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Low-Temperature Sintering of 0·99 SnO_2–0·01 CuO: Influence of Copper Surface Diffusion

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Abstract

The influence of CuO on the surface reactivity and on the shrinkage behaviour of a SnO_2 powder has been studied at low temperature ($T \leq 900°C$). Surface diffusion of copper ions, effective at a temperature as low as 400°C, results in an homogeneous distribution of copper cations on the grain surfaces. The powder's ability to fix water and oxygen-derived species is then modified. Simultaneously to the formation of oxygen vacancies in the outer part of the grains, a densification phenomenon is observed at 850°C. The corresponding shrinkage kinetics can be fitted using the model proposed by Scherer to describe viscous flow sintering of a low-density array of particles. A relation between the atomic defects present near the surface of the grains and the viscous flow-like behaviour is suspected. Copyright © 1996 Elsevier Science Ltd

1 Introduction

Pure SnO_2 is known to be very difficult to densify by natural sintering, i.e heat treatment gives rise to an increase of the size of both pores and grains.[1,2] However, addition of a small amount of CuO (1 molar %) favours densification. High-density ceramics (i.e. 98% of the theoretical density) can be obtained after sintering at 1150°C. We have shown, in a previous work, that the fast shrinkage observed at this temperature is related to the presence of a copper oxide-rich liquid phase.[3]

In addition, we have observed that the presence of CuO also promotes the densification of SnO_2 at temperatures (850 and 900°C) lower than that of the liquid phase formation (≈ 940°C).[4] At such low temperatures, grain surface diffusion can be the predominant matter transfer process. Therefore, the purpose of this work is to identify the contribution of the interface to the phenomena involved in the slow densification observed when $T < 940°C$.

2 Experimental Procedure

2.1 Preparation of the green compacts

SnO_2 (Aldrich 99·9%) and CuO (Prolabo Normapur 99%) were used as starting powders. Their specific surface areas were 7·3 and 14·8 $m^2.g^{-1}$, respectively. In order to get 0·99 SnO_2–0.01 CuO molar mixture, appropriate quantities of the powders were mixed in an agate ball mill in pure ethanol. After calcination for 3 h in air at 400°C, the powder mixture was uniaxially pressed to form cylindrical samples (6 mm diameter). The density of the green samples was 3·6 ± 0·1 g cm^{-3}.

2.2 Determination of the shrinkage kinetics

The isothermal shrinkage rate was determined at 850 and 900°C in air, using a Netzch dilatometer. The furnace was heated at the desired temperature and then the green sample, set on the measuring device, was introduced in 5 min into the isothermal zone. The shrinkage evolution was recorded during 80 min.

2.3 Study of water and oxygen sorption phenomena

SnO_2 is known as a material that chemisorbs oxygen and water easily.[5,6] These phenomena are also dependent on the grain surface composition. Therefore, study of the exchange between gas phase and SnO_2-based materials, using thermogravimetric analysis, can give information on an eventual evolution of the grain surface composition during heat treatment. Further insights in the sintering mechanisms of 0·99 SnO_2–0·01 CuO mixture can then be deduced since the composition of the surface of the grains is one of the parameters that control the sinterability of a ceramic powder at low temperature.

Thermogravimetric measurements were performed using a Setaram MTB 10-8 equipment. The equipment accuracy was 10 μg with an initial sample weight of about 700 mg. The behaviour of four samples was investigated: (i) a pure SnO_2 powder calcined at 400°C for 3 h, (ii) a 0·99 SnO_2–0·01 CuO powder calcined at 400°C for 3 h,

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Table 1. Definitions of the main terms used in section 3

m_O	Initial mass of a sample
m_{H_2O}	Mass attributed to water desorbed during heating
m_{O_2}	Mass attributed to oxygen adsorbed during cooling
n	Number of cationic positions on the grain surface per gram of material
n_{Sn}	Number of Sn on the grain surface per gram of material [$n_{Sn}/n = 1$ for "pure" SnO_2]
n_{H_2O}	Number of H_2O molecules desorbed per gram of material
n_{Cu}	Number of Cu lying in substitutional position on the grain surface per gram of material [$n_{Cu}/n = 1 - n_{H_2O}/n$]
n_{V_O}	Number of oxygen vacancies on the grain surface per gram of material [corresponding to O_2 molecules adsorbed during cooling]
n_V	Number of surface oxygen vacancies per gram due to Cu distribution [$n_V/n = n_{V_O}/n - (n_{V_O}/n)$ pure $SnO_2 = n_{V_O}/n - 0{\cdot}18$]

(iii) a 0·99 SnO_2–0·01 CuO calcined powder sintered at 850°C for 20 min, (iv) a 0·99 SnO_2–0·01 CuO calcined powder sintered at 850°C for 60 min. Each specimen was prepared as a cylindrical pellet and presented almost the same initial density ($\approx$ 3·6 g cm^{-3}). The samples were heated in flowing air at 200°C h^{-1} up to 800°C or 850°C, then held for 15 min in a dried oxygen flow, before cooling down to 20°C at 200°C h^{-1} in the same atmosphere. The recorded weight changes were corrected for buoyancy force changes. The BET specific surface areas were determined using N_2 gas as adsorbate at 77 K with a Micromeritics 2100 E apparatus. From TGA and BET measurements, numbers of species present on the surface of the grains have been calculated. Definitions of the terms used are given in Table 1.

3 Results and Discussion

3.1 Isothermal shrinkage kinetics

At 850 and 900°C, the evolution of the isothermal shrinkage, $|\Delta L/L_0|$, of 0·99 SnO_2–0·01 CuO samples versus sintering time, t, can be described by the relation:

$$|\Delta L/L_0| = A \,.\, t^p \qquad (1)$$

with $p = 0{\cdot}66 \pm 0{\cdot}02$. That value of p does not correspond to any of the known liquid-phase sintering mechanisms, i.e. $p \leq 0{\cdot}3$.[9] Furthermore, the fast initial densification step usually observed for this material during the liquid phase formation when $T_S \geq 940$°C is not observed. Those results lead us to consider that in this range of temperature (850–900°C) sintering does not involve a liquid phase. However, the influence of copper oxide on the densification rate is already marked for very short sintering time as it can be seen in Fig. 1 where the shrinkage kinetics at 850°C of 'pure' SnO_2 and of 0·99 SnO_2–0·01 CuO are compared. Such a behaviour suggests that the distribution of copper ions in SnO_2-based material occurs either during the calcination treatment at 400°C or very rapidly during the heating up to 850°C.

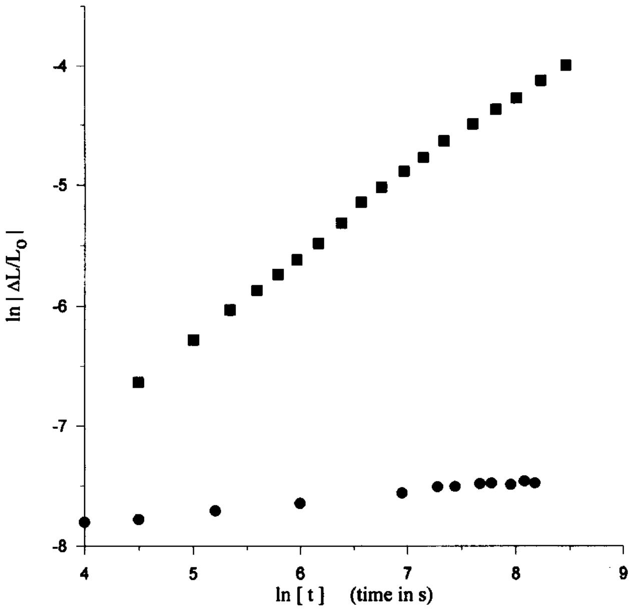

Fig. 1. Isothermal shrinkage at 850°C in air of (●) 'pure' SnO_2 and (■) 0·99 SnO_2–0·01 CuO materials.

3.2 Copper ion distribution after calcination at 400°C

The thermogravimetric study of water and oxygen sorption phenomena has been performed on green compacts of SnO_2 and 0·99 SnO_2–0·01 CuO powders previously calcined at 400°C in air for 3 h. The relative weight losses, $(m\text{-}m_O)/m_O$, related to desorption during heating up to 400°C in air, are reported in Fig. 2, where m_O and m are the weight of the sample measured in air at 20°C and at a temperature T, respectively. Considering the low amount of CuO in the mixture powder ($\approx$0·5 wt%), the difference between the two curves in Fig. 2 when $100 \leq T \leq 300$°C is too large to be attributed to sorption phenomena on CuO grains. Relative density (0·52) and specific surface area (7·3 m^2 g^{-1}) of the two samples being identical, only a modification of the SnO_2 grain surface composition can explain the difference in desorption behaviour. As a consequence, it can be considered that diffusion of copper ions on the surface of the SnO_2 grains occurred during the previous calcination treatment at 400°C.

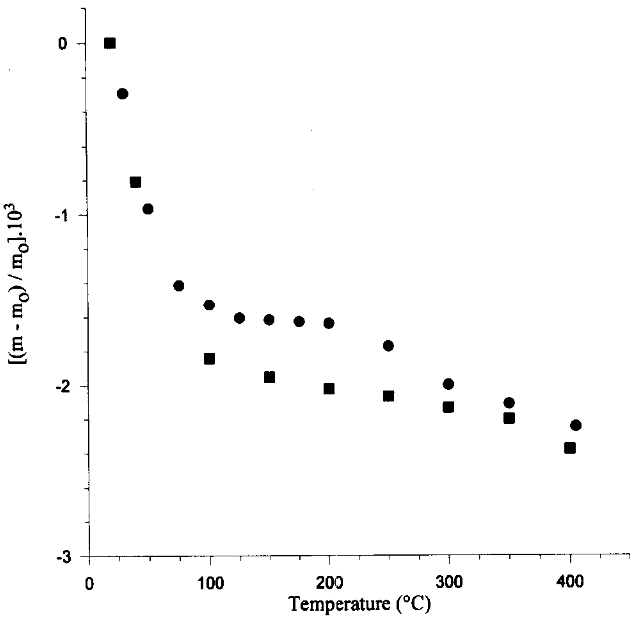

Fig. 2. Relative weight losses observed during the heating in air of calcined powders: (●) 'pure' SnO_2, (■) 0·99 SnO_2–0·01 CuO.

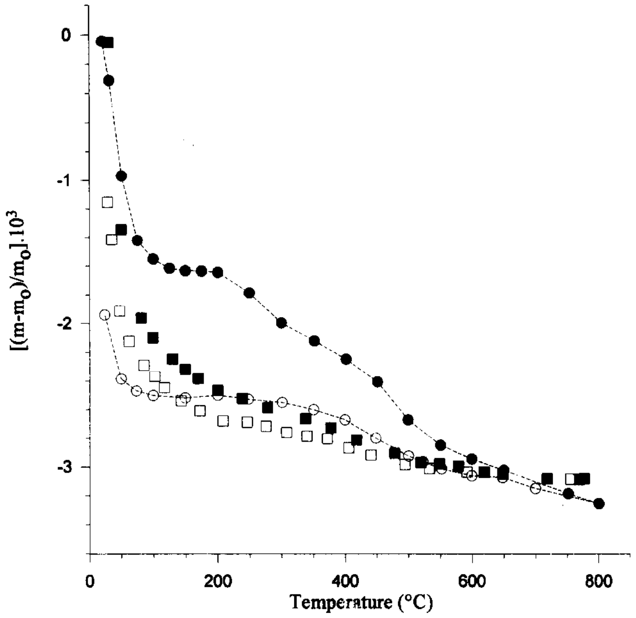

Fig. 3. Relative weight variations observed during heating in ambient air and cooling in dry oxygen of: calcined SnO_2 (● heating, ○ cooling) and 0·99 SnO_2–0·01 CuO calcined mixture sintered at 850°C for 20 min. (■ heating, □ cooling).

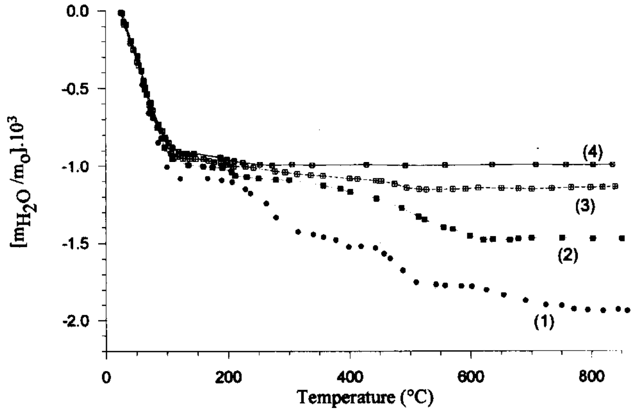

Fig. 4. Relative weight losses due to water loss during heating in air of: (1) calcined SnO_2, (2) calcined 0·99 SnO_2–0·01 CuO, (3) calcined 0·99 SnO_2–0·01 CuO sintered for 20 min at 850°C, (4) calcined 0·99 SnO_2–0·01 CuO sintered for 1 h at 850°C.

3.3 Evolution of grain surface composition during sintering at 850°C

3.3.1 Copper concentration

Many studies have been performed to determine the location of water and oxygen-derived species on rutile-type crystal surfaces.[7,8] Based on their conclusions, the following assumptions can be proposed in order to relate sorption phenomena to SnO_2 grain surface composition: (i) sorption of water-derived species (H_2O, OH^-, ...) is related to Sn cations[7] whereas Cu cations are not directly involved in this phenomenon,[9] (ii) O_2 molecules are chemisorbed at low temperature ($T < 200°C$) by oxygen vacancies,[7,9] (iii) on the grain surface, Cu cations are located in Sn position.[8]

The relative weight evolution versus temperature of a calcined SnO_2 powder and of a 0·99 SnO_2–0·01 CuO calcined mixture sintered for 20 min in air at 850°C is presented in Fig. 3. Experiments performed in dry atmosphere have shown that after a first heating up to 800°C, the weight changes observed during further heat treatments are reversible and are not dependent on the difference of oxygen partial pressure existing between dry air and dry oxygen. Therefore, the difference observed in the TGA curves between the heating in ambient air and the cooling in oxygen must be due to water species departure. Results reported in Fig. 4 (curves (3) and (4)) show for a 0·99 SnO_2–0·01 CuO sample that the longer the sintering time at 850°C, the weaker the water loss during the heating up to 850°C.

Assumption (i) relative to the role of Sn cations in water adsorption phenomena leads to association of the observed behaviour to a decrease of the tin cation number per gram of material (n_{Sn}) on the grain surface when CuO is present in the sample. BET measurements revealed that specific surface area was not significantly modified by sintering at 850°C or by thermogravimetric heat treatment; specific surface area variations were always lower than 5%. This effect appears strongly enhanced during sintering at 850°C (curves (3) and (4) in Fig. 4). As the specific surface area remains almost constant, the corresponding decrease of the n_{Sn}/n ratio must be related to the progressive substitution of tin by copper on the surface of the grains.

According to Jones and Hockey[7] the surface of a rutile-type structure is composed of 60% of (110) planes, 20% of (101) planes and 20% of (100) planes.

Table 2. Relative weight losses (m_{H_2O}/m_O) due to water loss during heating up to 800°C and corresponding numbers of H_2O and Cu per normal cationic position on the grain surface

	SnO_2	*0·99 SnO_2–0·01 CuO*		
	3 h 400°C	*3 h 400°C*	*3 h 400°C 20 min 850°C*	*3 h 400°C 1 h 850°C*
m_{H_2O}/m_O	$1·9 \times 10^{-3}$	$1·5 \times 10^{-3}$	$1·1 \times 10^{-3}$	$1·0 \times 10^{-3}$
n_{H_2O}/n	1·02	0·79	0·61	0·54
n_{Cu}/n	0	0·23	0·41	0·48

Assuming a similar partition in SnO_2 and taking into account the equivalent area of a tin cation on each type of plane, the value of n calculated from $S_{BET} = 7·3$ m^2 g^{-1} should be $6·2 \times 10^{19}$ atom g^{-1}. The relative water weight loss, m_{H_2O}/m_O, and the relative number of H_2O molecules desorbed per gram of material, n_{H_2O}/n, are reported in Table 2 for each type of sample. The n_{H_2O}/n value is close to 1 for 'pure' SnO_2. This result leads us to assume that, at room temperature, one H_2O species is bound to one Sn cation. In the absence of interaction between Cu and H_2O (assumption (i)) the difference ($1 - n_{H_2O}/n$) should be representative of the relative amount, n_{Cu}/n, of copper lying in substitutional position on the grain surface. The corresponding values reported in Table 2 agree with a progressive spreading of copper on the surface of the SnO_2-based grains during heat treatment.

3.3.2 Oxygen vacancy concentration

The increase of weight observed during cooling in oxygen from 200°C to 20°C must be related to oxygen adsorption on grain surfaces. The corresponding ratios m_{O_2}/m_O are given in Table 3. When CuO is present in the initial mixture, m_{O_2}/m_O increases with the temperature and the time of the pre-treatment. Assuming that one O_2 molecule is adsorbed by one oxygen vacancy,[7,9] the number of oxygen vacancies per cationic site on the grain surface, n_{V_O}/n, can be determined. The corresponding values reported in Table 3 lead to the consideration that the distribution of copper ions on the surface is associated to the formation of oxygen vacancies. Although copper ions migrate on tin oxide grains during isothermal heat treatment of 0·99 SnO_2–0·01 CuO at 850°C, no weight change is observed (Fig. 5). Therefore, a simple reaction can be proposed to summarise the whole process:

$$CuO \xrightarrow{SnO_2} Cu''_{Sn} + V_O^{\cdot\cdot} + O_O \qquad (2)$$

Since $n_{V_O}/n = 0·18$ for pure SnO_2 grains, some oxygen vacancies already exist without any CuO addition. The difference $n_{V_O}/n – 0·18 = n_V/n$ can be considered as characteristic of the relative amount of surface oxygen vacancies due to copper distribution (Table 3). The n_V/n_{Cu} ratios, reported in Table 3, are almost independent of pre-treatment conditions. The value, $n_V/n_{Cu} = 0·65$, seems to be characteristic of the grain surface of 0·99 SnO_2–0·01 CuO material. It differs significantly from the one imposed by reaction (2), i.e., $n_V/n_{Cu} = 1$. In the absence of weight change during heat treatment at 850°C (Fig. 5), this discrepancy indicates that about 35% of the oxygen vacancies formed during distribution of copper on the grain surface are unable to chemisorb oxygen. Two possibilities can be proposed to explain that effect: location of oxygen vacancies inside the grains or formation of clusters on the grain surface involving copper ions and oxygen vacancies. In the latter case, all vacancies would be located on the grain surface and would not contribute to the shrinkage.

3.4 Modelling of the low-temperature sintering

The p exponent characteristic of the shrinkage kinetics at 850 or 900°C is 0·66 ± 0·02. This value does not correspond to any known model involving

Table 3. Relative weight variations due to oxygen adsorption during cooling from 200 to 20°C and surface defects relative concentrations

	SnO_2	*0·99 SnO_2–0·01 CuO*		
	3 h 400°C	*3 h 400°C*	*3 h 400°C 20 min 850°C*	*3 h 400°C 1 h 850°C*
$(m_{O_2}/m_O)_{200-20°C}$	$0·6 \times 10^{-3}$	$1·1 \times 10^{-3}$	$1·5 \times 10^{-3}$	$1·6 \times 10^{-3}$
n_{V_O}/n	0·18	0·33	0·45	0·49
n_{Cu}/n	0	0·23	0·41	0·48
n_V/n	—	0·15	0·27	0·31
n_V/n_{Cu}	—	0·65	0·66	0·64

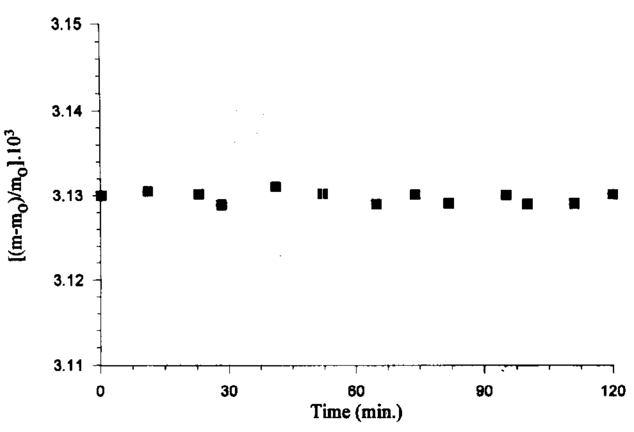

Fig. 5. Relative weight variation during sintering at 850°C in air of a calcined 0·99 SnO_2–0.01 CuO mixture. The sample was heated up to 850°C in 5 min.

solid-state sintering. Furthermore, Frenkel proposed that, under the influence of surface tension, crystalline bodies can display a viscous flow similar to that of amorphous bodies.[10] The possible presence of a large number of vacancies inside the grains would support such a behaviour quite well. As a consequence, shrinkage evolution of our ceramics can be compared with that associated with a viscous flow mechanism. Using Scherer's approach,[11] the sintering rate of a model structure is determined based on the assumption that the energy dissipated in the viscous flow is equal to the energy gained by the decrease in surface area during sintering. That ideal geometry (Fig. 6a) corresponds to a porous microstructure[11,12] constituted of cylinders arranged in a cubic array (length of side: 1). The cylinder radius, α, is expected to represent the average particle radius. This description is in agreement with the microstructure observed in a 0·99 SnO_2–0·01 CuO calcined sample sintered for 16 min at 900°C (Fig. 6b).

Scherer has expressed the theoretical variation of the relative density, ρ/ρ_{th}, as a function of the reduced time, $x_t = K)(t-t_O)$. ρ is the apparent density at t and ρ_{th} is the theoretical density. t_O is the fictitious time at which $\alpha/1 = 0$. The value of K is given by:

$$K = \gamma \,.\, (\rho_{th}/\rho_O)^{1/3} \,/\, (\eta \,.\, l_O) \qquad (3)$$

where γ is the specific surface excess of free energy, ρ_O the initial apparent density, η the 'viscosity' and l_O the initial value of l. The plot of ρ/ρ_{th} versus x_t is given in Fig. 7.

Assuming an isotropic shrinkage, ρ/ρ_{th} can be calculated for each value of t using the isothermal dilatometric experiments (ρ_{th} = 6·95 g cm^{-3}). Those experimental data can be fitted to the theoretical curve (Fig. 7) to deduce the reduced time abscissas, x_t. Since K and t_O are not time-dependent for a given sintering temperature, a linear relationship

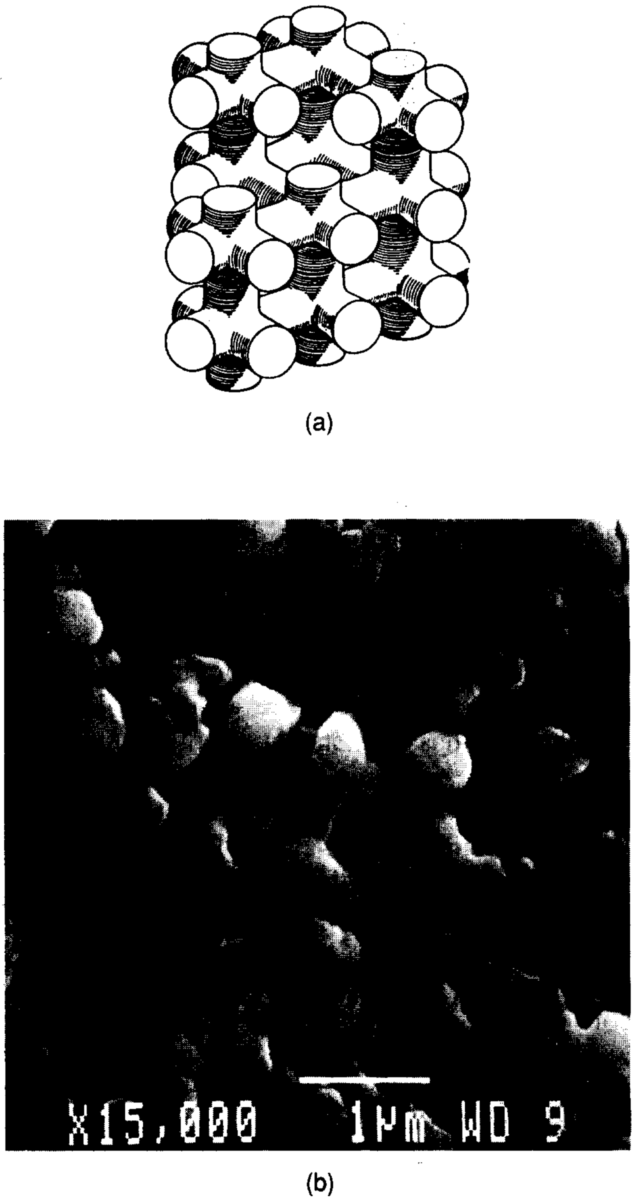

Fig. 6. (a) Idealized microstructure geometry used in the Scherer's model (from Ref 11). (b) microstructure of a 0·99 SnO_2–0·01 CuO ceramic sintered for 16 min at 900°C.

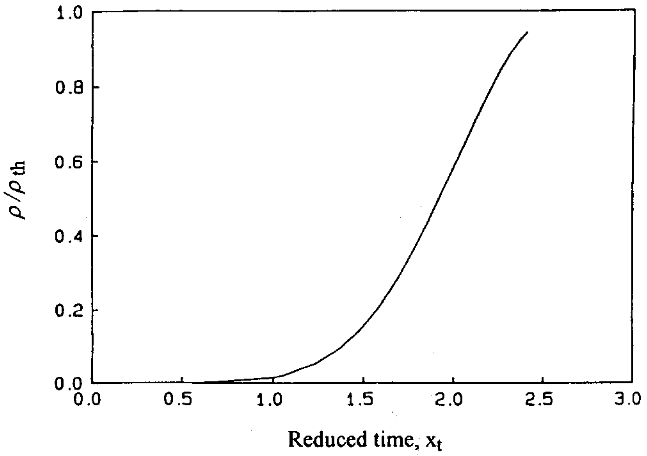

Fig. 7. Theoretical evolution of ρ/ρ_{th} versus reduced time corresponding to a viscous-flow sintering using the microstructure geometry described in Fig. 6(a).

is expected between the reduced and the sintering times if the Scherer's model is applicable. The plot of the experimental sintering times, t, versus x_t is given for T_S = 850, 900 and 940°C in Fig. 8. The straight lines obtained for 850 and 900°C suggest that the shrinkage behaviour of a 0·99 SnO_2–0·01 CuO calcined mixture is similar to the one observed at these temperatures during a viscous-flow sintering. The K values determined from the slopes (K^{-1}) of the straight lines are $1{\cdot}1 \times 10^{-5}$ and $3{\cdot}4 \times 10^{-5}$ s^{-1} at 850 and 900°C, respectively. The evolution of K with T_S is in agreement with the expected variation of the viscosity with the temperature (eqn (3)). The non-linear behaviour observed at T_S = 940°C, the temperature at which the sintering is controlled by a liquid phase,[4] confirms the specific nature of the low-temperature ($T_S \leq 900$°C) shrinkage mechanism for 0·99 SnO_2–0·01 CuO powders.

In fact, it is not necessary for the whole material to be viscous to observe a viscous-flow type shrinkage. It has been shown recently that a packing of hard particles coated by a 'soft' phase can sinter at a rate comparable to that of particles without a rigid core, i.e. following a viscous-flow mechanism, provided the thickness of the viscous layer is sufficient.[13,14] In the case of spherical particles, Jagota[13] showed that a normalised coating thickness t/R = 0·2 (R is the radius of the hard core of the grain) is sufficient to reach full density at almost the same rate as the viscous material. Moreover, when the relative density of the material remains low, its sintering kinetics is the same as that of the coating for a value of t/R as low as 0·1. Considering that the relative density of the 0·99 SnO_2–0·01 CuO ceramics described in this paper was lower than 56%, a thick disordered layer near the surface of the grains, possibly due to the formation of oxygen vacancies inside the grain during the copper distribution, could play the role of that viscous layer. Its thickness was estimated, applying Jagota's approach to our shrinkage and using the size of the grains deduced from specific area measurements (r = 0·06 μm). A value of the order of a nanometre, which seems rather likely.

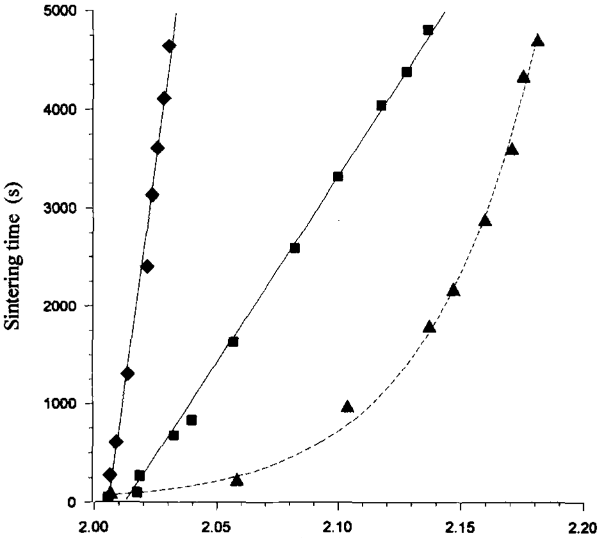

Fig. 8. Evolution of the sintering time of 0·99 SnO_2–0·01 CuO calcined samples versus reduced time obtained from Fig. 7. Sintering temperatures were: ◆ 850°C, ■ 900°C and ▲ 940°C.

4 Conclusion

A small addition (1 molar %) of copper oxide results in a large change in the shrinkage behaviour at low sintering temperature, 800 or 850°C, compared to 'pure' SnO_2. In this range of temperature, occurrence of a liquid phase appears doubtful. Study of the influence of temperature on the weight evolution of various 0·99 SnO_2–0·01 CuO heat-treated powders has allowed us to follow the distribution of copper ions and free oxygen vacancies on the grain surface. First, distribution of copper ions occurs through surface diffusion at temperatures as low as 400°C. Second, at higher temperatures (850–900°C) a part of oxygen vacancies are not able to chemisorb O_2 molecules. Simultaneously, densification is observed and its kinetics can be fitted by the model proposed by Scherer to describe viscous-flow sintering. The possible location of oxygen vacancies which are not free on the surface of the grains, within a thick layer, could then be related to that unusual shrinkage behaviour. That layer (≈ nm) would play the role of a viscous coating of the SnO_2 grains.

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