

Sintering mechanisms of 0.99 SnO₂–0.01 CuO mixtures

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The densification kinetics of 0.99 SnO₂–0.01 CuO molar mixtures have been studied between 850 and 1150 °C. Both experimental analyses and theoretical modelling show the role of a liquid phase for sintering temperatures $T_s \geq 940$ °C: sintering is controlled by a liquid phase after a fast shrinkage due to grain rearrangement. The analytical formulation of the shrinkage behaviour suggests that dissolution at the solid–liquid interface is the limiting process when $T_s \leq 1000$ °C and diffusion is the limiting step at higher temperatures.

1. Introduction

Pure SnO₂ is known to be very difficult to densify by natural sintering, i.e. the heat treatment gives rise to both an increase of the size of pores and grains [1, 2]. However, additives such as Li₂O, CuO, MnO₂ or ZnO favour the densification [3–6]. As described previously [7], addition of a small amount of CuO (1 mol%) leads to high-density ceramics, for instance 98% theoretical density after a 2 h sintering treatment at 1150 °C. The fast shrinkage observed at this temperature appeared to be related to the existence of a liquid phase in the Cu–O system at temperatures higher than 1090 °C in air.

A preliminary study has shown that presence of copper oxide can also drastically change the sintering behaviour of SnO₂ at temperatures noticeably lower than 1090 °C. The purpose of this work is to determine the origin of the fast shrinkage observed between 850 and 1150 °C.

2. Experimental procedure

2.1. Preparation of the green compacts

SnO₂ (Aldrich 99.9%) and CuO (Prolabo Normapur 99%) were used as starting powders. Their specific surface areas were 7.3 and 14.8 m² g⁻¹, respectively. The average SnO₂ grain radius, determined from transmission electron microscopy (TEM) observations and BET measurements, was 0.06 μm.

In order to obtain 0.99 SnO₂–0.01 CuO molar mixtures, appropriate quantities of powders were mixed in pure ethanol, in an agate ball mill. After calcination in air at 400 °C for 3 h, the powder mixtures were uniaxially pressed at 100 MPa to form cylindrical samples (6 or 8 mm diameter). The density of the green samples was 3.6 ± 0.1 g cm⁻³.

2.2. Determination of the densification rate

The isothermal shrinkage rate was measured at various temperatures in air, using a Netzch dilatometer. The samples were 6 mm diameter pellets with a thickness of about 2.5 mm. The furnace was heated at the desired temperature ($850 \leq T_s \leq 1150$ °C) and the specimen, set on the measuring device, was then introduced in 5 min into the isothermal zone. The shrinkage evolution was recorded during 80 min.

2.3. Preparation and characterization of the ceramics

Some samples (8 mm diameter) were sintered in a regular furnace in air at a temperature, T_s , in the range $850 \leq T_s \leq 1150$ °C for a time, t ($15 \leq t \leq 80$ min). The heat treatment was the same as that of the dilatometric experiments. After sintering, the ceramics were cooled to room temperature in 10 min. The apparent relative density was determined from the Archimedes method [8]. The average grain radius was estimated from scanning electron microscopy (SEM) images performed on polished and thermally etched samples ($T_{\text{etching}} = T_s - 50$ °C, $10 \leq t_{\text{etching}} \leq 30$ min). A linear intercept method was used [9].

3. Results

The influence of the sintering time, t , on the relative shrinkage, $|\Delta L/L_0|$, is shown in Fig. 1 for different sintering temperatures. For each temperature, the experimental variation of $\ln(|\Delta L/L_0|)$ versus $\ln(t)$ is well described by a succession of linear relationships. Therefore, the isothermal shrinkage behaviour can be

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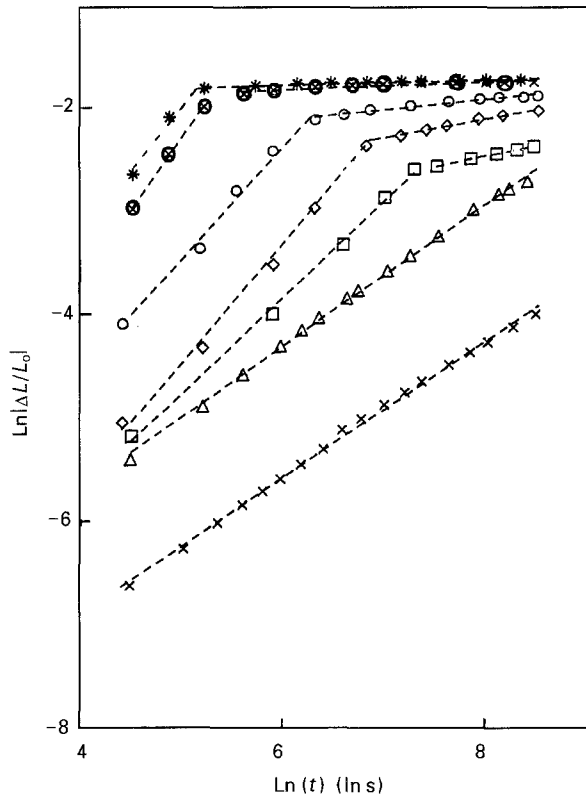


Figure 1 Influence of the sintering time, t , on the relative shrinkage, $|\Delta L/L_0|$, of 0.99 SnO₂-0.01 CuO ceramics sintered in air at $T_s =$ (x) 850 °C, (Δ) 900 °C, (\square) 940 °C, (\triangleleft) 970 °C, (\circ) 1000 °C, (\otimes) 1100 °C and ($*$) 1150 °C.

described according to the general form

$$|\Delta L/L_0| = At^p \quad (1)$$

The influence of the sintering time, t , on the average grain radius, r , is given in Fig. 2 for $T_s = 970, 1000$ and 1150 °C. When $T_s < 940$ °C, it was not possible to determine r accurately due to the low density of the samples. The linear evolution of $\ln(r)$ versus $\ln(t)$ led to the following expression

$$r = Bt^a \quad (2)$$

All p and a values determined from experimental measurements are reported in Fig. 3 as a function of t and T_s . Four different t - T_s domains can be identified, depending on p or a values.

4. Discussion

4.1. Liquid-phase sintering

In a previous work, we have shown that the sintering of 0.99 SnO₂-0.01 CuO samples heated at 1150 °C is controlled by the liquid that exists in the copper-oxygen system in air at $T > 1090$ °C [7]. In that case, the shrinkage behaviour is well described by a liquid-phase sintering mechanism limited by diffusion with grain growth controlled by grain-boundary impurities or intergranular phases [7]. The corresponding p and a exponents, defined by Equations 1 and 2 respectively, were found to be equal to 0.05 and 0.20.

For $T_s \geq 1000$ °C and for the longer sintering times (Fig. 3) the p and a values determined experimentally

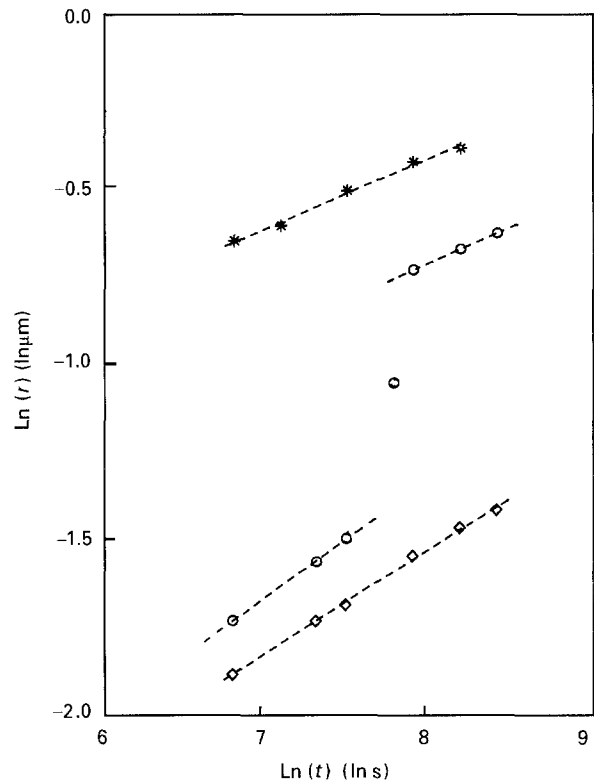


Figure 2 Influence of the sintering time, t , on the average grain radius, r , of 0.99 SnO₂-0.01 CuO ceramics sintered in air at (\diamond) 970 °C, (\circ) 1000 °C and ($*$) 1150 °C.

are the same as those previously reported for $T_s = 1150$ °C. Therefore, the mechanisms involved at 1150 °C should also be considered as predominant when $T_s \geq 1000$ °C. Actually, the intergranular phase observed by TEM (Fig. 4) in a ceramic sintered at 1000 °C for 30 min and quenched to room temperature, is in agreement with the presence of a liquid phase during the process. During the first sintering step, a fast shrinkage occurs; p values are larger than 1 and are increasing with T_s . Such a behaviour is often considered as characteristic of grain rearrangement [10]. The liquid phase which appears during this initial stage must act as a lubricant.

The kinetic trend observed during the beginning of the process at 970 and 940 °C is similar to that described above. Such a behaviour suggests that a liquid phase already exists at $T_s = 940$ °C in 0.99 SnO₂-0.01 CuO materials.

The p and a values determined when $940 \leq T_s \leq 1000$ °C for the second sintering stage are also compatible with the existence of a liquid. When liquid-phase sintering is controlled by dissolution, the following law can be used to describe the shrinkage [10]

$$|\Delta L/L_0| = kr^{-1}t^{0.5} \quad (3)$$

Introduction of the experimental shrinkage variation, $|\Delta L/L_0|_{\text{exp}} = A_1 t^{0.16}$, in Equation 3 leads to the following theoretical grain radius growth formulation

$$r_{\text{th}} = k't^{0.34} \quad (4)$$

The exponent 0.34 is in good agreement with the experimental value $a = 0.32 (\pm 0.04)$ reported in Fig. 3. Therefore, when the sintering temperature is in the

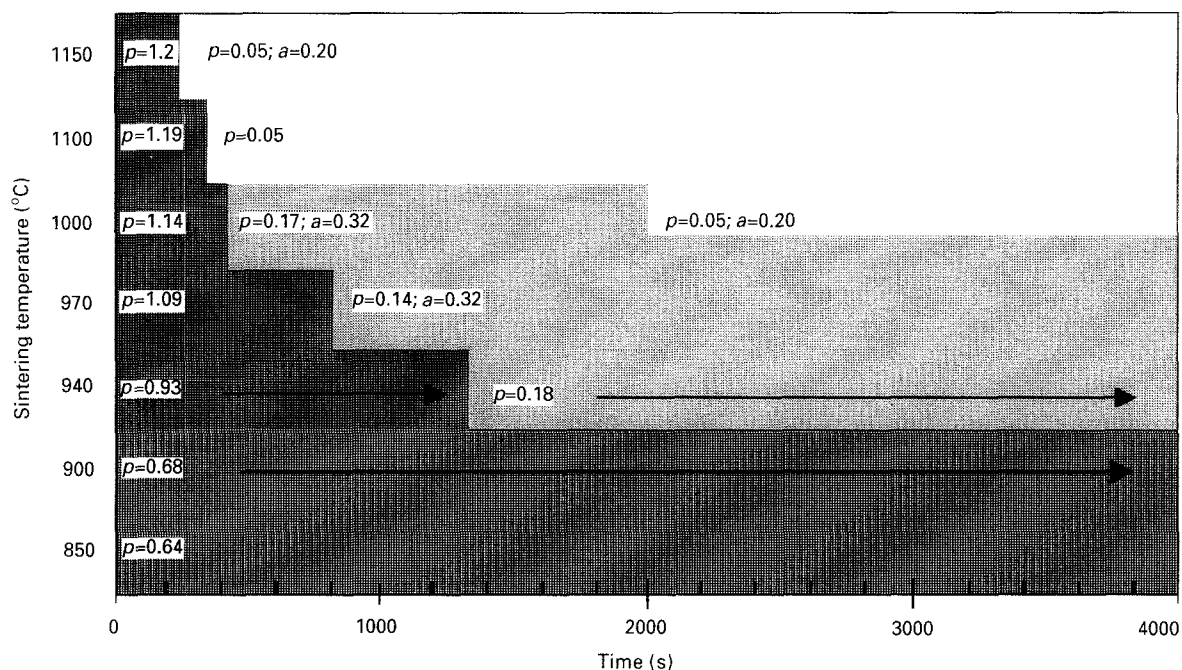


Figure 3 Values of the p in Equation 1 ($|\Delta L/L_0| = At^p$) and of the a in Equation 2 ($r = Bt^a$), depending on the sintering conditions (temperature, T_s (°C) and time, t (s)).



Figure 4 Intergranular phase in a 0.99 SnO₂-0.01 CuO ceramic sintered in air at 1000 °C for 30 min and quenched at room temperature.

940–1000 °C range, the second sintering step can be considered as liquid-phase controlled with a shrinkage rate limited by dissolution. The a exponent value suggests that the corresponding grain growth can be described by an Ostwald ripening mechanism [11].

Those results indicate that a liquid phase exists in the Sn–Cu–O₂ system at a temperature (940 °C) lower than 1090 °C which is the eutectic temperature of the Cu–O system. However, the amount of intergranular phase observed after quenching of the ceramics was always too weak to allow the determination of the liquid composition.

The sintering behaviour observed at 1000 °C clearly points out the different contributions of the liquid phase to the sintering process. During the first 7 min, the formation of the liquid favours the grain rearrangement. Then the sintering kinetics is controlled by a dissolution–recrystallization process. When the deposited layer is thin enough ($7 \leq t \leq 30$ min), dissolution is the limiting step. Later on ($t \geq 35$ min) diffusion through the deposited material becomes the slowest process. That change in the limiting process is associated with a change in the grain-growth mechanism (Fig. 2). For longer sintering time ($t = 15$ h) no further intergranular phases can be detected in the ceramics by TEM, and copper is homogeneously distributed within SnO₂-based grains. The comparison between the sintering behaviour at 940 and 1150 °C leads us to conclude that the lower the sintering temperature, the longer is the dissolution-limited step.

4.2. Low-temperature mechanism ($T_s \leq 900$ °C)

The fast initial densification step, characteristic of rearrangement phenomena, is not observed during sintering at 850 or 900 °C (Fig. 1). Furthermore, the p values obtained at those temperatures (0.66 ± 0.02) cannot be associated with any of the known liquid-phase sintering mechanisms. Then, there is no evidence for the presence of a liquid phase in this range of sintering temperatures.

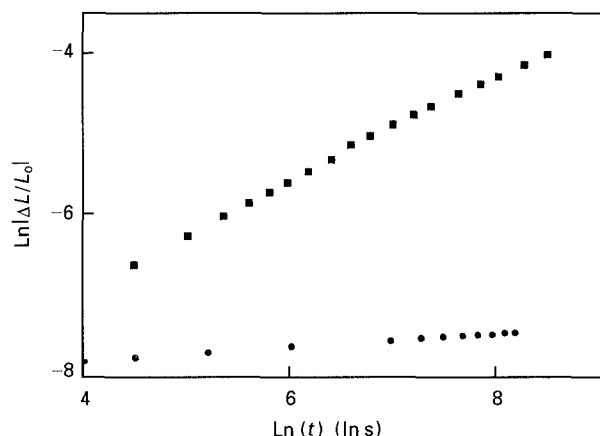


Figure 5 Shrinkage evolution during sintering at 850°C in air of (●) "pure" SnO₂ and (■) 0.99 SnO₂-0.01 CuO materials.

The isothermal shrinkage behaviour observed at 850°C for "pure" SnO₂ and 0.99 SnO₂-0.01 CuO materials is reported in Fig. 5. The copper oxide influence on the shrinkage rate is straightforward, even for short sintering times (5 min). Such a behaviour suggests that the repartition of copper ions in SnO₂-based material is very fast, or occurs during the presintering process, i.e. during calcination at 400°C or during heating to 850°C (in 5 min). Surface diffusion must contribute to the copper distribution and then to the microstructural evolution.

5. Conclusion

The densification of SnO₂ is strongly enhanced by addition of a small amount of copper oxide. When the sintering temperature is equal to or higher than 940°C, that effect is mainly due to the existence of a liquid in the Sn-Cu-O₂ system. The roles of the

liquid phase during sintering can be summarized as follows: (i) it favours grain rearrangement, (ii) it ensures matter transfer in a second step, (iii) it controls the densification process with a dissolution-limiting step when the sintering temperature is between 940 and 1000°C and with a diffusion-limiting step at higher temperature.

When the sintering temperature is lower than 940°C, the improvement of the densification ability of SnO₂, due to copper oxide, should be related to a fast copper repartition on the SnO₂-based grain surface.

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