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Slip casting and sintering of monodispersed TiO_2 particles

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Monodispersed TiO_2 particles were used to prepare a uniformly packed green compact with a high relative density by slip casting. A suspension consisting of monodispersed TiO_2 particles, solvent and binder was cast in the mould. The sintering behaviour of the green compact was investigated. The green compact could be sintered to a relative density of $> 99\%$ by treatment at 1050 °C for 120 min. The average grain size of the sintered body was 1.26 μm without abnormal grain growth. The green sheet cast on a glass board could be densified with no grain growth. The experimentally obtained relation between densification rate and grain size indicated a volume diffusion mechanism according to Coble's equation.

1. Introduction

Particle characteristics such as particle size, size distribution, shape [1] and state of agglomeration [1–3], and particle packing in the green compact, influence the densification behaviour and microstructure development. On the other hand, the initial [4, 5], intermediate [6–8] and final stages of sintering [6] have already been studied using the models proposed by several workers using powders such as Al_2O_3 [9], Fe_2O_3 [9], ZnO [10] and Ag [11]. They were discussed in terms of the densification rate and grain size during sintering. Commonly, the densification phenomena observed during sintering of the powders show microstructure development involving an abnormal grain growth with increasing temperature. So far, there has been a large gap between real powders and the sintering of model powders.

Recently, monodispersed and highly sinterable powders have been noted as ideal ceramic raw materials. Barringer and Bowen [12] have proposed that uniformly packed green microstructure composed of monodispersed particles leads to a faster densification rate and shorter densification time without grain growth. Preparation and sintering of monodispersed TiO_2 particles have been reported by Barringer *et al.* [13]. They indicated that the intermediate stage of the sintering mechanism of monodispersed TiO_2 particles was a volume diffusion. Jean and Ring [14] demonstrated that monodispersed TiO_2 particles could be synthesized by using a surfactant such as hydroxypropylcellulose (HPC) to inhibit agglomeration and sintered densely at 1050 °C. This shows the advantage of HPC, which can produce a uniform and fine-grained microstructure. Edelsen and Glaeser [15] indicated that the microstructure of monodispersed TiO_2 powders constituted primary particle-influenced sintering behaviour. In particular, the important thing taken into consideration in the densification is that metal alkoxide-derived monodispersed TiO_2 particles give porous agglomerates of a fine primary unit.

Significant grain growth during the sintering is known to occur in the compact made by a die press because of inhomogeneous particle packing. Sordelet and Akinc [16] reported that the compact of monodispersed Y_2O_3 powder made by a die press showed large grain growth. However, they also suggested that compact fabrication should be improved by sedimentation or slip casting. We noted slip casting as an ideal shaping process because slip and tape casting of ceramics offers the possibility of making complex shapes, and it is widely used in the production of ceramic capacitors, substrates for electronic circuits and ceramic packages. Studies of the slip casting and rheological behaviour of suspensions have already been done by several workers [17, 18]. The rheological characteristics of the slurry influence the dispersion state of particles and the particle packing in a green compact. Sacks and co-workers demonstrated that a slurry of Al_2O_3 powders with a narrow size distribution [19] or monodispersed SiO_2 powders [20, 21] could be prepared by controlling rheological properties such as the viscosity and zeta potential of the slurry, so as to produce fine-grained microstructure. In this article, the sintering behaviour of monodispersed TiO_2 particles produced by various casting processes is described. In addition, the intermediate stage of the sintering mechanism of monodispersed TiO_2 particles is discussed.

2. Experimental procedure

2.1. Particle preparation

Monodispersed TiO_2 particles were prepared by hydrolysis of titanium tetra-ethoxide (Ti $(OC_2H_5)_4$, 99 %) in a dilute alcohol solution. Two ethanol solutions were mixed using a stirrer to give concentrations of 0.1 $mol\,l^{-1}$ for Ti $(OC_2H_5)_4$ and

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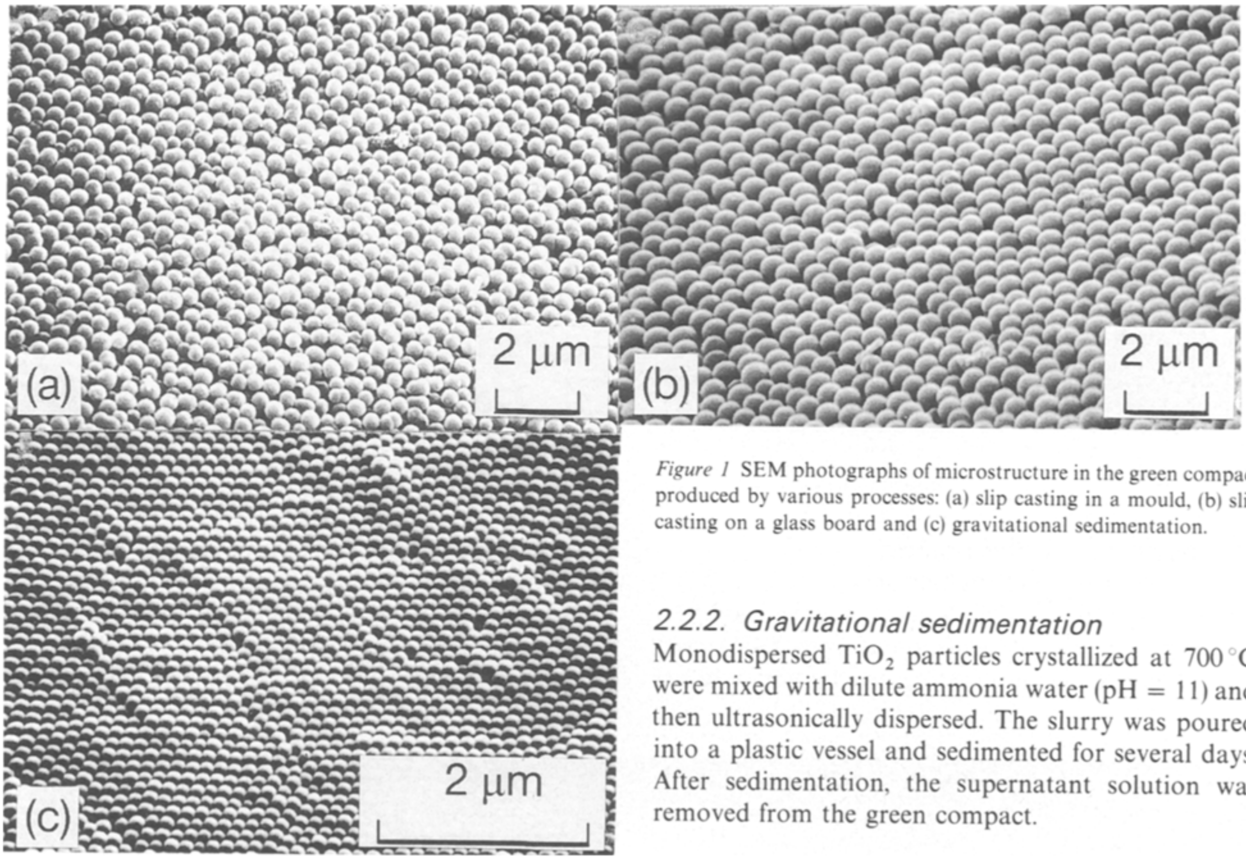

Figure 1 SEM photographs of microstructure in the green compact produced by various processes: (a) slip casting in a mould, (b) slip casting on a glass board and (c) gravitational sedimentation.

0.3 mol l^{-1} for H_2O. After mixing, $TiO_2 \cdot nH_2O$ particles were formed and aged in the mother liquid at 50 °C for 5 h using a water bath. As-prepared particles were separated from the mother liquid by centrifugation. $TiO_2 \cdot nH_2O$ particles were repeatedly washed in the ethanol solution. $TiO_2 \cdot nH_2O$ particles were hydrothermally treated in water at 80 °C for 2 h. Amorphous $TiO_2 \cdot nH_2O$ particles were weakly crystallized to form anatase.

2.2. Green compact production

2.2.1. Slip casting

Monodispersed TiO_2 particles used in slip casting were slowly heated to 700 °C and kept there for at least 2 h. The size of monodispersed TiO_2 particles decreased from 0.5 µm (as-prepared) to 0.45 µm. The particles were crystallized to rutile and loosely agglomerated. The particles were then fully dispersed in ethanol two or three times using an ultrasonic dispersion system. After dispersion, the ethanol solution was removed from the particles using a centrifuge. Binder, solvent and plasticizer were added to the particles and mixed for 24 h at room temperature. Either polyvinylbutyral or polyvinylalcohol was used as a binder. Methyl isobutyl ketone (MIBK) with ethanol was used as a solvent (weight ratio = 3 : 1). A slip consisting of monodispersed TiO_2 particles, solvent and binder was cast in a plaster of Paris mould or on a glass board. The solid loading of TiO_2 particles in the slip was 8–20 wt %. After casting, the green compacts were removed from the mould.

2.2.2. Gravitational sedimentation

Monodispersed TiO_2 particles crystallized at 700 °C were mixed with dilute ammonia water (pH = 11) and then ultrasonically dispersed. The slurry was poured into a plastic vessel and sedimented for several days. After sedimentation, the supernatant solution was removed from the green compact.

2.2.3. Burn-out and sintering

The cast compact and sheet were dried for 24 h at room temperature and heated for 24 h at 60 °C and further for 24 h at 200 °C. The binder and solvent were almost burnt out by calcination at 500 °C. The dimensions of the green compact made from the mould were 1 cm diameter × 0.5 cm. On the other hand, the dimensions of the green sheet made on a glass board was 5 cm × 5 cm × 0.1 cm. The dimensions of the gravitationally sedimented compact were 1 cm diameter × 0.5 cm. All green compacts were introduced into an electric furnace and sintered at various temperatures from 900 to 1200 °C.

The constituents of the slurry used in slip casting and the bulk density are summarized in Tables I and II. A slip casting can produce dense compacts with a greater packing density in comparison with a die press.

TABLE I Slip casting system

Constituent	Content (wt %)
Powder	8–20
Solvent	60–89
Binder	0.5–2
Plasticizer	0.5–1

TABLE II Green density

Compact fabrication	Density (%)
Slip casting	60.5–70.4
Die press	51.5–56.4
Sedimentation	69.0–72.0

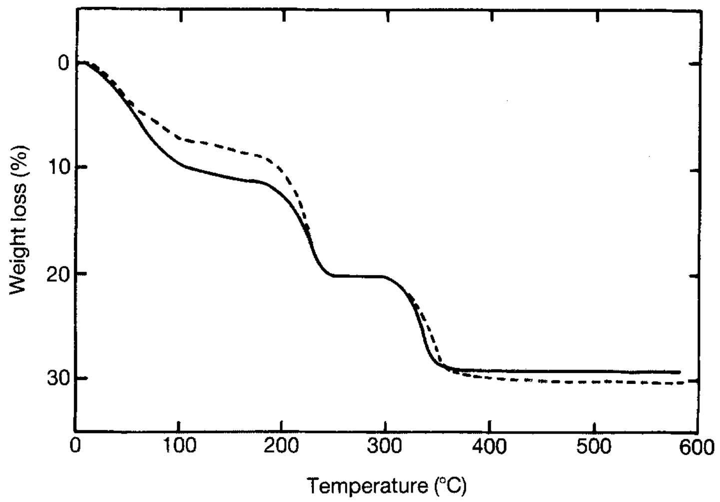

Figure 2 TGA curves for the top and bottom surfaces of a green compact: (---) top surface, (—) bottom surface.

3. Results and discussion

3.1. Green compact evaluation

Fig. 1 shows SEM photographs of green compact microstructure consisting of monodispersed TiO_2 particles, produced by slip casting and by gravitational sedimentation. The particles of green compacts were uniformly packed and not agglomerated. A uniform distribution of pores was observed by SEM.

Fig. 2 shows thermogravimetric analysis (TGA) of a green compact under an air atmosphere. The weight

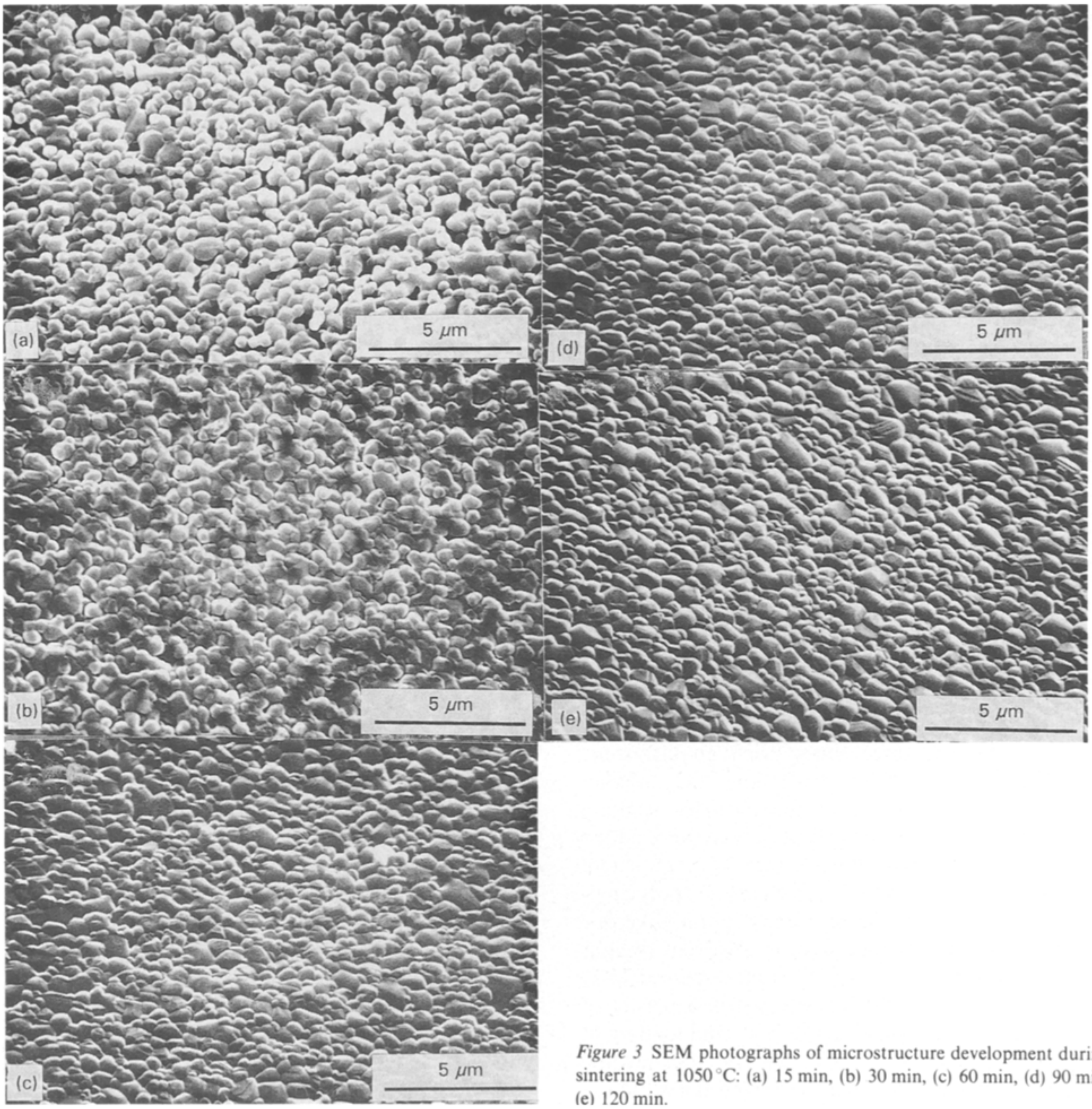

Figure 3 SEM photographs of microstructure development during sintering at 1050 °C: (a) 15 min, (b) 30 min, (c) 60 min, (d) 90 min, (e) 120 min.

loss due to decomposition of the solvent is about 20 % from room temperature to 300 °C. The weight loss from 300 to 500 °C is attributed to decomposition of the binder. TGA curves at the top and bottom of the green compact show a similar behaviour. This shows that the particles are not settled during casting and are well dispersed in the binder and solvent.

3.2. Sintering behaviour of slip-cast compact

Fig. 3 shows the changes in green microstructure during sintering at 1050 °C for 120 min. Pores were appreciably observed in the microstructure until a time of 30 min and a relative density of 85 %. No large pores existed and the pore size was relatively uniform by SEM observation. When the sintering time was more than 60 min and the relative density 92 %, the grains were developed and densification began to occur. The relative density was > 99 % at 120 min and no abnormal grain growth was observed. Hence, the particle packing density and uniformity of porosity controlled the microstructure during the densification process. Therefore, a uniformly packed green microstructure made by slip casting will rapidly sinter to theoretical density with no abnormal grain growth.

Fig. 4 shows the isothermal sintering data as a plot of relative density (theoretical density of rutile = 4.25 g cm^{-3}) as a function of sintering time. Sintering in air was done for various times at temperatures from 900 to 1200 °C. The sintering temperature promoted grain growth during the densification. The densification rate observed in Fig. 4 increased rapidly as the temperature was increased from 900 to 1200 °C. The densification rate was significantly slower at 900 °C than at 1200 °C. Even after sintering at 900 °C for 10 h, the relative density was only 80 %. A time of 10 h was required to reach the theoretical density at 1000 °C, whereas less than 15 min was required at 1200 °C. The densification rate of TiO_2 at each sintering temperature was faster than that reported by Barringer *et al.* [13]. This means that the particle packing and distribution of pores in a slip-cast compact is more uniform.

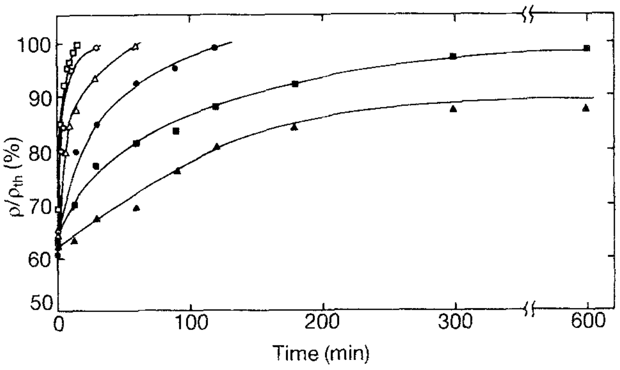

Figure 4 Relative density of slip-cast TiO_2 particle compact as a function of sintering time for different sintering temperatures: (▲) 900 °C, (■) 1000 °C, (●) 1050 °C, (△) 1100 °C, (○) 1150 °C, (□) 1200 °C.

Fig. 5 shows the microstructure of TiO_2 sintered at various temperatures. The grains in the microstruc-

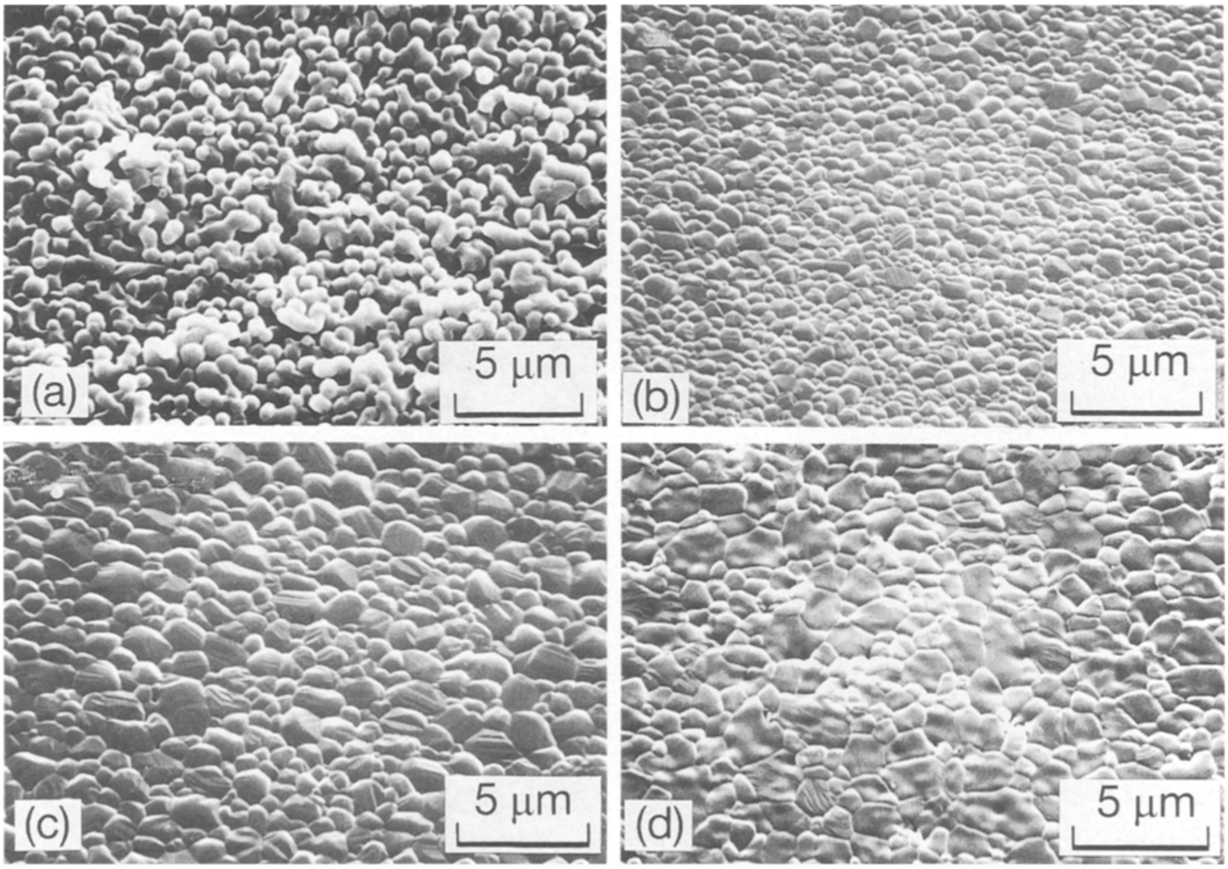

Figure 5 Microstructure development at different sintering temperatures: temperature and relative density (a) 900 °C, 77.6 %; (b) 1100 °C, 98.4 %; (c) 1150 °C, 99.6 %; (d) 1200 °C, 99.9 %.

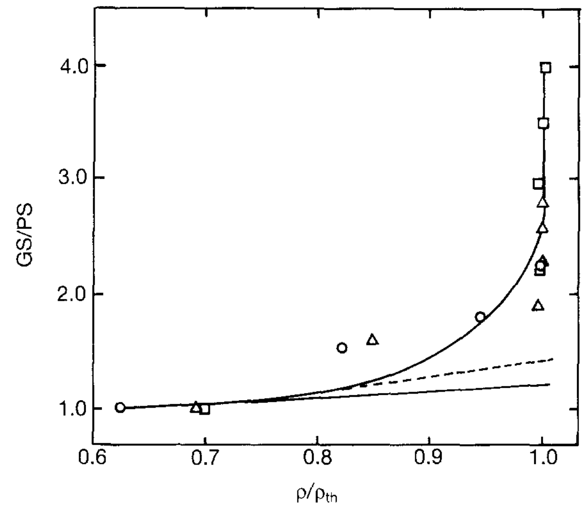

Figure 6 Relative grain size as a function of relative density for different sintering temperatures and processes: slip casting at (○) 1000 °C, (△) 1050 °C, (□) 1200 °C and (---) sedimentation at 1050 °C for PS = 0.45 μm; (—) green sheet at 1100 °C for PS = 0.2 μm.

ture developed as the sintering temperature increased. The grains were not developed at 900 °C when the relative density was 77.6 %, but the pore size was uniform from SEM observation. The initial stage of sintering was observed on treatment at 900 °C for 90 min. However, the sintering showed the final stage a temperature above 1050 °C for the same time of treatment.

Fig. 6 shows the change of the relative grain size, i.e. grain size (GS) divided by particle size (PS). Grain growth occurred rapidly as the temperature was increased. However, little grain growth occurred until the relative density became greater than 99 % (GS/PS = 2.5) at 1050 °C for 90 min. The behaviour of grain growth was similar to that observed by Barringer *et al.* [13]. The relative grain size was about 4.0 at 1200 °C for 90 min. Grain growth observed in the slip-cast compact may have been due to the presence of inhomogeneous particle packing regions in the green microstructure.

3.3. Sintering of green sheet

As another approach, a green sheet was made by pouring the slurry of monodispersed 0.2 μm TiO_2 particles on to the glass board. Fig. 7 shows SEM photographs of the microstructure on the surfaces of sheets sintered at various temperatures. Grains were not developed at 900 °C, similar to the sintering behaviour of slip-cast compact, but grain growth was also hardly observed at 1050 °C (GS/PS = 1.2). The retardation of microstructure development during densification resulted from several contributions, i.e. (a) the particles had a uniformly ordered array in the green compact, (b) the particle size was very small and the particles were not agglomerated, and (c) the microstructure in the particles was relatively dense during crystallization in comparison with that of the porous particles of 0.45 μm.

3.4. Sintering of gravitationally sedimented compact

Fig. 8 shows SEM photographs of the body sintered at 1050 °C for 90 min. The surface and fracture microstructures in the sintered body were almost the same and there was little grain growth due to the uniform particle packing (GS/PS = 1.45). The grain growth

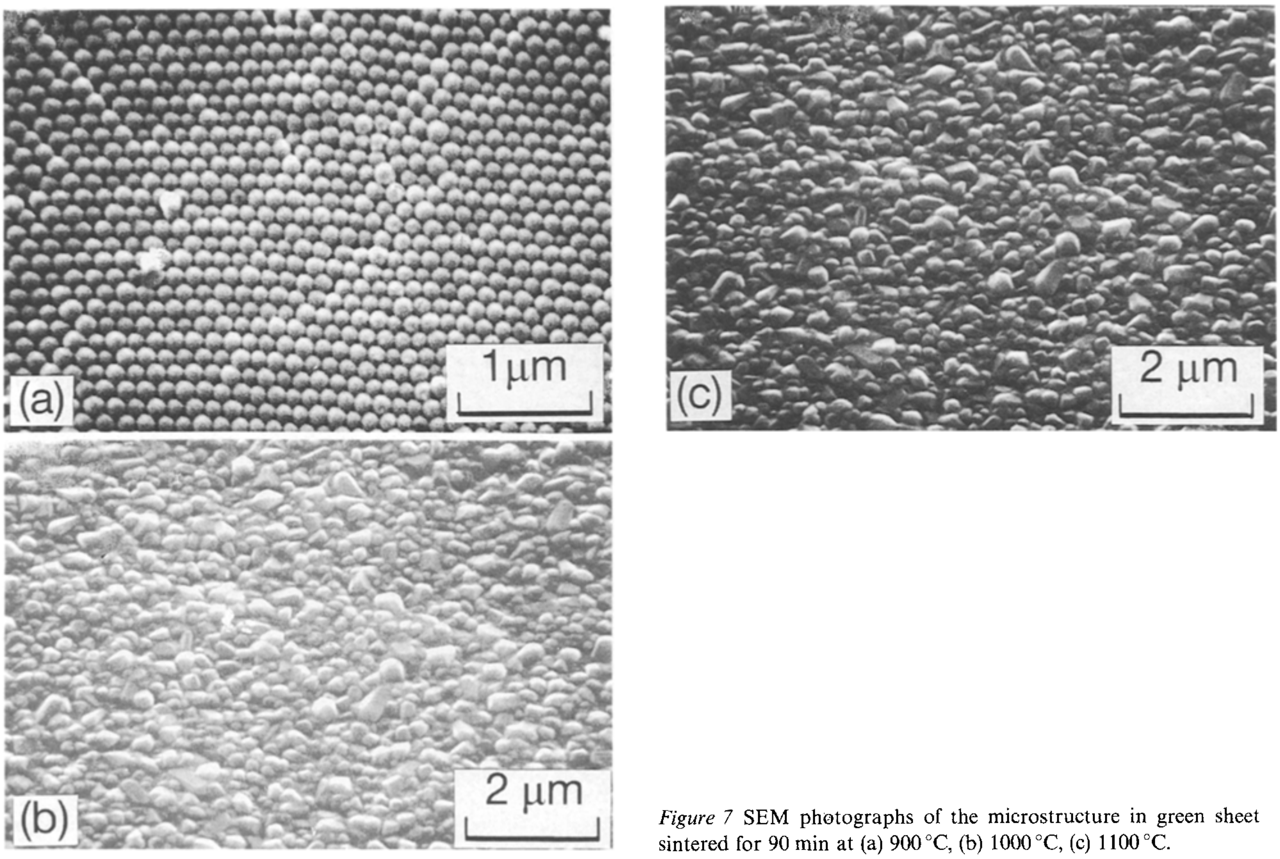

Figure 7 SEM photographs of the microstructure in green sheet sintered for 90 min at (a) 900 °C, (b) 1000 °C, (c) 1100 °C.

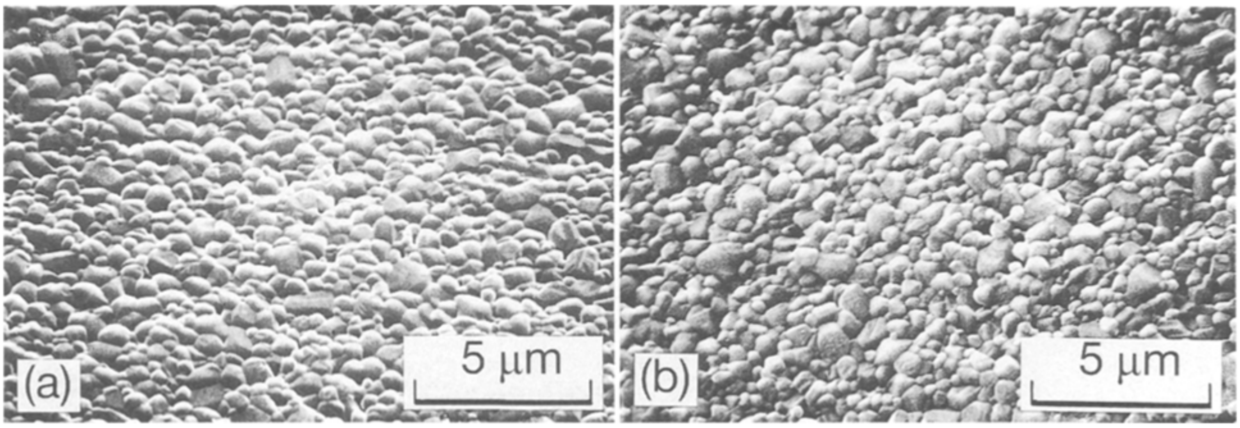

Figure 8 SEM photographs of microstructure in sedimented compact sintered at 1050 °C for 90 min: (a) top surface, (b) fracture surface.

was retarded in comparison with a slip-cast sintered body. However, it is not clear why larger grain growth occurred than in the sintering of a green sheet.

3.5. Intermediate-stage sintering mechanism

An intermediate-stage sintering model has already been introduced by Coble [6]. According to Coble equation's of intermediate-stage sintering

$$-\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{K\gamma\Omega D}{(\mathrm{GS})^m k_\mathrm{b} T} \qquad (1)$$

where P is the porosity, t the time (s), K a constant defined by the geometry, γ the surface free energy of TiO_2 ($600\,\mathrm{erg\,cm^{-2}}$ or $0.6\,\mathrm{J\,m^{-2}}$), Ω the molar volume ($3.13 \times 10^{-23}\,\mathrm{cm^3}$), D the diffusion coefficient, GS the grain size, k_b the Boltzmann constant ($1.38 \times 10^{-16}\,\mathrm{erg\,K^{-1}}$ or $1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$) and T the temperature (K). Equation 2 below was used instead of Equation 1 since P was not obtained from the experiments:

$$\frac{\mathrm{d}(\rho/\rho_\mathrm{th})}{\mathrm{d}t} = \frac{K\gamma\Omega D}{(\mathrm{GS})^m k_\mathrm{b} T} \qquad (2)$$

where ρ is the density and ρ_th the theoretical density. It appeared that the exponent m determined from Equation 2 was 3 in the case of a volume diffusion model. An exponent of grain size m, is, required to determine the mechanism of the intermediate stage of sintering. This is obtained from the data of grain size and densification rate (rate of change of relative density with sintering time). Fig. 9 shows a plot of ln (densification rate) versus ln (grain size). The exponent value given by the slope of the straight line is about -3. This corresponded to the slope introduced by Coble. This finding indicates that the mechanism of intermediate-stage sintering is a volume diffusion. This is supported by the data of Barringer *et al.* [13]. If the sintering mechanism is grain boundary diffusion, the exponent value must be 4. A value of 4 was not obtained from any of the experiments.

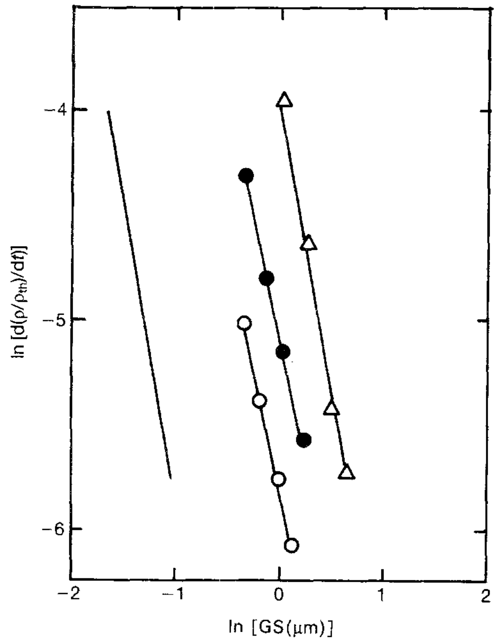

Figure 9 Log–log plots of grain size and densification rate: slip casting at (○) 1000 °C, (●) 1050 °C, (△) 1200 °C and (—) green sheet at 1100 °C. Slope = − 3.

To determine the activation energy for the intermediate stage of sintering, the densification rate equation (Equation 2) was written by using Equation 3,

$$D = D_\mathrm{o} \exp\left(-\frac{Q}{RT}\right) \qquad (3)$$

$$(\mathrm{GS})^3 k_\mathrm{b} T \frac{\mathrm{d}(\rho/\rho_\mathrm{th})}{\mathrm{d}t} = K\gamma\Omega D_\mathrm{o} \exp\left(-\frac{Q}{RT}\right) \qquad (4)$$

where D_o is the rate-controlling diffusion coefficient, assumed to be constant, Q is activation energy and R is the gas constant. Fig. 10 shows an Arrhenius plot for intermediate-stage sintering. The activation energy is given by the slope of the line for each temperature. The slope for each temperature yields an activation energy of $47.5\,\mathrm{kcal\,mol^{-1}}$ ($199\,\mathrm{kJ\,mol^{-1}}$). The rate-controlling diffusion coefficient is obtained by alternating the geometry factor, K. K varies according to the geometry of the grains during sintering. If the grain shape corresponds to a tetrakaidecahedron (a 14-sided polyhedron) on the basis of the sintering model, the value of K is 10 and then D_o is $3.21 \times 10^{-3}\,\mathrm{cm^2\,s^{-1}}$. This value of D_o is in accord with the value for oxygen tracer diffusion in TiO_2 ($D_\mathrm{o} = 2.0 \times 10^{-3}\,\mathrm{cm^2\,s^{-1}}$ [22]). Furthermore, when the grain

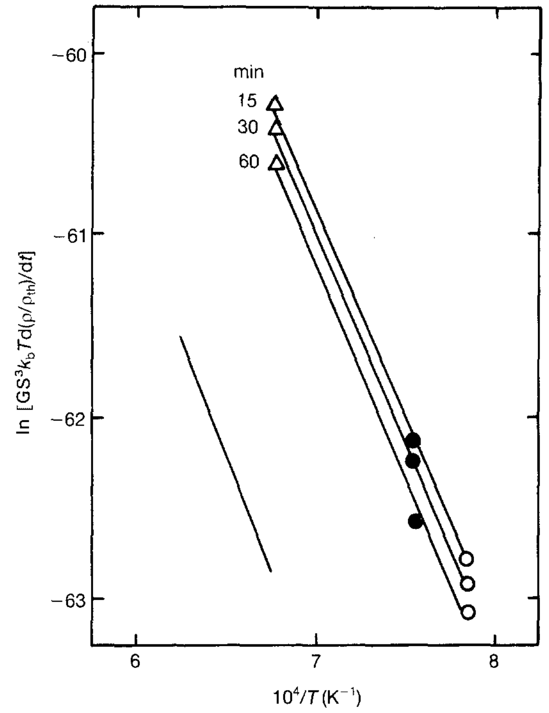

Figure 10 Arrhenius plot for intermediate-stage sintering on the basis of volume diffusion: slip casting at (○) 1000 °C, (●) 1050 °C, (△) 1200 °C and (—) green sheet at 1100 °C. $Q = 47.5$ k cal mol^{-1} (199 kJ mol^{-1}).

shape is that of either a cube or a dodecahedron, K is 151 and 98, respectively. D_0 is then, given by 2.12 $\times\ 10^{-4}$ and 3.24×10^{-4} cm^{2}s^{-1}. The diffusion coefficient is lower and the geometry of the grain is simple. As a result, the geometry of the grain may reasonably be considered as a tetrakaidecahedron.

4. Conclusions

Monodispersed TiO_2 particles were used to prepare a uniformly packed green compact with a high relative density by slip casting and sedimentation. A suspension consisting of monodispersed TiO_2 particles, solvent and binder was cast in a mould or on to a glass board. The sintering behaviour and intermediate-stage sintering mechanism of a green compact constituted of monodispersed TiO_2 particles was investigated. The green compact could be sintered to a relative density of > 99 % without abnormal grain growth. In particular, the green compacts made from a green sheet and by sedimentation led to a relative density of > 99 % with little grain growth. The experimentally obtained relation between densification rate and grain size showed a volume diffusion mechanism according to Coble's equation. The rate-controlling diffusion coefficient was in accord with the value for oxygen tracer diffusion in TiO_2.

References

1. M. F. YAN, *Mater. Sci. Eng.* **48** (1981) 53.
2. F. F. LANGE, *J. Amer. Ceram. Soc.* **67** (1984) 83.
3. F. D. DYNYS and J. W. HALLORAN, *ibid.* **67** (1984) 596.
4. W. D. KINGERY and M. BERG, *J. Appl. Phys.* **26** (1955) 1205.
5. D. L. JOHNSON and I. B. CUTLER, *J. Amer. Ceram. Soc.* **46** (1963) 541.
6. R. L. COBLE, *J. Appl. Phys.* **32** (1961) 787.
7. T. IKEGAMI and Y. MORIYOSHI, *J. Amer. Ceram. Soc.* **67** (1984) 174.
8. J. H. ROSOLOWSKI and C. GRESKOVICH, *ibid.* **58** (1975) 177.
9. R. L. COBLE, *ibid.* **41** (1958) 55.
10. L. F. NORRIS and G. PARRAVANO, *ibid.* **46** (1963) 449.
11. R. L. EADIE, G. C. WEATHERLY and K. T. AUST, *Acta Metall.* **26** (1978) 759.
12. E. A. BARRINGER and H. K. BOWEN, *J. Amer. Ceram. Soc.* **65** (1982) C-199.
13. E. A. BARRINGER, K. BROOK and H. K. BOWEN, "Material Science Research 15" (Plenum, New York, 1984) p.1.
14. J. H. JEAN and T. A. RING, *Amer. Ceram. Soc. Bull.* **65** (1986) 1574.
15. L. E. EDELSEN and A. M. GLAESER, *J. Amer. Ceram. Soc.* **71** (1988) 225.
16. D. J. SORDELET and M. AKINC, *ibid.* **71** (1988) 1148.
17. R. MORENO, J. REQUENA and J. S. MOYA, *ibid.* **71** (1988) 1036.
18. J. H. D. HAMPTON, S. B. SAVAGE and R. A. L. DREW, *ibid.* **71** (1988) 1043.
19. T. S. YEH and M. D. SACKS, *ibid.* **71** (1988) 841.
20. M. D. SACKS, *Amer. Ceram. Soc. Bull.* **63** (1984) 1510.
21. *Idem*, "Rheological Science in ceramic processing", edited by L. L. Herch and D. R. Ulrich, (Science of Ceramic Chemical Processing, Wiley Interscience, New York, 1986) p. 522.
22. S. MRAVEC "Defect and Diffusion in Solid", Materials Science Monographs (Elsevier, 1980) p. 437.

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