the addition of CuO [10–14]. Although a list of various potential additives has been suggested by Alder [15], their influence on the sintering properties (namely densification) and electrical conductivity has not been systematically investigated thus far.

This contribution presents new data on the influence of a series of oxide additives (individual and various combinations), namely Sb_2O_3, CuO, ZnO, Fe_2O_3, Cr_2O_3, TiO_2, MnO_2 and MoO_3 on the sintering capacity and electrical conductivity of the SnO_2-based ceramic materials. These data are considered to be of interest with respect to the development of stable electrodes, e.g. for the aluminium electrolysis (inert anodes [16]) and for the glass industry electrodes for the electric furnaces [17]. In both cases, a high density and electrical conductivity are imperative.

2. Experimental details

All the chemicals employed were of a reagent (p.a) grade. The oxide mixtures were obtained by wet homogenization of powders with a particle size of less than 60 µm. Pellets with various diameter, 10 to 20 mm, which were utilized in the density, relative shrinkage and electrical resistivity measurements, were obtained by pressing in a double-action cylindrical die at 50 MPa.

In the investigation into the sintering capacity of the SnO_2-based composites, the pellets were heated to 1200 °C at a rate of $10\,^{\circ}C\,min^{-1}$, kept for 30 min at this temperature and subsequently cooled at a rate of $20\,^{\circ}C\,min^{-1}$. The procedure employed was described in Part I of this series [14].

The pellets for resistivity measurements were subjected to a four hours thermal treatment at 1200 to 1300 °C and after cooling, the plate surfaces were polished and platinum plated to ensure a good electrical contact with the platinum discs of the pellet holder (Fig. 1).

The resistivity ρ was measured with a B-641 type Waine Kerr autobalance bridge in a low impedance

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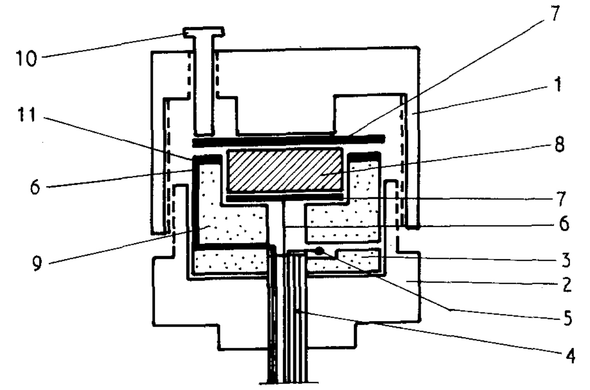

Figure 1 The pellet holder for conductivity measurements. 1, 2 refractory steel threated bodies; 3 boron nitride ring; 4 four channel insulator; 5 Pt–PtRh thermocouple; 6 platinum wire; 7 platinum electrodes; 8 semiconductor pellet; 9 boron nitride support; 10 stainless steel screw; 11 platinum ring.

scheme over a temperature range from 20 to 1000 °C. The shrinkage, $\Delta l/l_0$, of tested samples was determined by a NET 2 SCH dilatometer and the density d by the hydrostatic method (in mercury).

3. Results and discussion

The data on the relative shrinkage, bulk density and electrical conductivity of the oxide mixtures studied are listed in Table I. From a comparison of the corresponding values it becomes evident that the electrical conductivity is closely associated with the sintering capacity of the oxide mixtures. The highest conductivity values were determined for the CuO-containing samples, this apparently being the sole additive promoting the densification of SnO_2-based composites.

The dependence of the resistivity on the temperature for some selected samples is shown in Fig. 2. As evinced by curves 1 to 3 in Fig. 2, the ρ against t dependence for the ternary system SnO_2–Sb_2O_3–CuO exhibits a pronounced drop of resistivity in the temperature interval from 20 °C up to 100 to 500 °C, depending on the composition. Above the upper limit of this interval, the course of this dependence is virtually parallel with the x axis which indicates that the resistivity is independent of temperature. An entirely different picture is observed for the addition of ZnO and multicomponent additions of various oxides where the resistivity achieves a constant value only at essentially higher temperatures (curve 4) or it is strongly temperature dependent over the whole temperature range investigated (curves 5 and 6).

According to Fig. 2, the presence of Sb_2O_3 in the SnO_2-based composites ensures an exclusively extrinsic conductivity with activation energy ranging within 0.02 to 0.4 eV (curves 1 to 3). The linear slow variation of log ρ against $1/T$ is similar to that encountered in metals and suggests a direct dependence of electron mobility on temperature.

The ZnO-containing mixtures also exhibit the feature of a n-extrinsic semiconductor (curves 4 to 6), but there are regions corresponding to intrinsic semiconductors (973 to 1223 K, $U = 1.84$ eV) and to dopants (293 to 573 K, $\varepsilon_D = 0.66$ to 0.08 eV). The sections of curves between the two slopes correspond to the temperature range where the dopants are ionized. The temperature dependence of the resistivity thus represents the variation of charge carrier mobility with temperature.

Although the spectacular effect on the electrical conductivity of SnO_2 claimed for the addition of Sb_2O_3 [5–9] was not confirmed in this investigation and apparently can only be observed in the Sb_2O_3-doped SnO_2 single crystals, the experimental data summarized in Table I and shown in Fig. 2 confirm that Sb_2O_3 and CuO are the most effective additives as far as the sintering capacity and electrical conductivity of the SnO_2-based composites are concerned. Their influence has therefore been investigated within wider concentration limits in order to find the optimum compositon of the mixture.

The data on the specific influence of the individual additives and of their various combinations are listed in Table II. As mentioned above, the electrical conductivity is closely associated with the sintering capacity and consequently with the density of the SnO_2-based composites. Thus, although the conductivity of a SnO_2–Sb_2O_3 mixture with a low concentration of Sb_2O_3 is quite high at 1000 °C, it is still lower compared to the conductivity of SnO_2–CuO mixtures because of inadequate densification and decrease with increasing Sb_2O_3 content due to the deteriorating effect of antimony(III)oxide on the sintering capacity.

TABLE I Densification and electrical conductivity of various SnO_2-based ceramic materials at 970 °C

Sample	Composition (mass %)	$\Delta l/l_0$	d (g cm^{-3})	χ (S cm^{-1})
1	$98SnO_2 + 2ZnO$	0.077	5.68	0.105
2	$98SnO_2 + 2Sb_2O_3$	0.005	4.49	0.251
3	$98SnO_2 + 2CuO$	0.123	6.48	0.538
4	$98SnO_2 + 2La_2O_3$	0.005	4.51	0.198
5	$98SnO_2 + 1Sb_2O_3 + 1CuO$	0.117	6.22	0.590
6	$98SnO_2 + 2Sb_2O_3 + 2CuO$	0.137	6.57	0.716
7	$94SnO_2 + 2Sb_2O_3 + 2CuO + 2La_2O_3$	0.029	5.04	0.515
8	$95.5SnO_2 + 2Sb_2O_3 + 2CuO + 0.5TiO_2$	0.135	6.51	0.636
9	$94SnO_2 + 2Sb_2O_3 + 2CuO + 2TiO_2$	0.143	6.57	0.656
10	$95.5SnO_2 + 2Sb_2O_3 + 2CuO + 0.5MoO_3$	0.079	5.58	0.469
11	$94SnO_2 + 2Sb_2O_3 + 2CuO + 2MoO_3$	0.036	4.75	0.377
12	$88SnO_2 + 2ZnO + 2CuO + 2Cr_2O_3 + 2MnO_2 + 2La_2O_3 + 2Fe_2O_3$	0.082	5.87	0.513

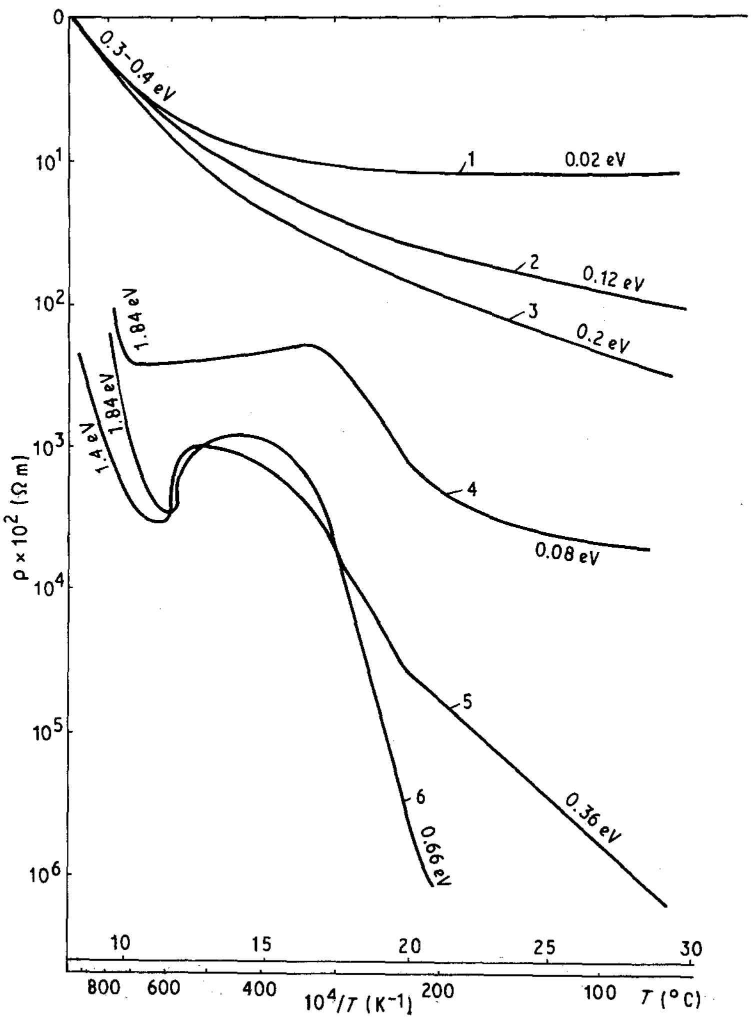

Figure 2 Dependence ρ plotted against temperature for SnO_2-based composites with different additives (mass %): (1, 2% Sb_2O_3 + 2% CuO; 2, 2% Sb_2O_3 + 1% CuO; 3, 2% Sb_2O_3 + 5% CuO; 4, 2% ZnO; 5, 2% ZnO + 2% CuO; 6, 2% ZnO + 2% CuO + 2% Cr_2O_3 + 2% MnO_2 + 2% La_2O_3 + 2% Fe_2O_3.)

The density and electrical conductivity of the SnO_2–CuO binary mixtures are less sensitive with respect to the CuO concentration. This is also true for the SnO_2–CuO–Sb_2O_3 ternary system. In the latter case, only small variations of the density and conductivity were observed when the CuO content was increased from 0.5 to 5 mass % at a constant Sb_2O_3 content of 2 mass %. The addition of Sb_2O_3 apparently does not deteriorate the densification of the composites in the presence of CuO, however, an increase of the Sb_2O_3 content from 2 to 6 mass % brought about only a slight increase of the conductivity of the composite.

TABLE II The dependence of the density and electrical conductivity on composition in the system SnO_2 + Sb_2O_3 + CuO at 970 °C.

Composition			d ($g\,cm^{-3}$)	χ ($S\,cm^{-1}$)
SnO_2 (mass %)	Sb_2O_3 (mass %)	CuO (mass %)		
99.8	0.2	–	4.78	0.458
98	2	–	4.49	0.251
95	5	–	4.34	0.136
90	10	–	4.19	0.116
98	–	2	6.48	0.538
96	–	4	6.50	0.620
96	2	2	6.57	0.716
94	4	2	6.30	0.730
92	6	2	6.20	0.738
97.5	2	0.5	5.01	0.498
97	2	1	6.37	0.678
95	2	3	6.40	0.699
93	2	5	6.37	0.677

These findings on the influence of the Sb_2O_3 and CuO additives are consistent with the phenomena observed in the investigation into the high-temperature interactions of tin(IV)oxide with antimony(III) and copper(II) oxides [14].

From an analysis of the data summarized in Table II it follows that raising the concentrations of Sb_2O_3 and CuO above 2 mass % apparently is ineffective with respect to the densification at sintering and, consequently to the electrical conductivity of SnO_2-based ceramic materials.

4. Conclusions

Based on experimental data, the following conclusions can be drawn on the influence of the oxide additives on the sintering capacity and electrical conductivity of the SnO_2-based composites.

(1) The electrical conductivity is closely associated with the density of the composite.

(2) From among various oxide additives tested, only CuO was found to promote the densification of the composite.

(3) The addition of Sb_2O_3, which is claimed to increase the electrical conductivity, is only effective in the presence of CuO addition.

(4). As optimum composition of SnO_2-based ceramic materials for stable electrodes, a mixture of 96 mass % SnO_2 + 2 mass % Sb_2O_3 + 2 mass % CuO can be recommended.

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References

1. E. E. KOHNKE, *J. Phys. Chem. Solids* **23** (1962) 1557.
2. C. G. FONSTAD and R. H. REDIKER, *J. Appl. Phys.* **42** (1971) 2911.
3. M. NAGASAWA and S. SHIONYA, *J. Phys. Soc. Jpn.* **30** (1971) 1213.
4. Z. M. JARZEBSKI and J. P. MARTON, *J. Electrochem. Soc.* **123** (1976) 299.
5. L. D. LOCH, *ibid.* **110** (1963) 1081.
6. H. E. MATTHEWS and E. E. KOHNKE, *J. Phys. Chem. Solids* **29** (1968) 653.
7. C. A. VINCENT and D. G. WESTON, *J. Electrochem. Soc.* **119** (1972) 518.
8. P. G. ORSINI, P. PERNICE and L. EGIZIANO, *ibid.* **128** (1981) 145A.
9. P. H. DUVINEAUD and D. REINHARD, *Sci. Ceram.* **12** (1984) 287.
10. M. R. PARICE, S. BOSU and A. PAUL, *ibid.* **11** (1983) 90.
11. M. N. KUCHERYAVYI and V. A. POLEVOV, *Steklo Keram.* **9** (1984) 12.
12. B. G. ALPIN, E. V. DEGTYAREVA, V. J. DROZD, N. V. BULKO and S. V. LYSAK, *Izv. Akad. Nauk SSR* **17** (1981) 923.
13. M. ROLIN and A. DUCOURET, *Bull. Soc. Chim. France* (1980) 799.
14. M. ZAHARESCU, S. MIHAIU, S. ZUCA and K. MATIASOVSKY, *J. Mater. Sci.* submitted.
15. H. ALDER, US Patent 4,057, 480 (1977).
16. K. BILLEHAUG and H. A. ØYE, *Aluminium* **56** (1980) 642.
17. T. CHVATAL, *Sprechsaal Keram. Glass Baust.* **B107** (1974) 1057.

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