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Influence of SnO on the Sintering Behaviour of Tin Dioxide

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Abstract: Fine tin dioxide powders were prepared by a precipitation procedure from sulphuric acid solution. The influence of calcination temperature, aging and tin monoxide addition on the compaction behaviour and the sinterability of these SnO_2 powders were studied. The presence of SnO leads to an increase of green ceramic densities and favours densification during sintering. So pure SnO_2 ceramics with relative densities between 0.40 and 0.64 can be obtained by use of SnO_2/SnO mixtures as starting materials and of special temperature and atmosphere programs for the sintering process. © 1997 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Sintering of tin dioxide, SnO_2, is characterized mainly by an absence of densification. The proposed sintering mechanisms are surface diffusion at low temperature[1] and evaporation–condensation at high temperature.[2] Nevertheless, dense SnO_2 ceramics have already been obtained by hot isostatic pressing[3] or in the presence of an additive like MnO_2,[4] CuO,[1,4–6] Li_2CO_3,[4] ZnO[4,6] or Nb_2O_5.[7,8] For example, manganese oxide is one of the most effective sintering additives since 0.86 cationic percent is sufficient to produce highly densified ceramics.

In comparison to the pure material, tin dioxide ceramics containing additives show differences in electrical and optical properties. In dependence on the amount of the additives, the colour can change from white to brown or black. Therefore, it is still a challenge to prepare dense and single phase SnO_2 ceramics without using hot isostatic pressing.

The phase equilibria in the Sn–SnO_2 system show the existence of the phases SnO_2, Sn_3O_4 and SnO. SnO_2 has the largest thermal stability of these phases. SnO decomposes to liquid Sn and Sn_3O_4 at temperatures above 270 °C. Sn_3O_4 melts incongruently above 450 °C to Sn and SnO_2.[9] Therefore, during heat treatment of SnO_2–SnO mixtures in air, liquid tin exists at relatively low temperatures before the oxidation to tin dioxide takes places at higher temperatures. The primary objective of the present study was the investigation of the sintering behaviour of SnO_2–SnO powder mixtures. The influence of the temporary presence of a phase consisting of liquid tin on the densification behaviour of tin oxide compacts has been studied using special temperature and atmosphere programs. The effect of SnO addition to SnO_2 powders was investigated also in regard to the compaction behaviour under different forming pressures.

2 EXPERIMENTAL

The preparation of the SnO_2 powders was described in detail previously.[10] Tin granules (Prolabo, Normapur) were attacked by hot concentrated (94.7%) sulphuric acid. After cooling, the solution was filtered and the filtrate was diluted in cold water. This tin (IV) solution was hydrolysed with aqueous ammonia (1.6%) at 80 °C at a pH of 7.0. The hydrated tin dioxide precipitate was then divided into two parts. Part A was washed with distilled water for complete removal of the remaining sulphate. Part B was aged for four weeks in its own solution, the pH was kept constant at 7.0, and then washed like A. All filtered precipitates were dried at 160 °C for 15 h and calcined at 400 or 700 °C for 15 h. SnO was prepared by a method described by Fraenkel and Snipischski[11] using $SnCl_2 \cdot 2H_2O$ (Merck KGaA, Darmstadt) as starting material. The powder was dried at 110 °C.

SnO_2–SnO mixtures with the molar composition 100–0, 95–5, 90–10, 75–25 or 50–50 were prepared using a ball mill. Cylinders (diameter = 8 mm and thickness = 3 mm) were obtained at room temperature after compaction using an uniaxial pressure of 50, 100, 150 or 200 MPa. The sintering was performed in a tubular furnace using the following program:

- 1 h at 600 °C in argon, to favour the formation and the distribution of liquid Sn in the ceramic bodies before oxidation,
- 2 h in oxygen at 800, 1000, 1100, 1200 or 1400 °C,
- cooling to room temperature in 15 min.

The specific surface area of the powders was determined using the BET method (nitrogen adsorption) and the average grain size was calculated assuming spherical grains. The density of the compacted powders was calculated using geometrical measurements of sample shape and weight. Total pore volume, specific surface area and average pore diameter of the compacts were determined by mercury porosimetry using the Washburn equation.[12] Surface characterization of the sintered ceramics was carried out by scanning electron microscopy (SEM).

Table 1. Properties of the starting SnO_2 powders

Calcining temperature	SnO_2 A		SnO_2 B		SnO
	400	700	400	700	
Specific surface area (m^2/g)	47	7	37	10	72
dBET (μm)	0.02	0.12	0.02	0.09	0.01

3 RESULTS AND DISCUSSION

Characteristics of the pure SnO_2 powders and of the SnO powder are summarized in Table 1. As usual, the specific surface area of pure SnO_2 decreases with rising calcination temperature. The main difference between A and B materials was reported elsewhere.[10] The aged powder (B) contains more microstrains than the fresh one. Scanning electron microscopic observations show the presence of large agglomerates in both cases. Values of morphological properties of green ceramics are reported in Table 2 for different forming pressures or compositions. The SnO_2 powders were calcined at 400 °C in this case. The green density ρ_0 of pure SnO_2 samples increases with pressure and reaches values higher than 40% of the theoretical density ρ_{th} for 200 MPa (ρ_{th} $SnO_2 = 6.95$ g/cm^3).

Figure 1 shows the pore size distribution of SnO_2 A samples after compaction at different pressures. Powder B shows a similar behaviour. A bimodal distribution does not exist. Agglomerates observed on SEM images are weak enough to be broken during compaction. The influence of SnO on the microstructure of tin dioxide green ceramics was studied for SnO_2 A powder calcined at 400 °C. Results reported in Table 2 show that the green density increases with the amount of tin monoxide, although the theoretical density of SnO (6.45 g/cm^3) is smaller than that of SnO_2. Such a behaviour can be explained either by a lubricant effect of SnO, which would favour the compaction of SnO_2, or by the presence of very small tin monoxide particles located in tin dioxide pores. The influence of SnO amount on the green density and the specific surface area is similar to that of forming pressure — the lubricant effect seems to be more probable. Table 3 shows the densities of SnO_2 and SnO_2–SnO samples before and after sintering at 800 °C, 1000 °C, 1200 °C and 1400 °C. The

Table 2. Influence of forming pressure and of SnO addition on the microstructure of green ceramics obtained from SnO_2 powders calcined at 400 °C

Sample composition	Forming pressure (MPa)	Density (g/cm^3)	Total pore volume (cm^3/g)	Specific surface area (m^2/g)	Average pore diameter (μm)
SnO_2 A	0.5	2.22	0.31	47	0.032
	1.0	2.35	0.28	50	0.027
	1.5	2.65	0.23	51	0.025
	2.0	2.97	0.19	52	0.022
SnO_2 B	0.5	2.48	0.26	37	0.025
	1.0	2.67	0.23	39	0.021
	1.5	2.88	0.20	41	0.018
	2.0	3.08	0.18	42	0.017
0.95 SnO_2 A-0.05 SnO	1.5	2.88	0.20	53	0.023
0.90 SnO_2 A-0.10 SnO	1.5	2.97	0.19	55	0.022
0.75 SnO_2 A-0.25 SnO	1.5	3.12	0.18	58	0.020
0.50 SnO_2 A-0.50 SnO	1.5	3.50	0.15	61	0.016

density increase of pure SnO_2 specimens with temperature is very weak for temperatures higher than 800 °C. The same behaviour is observed for mixtures prepared using SnO_2 powders calcined at 700 °C which are strongly agglomerated, too. The highest densities after sintering at 1400 °C are 4.44 $g{\cdot}cm^{-3}$ for 0.50 SnO_2 A (400)–0.50 SnO (64% of ρ_{th}) and 4.48 $g{\cdot}cm^{-3}$ for 0.50 SnO_2 B (400)–0.50 SnO (64%).

The effect of SnO addition on the sintering of SnO_2 powders calcined at 400 °C is quite different. Sample density increases with SnO content and sintering temperature. Values of ρ_{800}/ρ_0 and ρ_{1400}/ρ_0 are reported in Table 4 for samples prepared from SnO_2 B powder calcined at 400 °C.

Those results confirm the strong influence of SnO on the sintering behaviour of tin dioxide. The variation of density up to 800 °C (ρ_{800}/ρ_0) is dependent on the amount of tin monoxide in the green sample. In that range of temperature, tin monoxide must be decomposed in liquid Sn and Sn_3O_4 ($T > 270$ °C). Further, Sn_3O_4 must be transformed in liquid Sn and SnO_2 ($T > 450$ °C).[9] Simultaneously, liquid tin must slowly react with the oxygen of the surrounding atmosphere. Nevertheless, the higher the SnO content the larger is the amount of transmitting liquid tin.

Between 800 and 1400 °C, the effect of the presence of tin monoxide in the green sample is important and independent of its amount. The

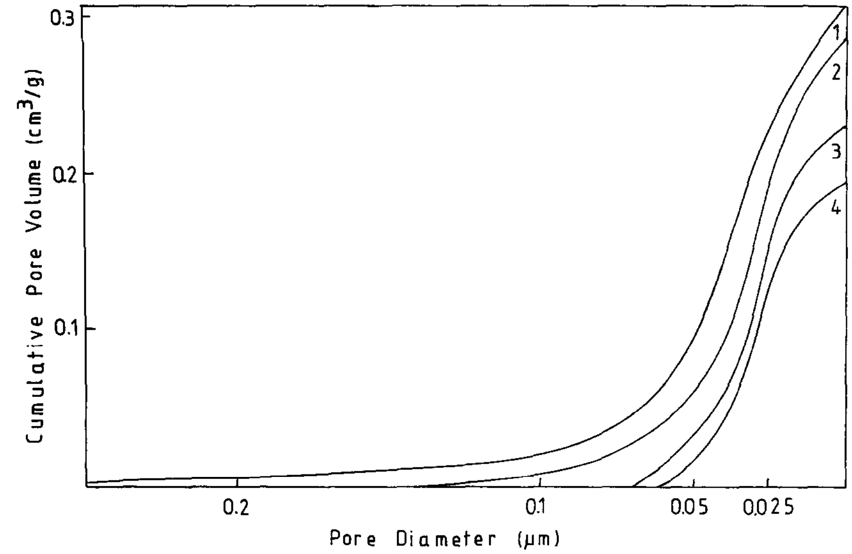

Fig. 1. Pore size distribution of SnO_2 A powder calcined at 400 °C after compaction at different pressures; 1 = 0.5 MPa, 2 = 1.0 MPa, 3 = 1.5 MPa, 4 = 2.0 MPa.

Table 3. Densities of different SnO_2 and SnO_2–SnO compacts before and after sintering at 800, 1000, 1200 and 1400 °C

Sample	Calcination temperature of SnO_2 (°C)	Green density ρ_0 (g/cm^3) (Forming pressure 1.5 MPa)	800 °C	1000 °C	1200 °C	1400 °C
SnO_2 A	400	2.65	2.78	2.82	2.85	2.85
SnO_2 A	700	2.86	2.86	2.86	2.92	3.05
SnO_2 B	400	2.88	2.89	2.90	2.90	2.90
SnO_2 B	700	2.97	2.98	2.98	2.99	3.06
0.95 SnO_2 A–0.05 SnO	400	2.88	3.03	3.20	3.35	3.36
0.90 SnO_2 A–0.10 SnO	400	2.97	3.08	3.23	3.41	3.48
0.75 SnO_2 A–0.25 SnO	400	3.12	3.29	3.45	3.58	3.60
0.50 SnO_2 A–0.50 SnO	400	3.50	3.92	4.28	4.43	4.44
0.95 SnO_2 A–0.05 SnO	700	3.34	3.34	3.35	3.37	3.38
0.90 SnO_2 A–0.10 SnO	700	3.40	3.41	3.41	3.46	3.48
0.75 SnO_2 A–0.25 SnO	700	3.46	3.47	3.47	3.50	3.52
0.50 SnO_2 A–0.50 SnO	700	3.58	3.59	3.59	3.61	3.64
0.95 SnO_2 B–0.05 SnO	400	3.02	3.16	3.28	3.45	3.47
0.90 SnO_2 B–0.10 SnO	400	3.09	3.22	3.38	3.54	3.59
0.75 SnO_2 B–0.25 SnO	400	3.23	3.41	3.58	3.71	3.76
0.50 SnO_2 B–0.50 SnO	400	3.60	4.08	4.35	4.45	4.48
0.95 SnO_2 B–0.05 SnO	700	3.40	3.42	3.43	3.48	3.50
0.90 SnO_2 B–0.10 SnO	700	3.49	3.49	3.50	3.51	3.52
0.75 SnO_2 B–0.25 SnO	700	3.58	3.58	3.59	3.60	3.62
0.50 SnO_2 B–0.50 SnO	700	3.69	3.70	3.71	3.73	3.75

relative density increases about 10% for all those samples containing SnO. This value is too high to be interpreted as the results of tin oxidation. The corresponding values $\Delta m/m$ are given in Table 4.

The increase of density of compact samples prepared from SnO_2 powder calcined at 400 °C is also demonstrated by the decrease of the cumulative pore volume. Figure 2 shows results of pore size measurements of SnO_2 A based samples after sintering at 1200 °C. All tablets were oxidized completely to SnO_2 at the end of the procedure. The sample corresponding to $x = 0.50$ shows the smallest cumulative pore volume, which is in accordance with the measured highest density. The pore size increase with rising x can be attributed to both grain growth and pore coalescence. Figure 3 shows the electron micrographs of the samples 0.95 SnO_2 A–0.05 SnO (a) and 0.50 SnO_2 A–0.50 SnO (b) after the sintering procedure. The micrographs confirm the porosity measurements showing the increase of pore size and grain size with rising SnO amount. It is remarkable that a bimodal distribution curve is found for the two samples with the

Table 4. Relative densities of x SnO–(1−x) SnO_2 samples. SnO_2 B powder calcined at 400 °C. ρ_{800} and ρ_{1400} correspond to sample densities after sintering at 800 and 1400 °C, respectively. $\Delta m/m$ is the relative weight change caused by oxidation of SnO

SnO content	ρ_{800}/ρ_0	ρ_{1400}/ρ_0	$\Delta m/m$
0	0.002	0.002	0
0.05	0.046	0.098	0.004
0.10	0.042	0.103	0.007
0.25	0.056	0.093	0.018
0.50	0.133	0.098	0.036

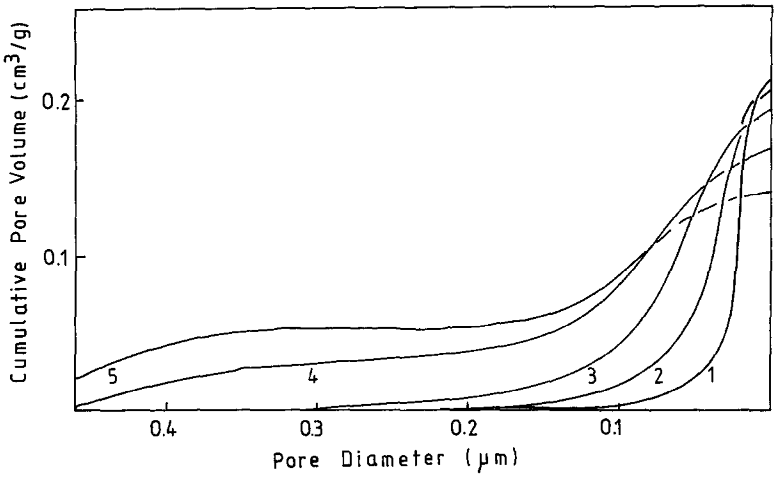

Fig. 2. Pore size distribution of x SnO–(1−x)SnO_2 mixtures pressed at 1.5 MPa after sintering at 1200 °C and complete oxidation to SnO_2 (SnO_2 A powder calcined at 400 °C); (1) $x = 0$, (2) $x = 0.05$, (3) $x = 0.10$, (4) $x = 0.25$, (5) $x = 0.50$.

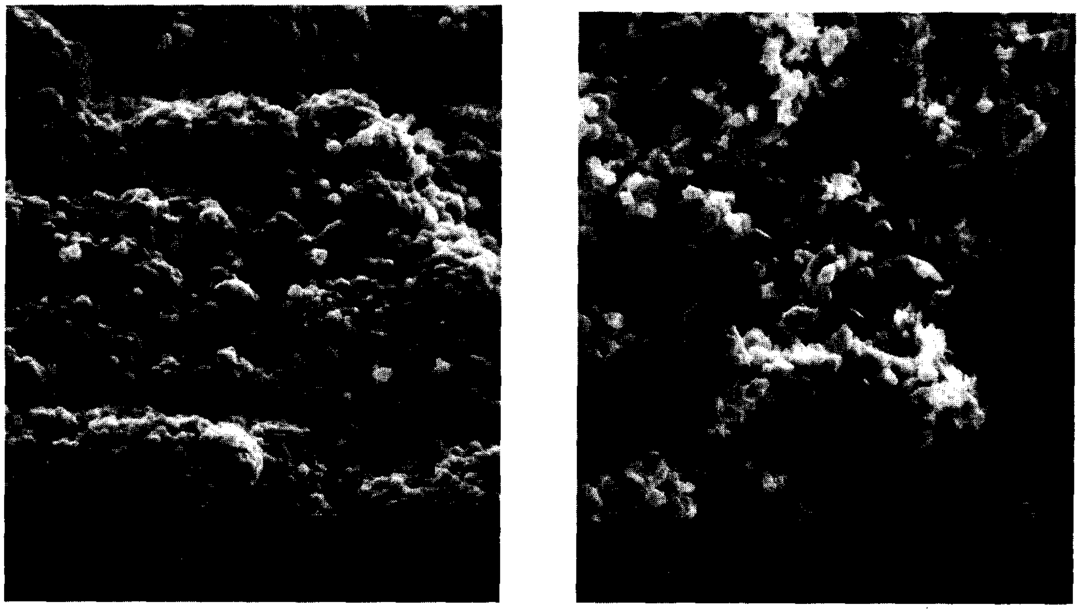

Fig. 3. SEM micrographs of: (a) 0.95 SnO_2 A–0.05 SnO; (b) 0.50 SnO_2 A–0.50 SnO after sintering at 1200 °C and complete oxidation to SnO_2 (SnO_2 A powder calcined at 400 °C).

highest SnO amount in the starting mixture. The reason for this should be the morphological difference between the SnO_2 and SnO powders leading to a more complex sintering mechanism in cooperation with the global oxidation of SnO to SnO_2.

4 CONCLUSIONS

The addition of tin monoxide improves the compaction behaviour of tin dioxide powders and, for very fine grained SnO_2, the densification during sintering. The SnO additive is not efficient enough for obtaining very dense ceramics. However, a relative density of 0.64 can be obtained after sintering at 1400 °C using special temperature and atmosphere programs. The SnO effect is attributed to the intermediate formation of liquid tin during the sintering process. SnO appears to be an efficient sintering additive when porous pure SnO_2 ceramics with relative densities 0.40 and 0.64 are sufficient.

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