Sintering of undoped SnO_2
(Sinterização de SnO_2 não dopado)

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Abstract

Pure SnO_2 sintering was studied by constant heating rate and isothermal sintering. The constant heating rate study showed no macroscopic shrinkage during the sintering process up to 1500 °C. Pore size distribution measurements, using gas desorption, and grain size and crystallite size measurements of isothermally sintered samples showed no formation of non-densifying microstructures during the sintering process. These results are a strong indication that densification was prevented by thermodynamic factors, mainly the high ratio of γ_{GB}/γ_{SV}. An explanation, based on the nature of covalent bonding and the balance between attractive and repulsive forces, was proposed to explain the high γ_{GB}/γ_{SV} ratio in SnO_2.
Keywords: sintering, SnO_2, microstructure.

Resumo

A sinterização de SnO_2 puro foi estudado por taxa constante de aquecimento e por sinterização isotérmica. O estudo de taxa constante de aquecimento mostrou que não ocorre retração macroscópica durante o processo de sinterização até temperaturas de 1500 °C. Medidas de distribuição de tamanho de poros, usando adsorção de gás, tamanho de grão e tamanho de cristalito para amostras sinterizadas isotermicamente mostrou a não formação de uma microestrutura não-densificante durante o processo de sinterização. Estes resultados são um forte indicativo que a densificação foi inibida por fatores termodinâmicos, principalmente o alto valor da razão de γ_{GB}/γ_{SV}. Uma explicação, baseada na natureza covalente da ligação química e no balanço entre forças atrativas e repulsivas, é apresentada para explicar o alto valor da razão γ_{GB}/γ_{SV} no SnO_2.
Palavras-chave: *sinterização, SnO_2, microestrutura.*

INTRODUCTION

It is a well known fact that the sintering of pure non-oxide covalent compounds (SiC, Si_3N_4, and others) is controlled by a non-densifying mechanism. This mechanism leads to a grain growth process devoid of macroscopic shrinkage or densification.

Similarly to the non-oxide covalent compounds, sintering of tin oxide (SnO_2) is controlled by a non-densifying mechanism [1-3]. Semi-empirical and *ab initio* theoretical calculations have shown a high degree of covalent bonding between Sn and O [4, 5]. This result suggests that the predominance of the non-densifying mechanism in the SnO_2 is related to the nature of the chemical bond and could be similar to the one observed in non-oxide covalent compounds.

In spite of this unequivocal conclusion, the non-densification of SnO_2 is not well known. In a recent paper [1], it was shown that, at a low temperature, sintering of ultra-fine SnO_2 powder is controlled by surface diffusion and, at high temperature, the sintering process is controlled by the evaporation-condensation process. Thus, sintering of pure SnO_2 will always be governed by a non-densifying mechanism. Of course, in this work it was assumed that mechanisms such as surface diffusion and evaporation-condensation are non-densifying.

Recently Shi [6] analyzed the importance of surface diffusion on densification during the sintering process and proposed that surface diffusion is the most probable mass transport mechanism to promote particle coarsening and center approaching between particles or grains.

Greskovich [7] explains the non-densification of Si considering the development of a non-densifying microstructure. This idea is based on the fact that pore growth is promoted by the disconnection of the solid phase at various points of the microstructure. This phenomenon results basically from surface diffusion or evaporation-condensation and the development of a non-densifying microstructure takes into account local shrinkage. In that model, local shrinkage is due

to surface diffusion or evaporation-condensation processes. Lange suggests that the development of a non-densifying microstructure during sintering of a powder compact is caused by a de-sintering phenomenon similar to the one observed in the matrix of ceramic composites, thin films and fibers [8]. In this case, the local shrinkage is basically caused by the non-uniformity of the compact powder.

From the point of view of thermodynamics, it was proposed that during the sintering of covalent compounds, densification is prevented by a high ratio of grain-boundary to solid-vapor surface energies (γ_{GB}/γ_{SV}) [9]. High γ_{GB}/γ_{SV} ratios prevent densification, even of pores surrounded by three grains (in this situation γ_{GB}/γ_{SV} must be $>\sqrt{3}$). A pore surrounded by a small number of grains is thermodynamically unstable when the γ_{GB}/γ_{SV} ratio is lower than $\sqrt{3}$. A high γ_{GB}/γ_{SV} ratio could be related to the nature of the chemical bond, since it is often present in covalent compounds.

The main purpose of this work is to understand SnO_2 sintering and to find an answer to the question: "Why is densification not observed during SnO_2 sintering?"

EXPERIMENTAL PROCEDURE

Table I shows some of the physical characteristics of the SnO_2 powder used in this work. This powder was synthesized by the polymeric precursor method using a tin citrate aqueous solution prepared from $SnCl_2.2H_2O$ (Mallinckrodt Baker, USA, purity > 99.9%) and citric acid (E. Merck, Germany, purity > 99.9%). Ethylene glycol was added to the citrate solution at a mass ratio of 40:60 in relation to the citric acid to trigger a polymerization reaction. After polymerization at 120 °C for several hours, the solid resin was treated at 400 °C for 2 h. The resulting polymer was ground in a ball mill and calcined at 500 °C for 4 h in air. After this step, the powder was heat treated at 400 °C for 12 h in an air flow. An X-ray diffraction analysis of this powder showed a single SnO_2 tetragonal phase.

To study the sintering process, the powder was isostatically pressed, attaining a green density of 54% of the theoretical density. The samples were then sintered both in a dilatometer with a heating rate of 10 °C/min up to 1550 °C (model 402E Netzsch, Germany) and in a tube furnace for an isothermal study. Both experiments were performed in air.

The grain growth measurement of the sintered pellets was accompanied by the measurement of the surface area, using the BET method. The mean grain size was estimated from the surface area using the relation:

$$G_{BET} = 6/\rho_T.S_{BET} \quad (A)$$

where G_{BET} is the mean grain size, r_T the theoretical density, and S_{BET} the surface area.

Measurements of the surface area, hysteresis curve, and pore size distribution of the sintered pellets were obtained using nitrogen adsorption/desorption analysis. The Barret-Joyner-Halenda (BJH) method, considering the desorption curves, was used to determine pore size distribution [11]. A Gaussian function was used to fit the pore size distribution curve.

The crystallite size of the sintered pellets was determined using the diffraction peaks of the (110) and (101) SnO_2 planes and the Scherrer equation:

$$G_{DRX} = \lambda K/\beta \cos\theta \quad (B)$$

where λ is the wavelength ($CuK_{\alpha 1}$), θ the diffraction angle, K a constant, and b the corrected half-width of the diffraction peak. In this study, the diffraction peak profile was fitted using a pseudo-Voigt function to calculate the full width at half maximum (FWHM). Only $CuK_{\alpha 1}$ radiation was considered; $CuK_{\alpha 2}$ radiation was subtracted via a computer software program (FIT Program, Diffract AT, Siemens, Germany). The β value was determined considering the following equation:

$$\beta = (B^2_{0bs} - b^2)^{1/2} \quad (C)$$

where B_{0bs} is the FWHM that is related to the sample and b is the FWHM of the external standard (quartz (SiO_2)).

Table I – Physical characteristics of the SnO_2 powder used in this work
[Tabela I – Caracterização física do pó de SnO_2 usado neste trabalho]

Surface area (m^2/g)	Mean particle size (nm)	Mean crystallite size (nm)
37	24	13

RESULTS AND DISCUSSION

Pore Evolution

The dilatometric results of the SnO_2 pellets showed no macroscopic shrinkage up to 1550 °C. These results suggest that no densification occurred during SnO_2 sintering.

Fig. 1 shows the pore size distribution curve, determined by the BJH method, for the SnO_2 pellets sintered at different temperatures. A mono-modal pore size distribution with a mean pore diameter of 15.1 nm can be observed at 500 °C (Fig.1a). With the increased sintering temperature (Fig 1b, 1c, 1d), an increase in pore diameter is observed, as well as a modification in the shape of the pore size distribution curve. With the increased temperature, the single mode pore population shifts to a bimodal pore population, with two pore diameters appearing most frequently.

The plot in Fig. 2 shows the total pore volume (V_T), measured by the BJH method as a function of the temperature. A decrease in V_T is observed between 500 °C and 600 °C and, from 600 °C to 900 °C, the V_T values are virtually constant. The decrease between 500 °C and 600 °C could be caused by a particle rearrangement, as suggested in [12] or it could be the result of localized shrinkage, since the decreased V_T value did not alter the macroscopic shrinkage. The analysis given in Figs. 1 and 2 suggests that the reduction in the V_T value modifies the pore

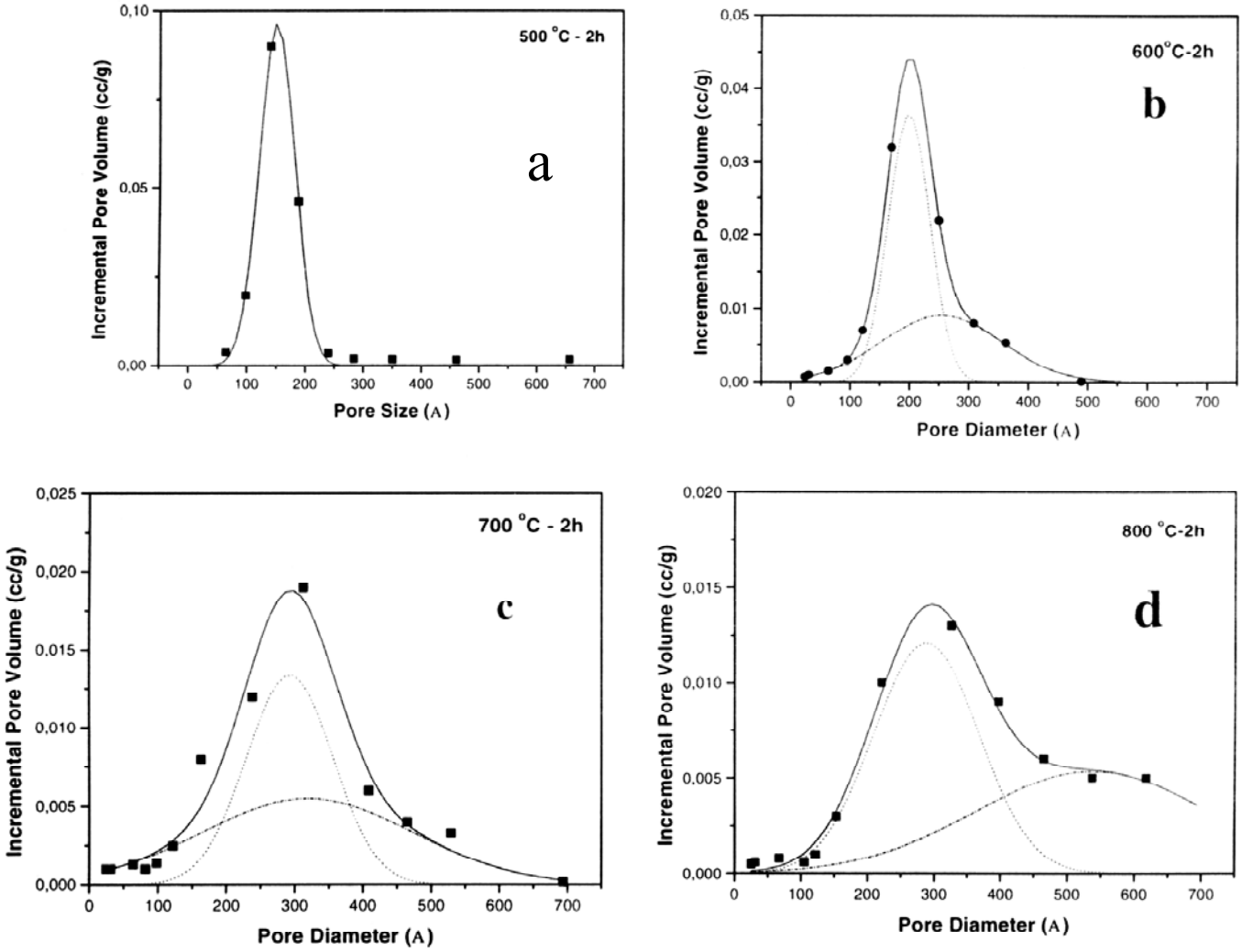

Figure 1: Pore size distribution for sintered samples in different temperatures.
[Figura 1: Distribuição de tamanho de poros para amostras sinterizadas em diferentes temperaturas.]

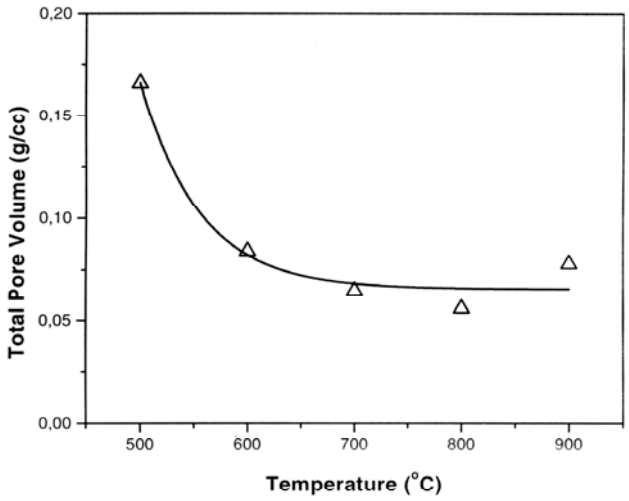

Figure 2: Total pore volume as function of sintering temperature (soaking time of 2 h).
[Figura 2: Volume total de poros em função da temperatura de sinterização (patamar de 2 h).]

size distribution curve, resulting in a bimodal pore population.

Fig. 3 shows the nitrogen adsorption/desorption curves for the SnO_2 pellets sintered at 500 °C and 800 °C for 2 h. The analysis in Fig. 3 displays a Type II adsortion/desorption curve and Type H-1 hysteresis for both pellets. These results suggest the presence of mesopores and open porosity with a cylindrical geometry [13, 14]. It should be noted that there was no change in pore geometry during the sintering process.

Grain size and crystallite size evolution

Fig. 4 presents the variation of grain (G_{BET}) and crystallite (G_{XRD}) sizes in the <110> direction as a function of the temperature for the pellets sintered for 2 h. At temperatures above 500 °C, grain sizes are always larger than crystallite sizes. However, in that temperature range, the crystallite and grain sizes are of the same order of magnitude (the G_{BET}/G_{XRD} ratio < 2). This suggests that grain sizes are formed by a single crystal and that no geometrical changes occur during the sintering process, but only an increase in grain size.

Table II – Mean Grain Size, Most Frequent Pore Diameter (d_{P1} and d_{P2}), and pore diameter-particle diameter ratio for the SnO_2 sintered pellet.
[Tabela II – Tamanho médio de grãos, diâmetro de poro mais freqüente (d_{P1} e d_{P2}) e razão diâmetro de poros/diâmetro de partículas para as pastilhas de SnO_2 sinterizadas.]

Sintering temperature (°C)	Mean grain size G_{BET}(nm)	Most frequent pore diameter d_{P1} (nm)	Most frequent pore piameter d_{P2} (nm)	d_{P1}: G_{BET}	d_{P2}: G_{BET}
500	29	15.1	———	0.52	———
600	37	19.9	25.5	0.54	0.69
700	51	29.2	31.8	0.57	0.62
800	68	28.9	53.8	0.43	0.79

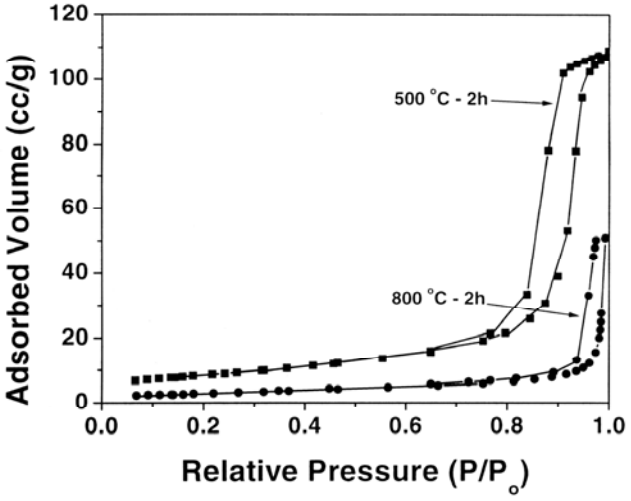

Figure 3: Adsorption/ desorption hysteresis curve for sintered pellets at 500 °C and 800 °C during 2 h.
[Figura 3: Curvas de histereses de adsorsão/desorsão para pastilhas sinterizadas a 500 °C e 800 °C durante 2 h.]

The constant G_{BET}/G_{XRD} ratio observed suggests that grain growth occurs by coalescence or by displacement of the grain boundary line toward the smaller particle [15], without densification of nanometric grain clusters. Cluster densification produces polycrystalline grains with G_{BET} bigger than G_{XRD} [16]. This result is an indication that the reduced pore volume observed between 500 °C and 600 °C is caused by rearrangements rather than by local shrinkages. Crystallite sizes measured in the <101> direction showed values similar to those measured in the <110> direction. These results indicated a non-preferential crystallite growth.

Discussion

The results reported in this work indicate that no macroscopic shrinkage is observed during pure SnO_2 sintering and that only pore and grain growth are observed during the heat treatment.

Table II shows the most-frequent pore diameter (d_p) of the two pore size populations (d_{P1} for the first and d_{P2} for the second pore size population), with the mean grain size (G_{BET}), and the d_P/G_{BET} ratio for the pellets sintered at different temperatures. It can be observed that the G_{BET} is larger than d_{P1} and d_{P2}, indicating that these pores are formed by primary particles. The small d_P/G_{BET} ratio suggests a small number of particles around a pore (small coordination number). The d_P/G_{BET} ratio is small even in the case of the larger pores (d_{P2}). These results suggest that a non-densifying microstructure was not formed during the SnO_2 sintering process.

Our analysis lead us to conclude that densification is prevented by thermodynamic factors, mainly the high γ_{GB}/γ_{SV} ratio. However, it is not clear why this ratio is so high in covalent compounds such as SnO_2. An analysis of this ratio shows that its high values may be due to a high value for γ_{GB} or a low value for γ_{SV} or to a combination of both. It is probable that both these effects occur in covalent compounds, i.e., high γ_{GB} and low γ_{SV} .

Considering the potential energy (E_p) of the interaction between two clusters of molecules, E_p is given by:

$$E_P = E_R + E_A \qquad (D)$$

where E_R is the repulsive energy and E_A is the attractive energy.

In a cluster formed by covalent molecules, there are few degrees of freedom to decrease E_R and to minimize E_p. This behavior is due to the nature of the covalent bond. In order to form covalent bonds between the clusters, the atoms must be arranged in such a way as provide the bonds with a fixed directional relationship to each other. Based on this point of view, the interaction between two clusters of covalent compounds normally results in a high value of E_p .

Considering the first law of thermodynamics:

$$dE = dq + dW \qquad (E)$$

where dE is the internal energy variation, dW is the work variation and dq is the heat variation.

In a system where dq = 0 (no heat transference), dE is given by:

$$dE = dW \qquad (F)$$

By definition, γ is written as:

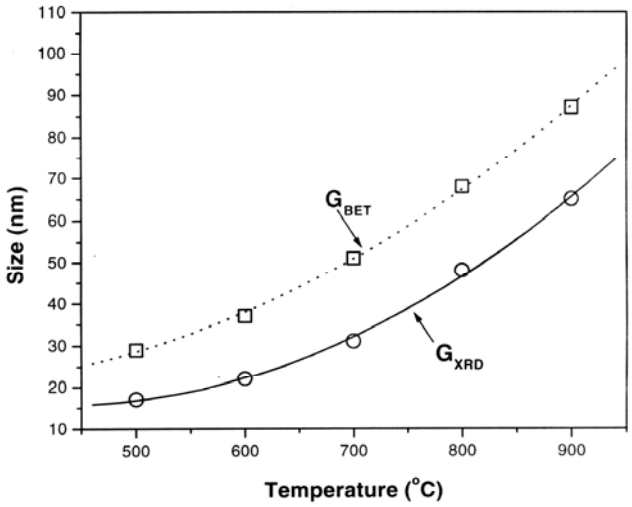

Figure 4: Grain size (G_{BET}) and crystallite size (G_{XRD}) as function of temperature.
[Figura 4: Tamanho de grão (G_{BET}) e tamanho de cristalito (G_{DRX}) em função da temperatura.]

$$dW = \gamma\, dA \quad (G)$$

where dA is the area variation. Based on equations (F) and (G), one can write the following relation:

$$dE = \gamma\, dA \quad (H)$$

or,

$$\Delta E = \gamma\, \Delta A \quad (I)$$

Considering that ΔE is equal to E_P, one can state that E_P is proportional to γ_{GB}. Thus, in a covalent solid, the γ_{GB} will be high due to the high value of E_P. The high E_P value stems from the high value of E_R and is related to the nature of the covalent bond. The most favorable condition for a low γ_{GB} value is a grain boundary formed by grains of the same crystallographic orientation or by a low angle grain boundary.

In addition to their high γ_{GB} value, covalent compounds may present a low γ_{SV} value due to the adsorption of impurities in the solid/vapor interface (pore). The adsorption of impurities decreases the number of broken chemical bonds, thus causing a decrease in the γ_{SV} value.

CONCLUSIONS

In this study it was observed that no macroscopic shrinkages occur during the pure SnO_2 pellet sintering process. The microstructures developed at different sintering temperatures showed that a non-densifying microstructure was not formed. This result strongly indicates that densification is prevented by thermodynamics factors, mainly the high γ_{GB}/γ_{SV} ratio. An explanation, based on the nature of the covalent bond and the balance between the attractive and repulsive forces, was proposed to explain the high γ_{GB}/γ_{SV} ratio in covalent compounds such as SnO_2.

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