

# Powder Processing for Fabricating $\text{Si}_3\text{N}_4$ Ceramics

*The strength of spray-dried  $\text{Si}_3\text{N}_4$  powders containing  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  is controlled by polymeric dispersant content, which also influences sintering properties of the ceramics.*

**H**ard agglomerates limit uniform consolidation of green compacts and leave large pores in the resultant sintered bodies. Consolidation of oxide ceramics<sup>1-6</sup> by slip-casting via dispersion of fine powders by pH adjustment in suspension reduces the tendency for aggregation and yields more uniform and dense green bodies. Also, ultra-high-pressure (up to 1 GPa) isostatic dry-pressing<sup>7,8</sup> of spray-dried granules can collapse the interaggregate pores in green bodies. This has resulted in nearly full densification of the green compacts by relatively low-temperature sintering of the oxides.

Usually, the densification of silicon nitride ceramics requires a sintering aid, e.g., alumina and yttria fine powders. Many types of dispersants have been used to obtain a uniform mixture of silicon nitride and sintering aid. These dispersants affect the microstructure and strength of the spray-dried granules. However, few studies have been made of the effects of the microstructure and strength of spray-dried granules on the sintered and mechanical properties of non-oxide ceramics.<sup>9-11</sup>

In our previous article,<sup>12</sup> the microstructure and strength of spray-dried granules of silicon nitride powders with sintering aids were shown to be a function of the state of powder agglomeration in suspension. Close-packed granules obtained by fine dispersion of particles increased granule strength and intergranular porosity in green compacts.

This article shows the effect of such intergranular porosity—controlled by the strength and structure of spray-dried granules—on the densification of green compacts during sintering. Furthermore, relationships between the fracture strength distribution of spray-dried granules and bending strength distributions of sintered bodies are discussed.

## The Experiment

Fine  $\text{Si}_3\text{N}_4$  powder (specific surface area (SSA) of 11.0 m<sup>2</sup>/g, SN-E10, Ube Industries, Yamaguchi, Japan) was mixed in water with 5 wt% ultrafine  $\text{Al}_2\text{O}_3$  (SSA of 151 m<sup>2</sup>/g, B-type, Iwatani International Corp., Tokyo) and  $\text{Y}_2\text{O}_3$  (SSA of 24.8 m<sup>2</sup>/g, Mitsubishi Chemical Ltd., Tokyo) powders and then ball-milled. The total amounts of solid powders and suspension were 0.5 kg and 0.0012 m<sup>3</sup>, respectively. Solid content in suspension was 38 wt%. Different concentrations of water-soluble polymeric dispersants<sup>12</sup> ( $C_D$  of 0, 1, 2 and 4 wt% maleic anhydride polymer, AKM0531, Nippon Oil & Fats Co. Ltd., Tokyo) were added to the suspensions. The viscosity of each suspension was determined with a concentric cylinder viscometer at a shear rate of 1 s<sup>-1</sup>. The size distribution of the aggregates in suspension was characterized by light scattering and diffraction methods.

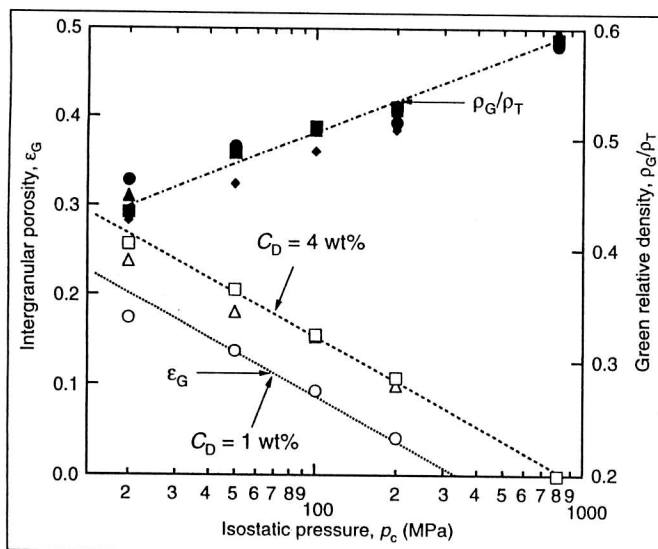
After they were mixed for 96 h, the granules were spray dried (Model CL-8, Ohkawara Kakohki Co. Ltd., Yokohama, Japan) at an

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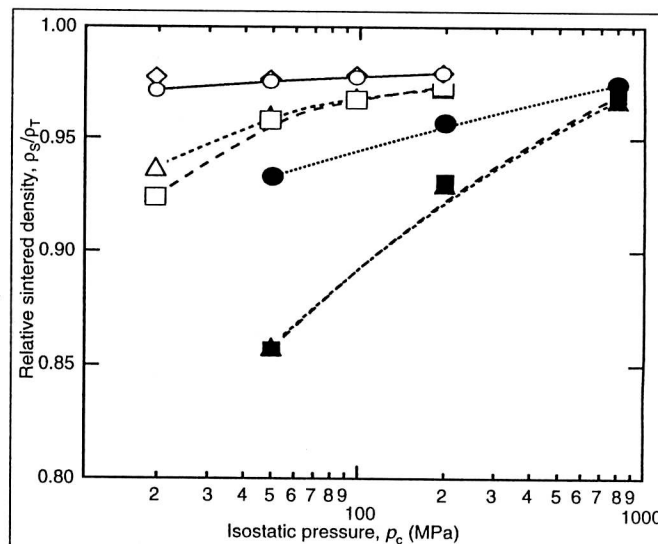
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Relationship between intergranular  $\epsilon_G$ , relative density of green bodies and isostatic pressure (open symbols are  $\epsilon_G$ , solid symbols are  $\rho_G/\rho_T$  and (( $\diamond$ )  $C_D = 0$  wt%, ( $\circ$ ,  $\bullet$ )  $C_D = 1$  wt%, ( $\triangle$ ,  $\blacktriangle$ )  $C_D = 2$  wt% and ( $\square$ ,  $\blacksquare$ )  $C_D = 4$  wt%).



Relationship between cold isostatic pressure and relative density of sintered  $\text{Si}_3\text{N}_4$  ceramics. Sintering temperature was (solid symbols) 1650°C and (open symbols) 1850°C (( $\diamond$ )  $C_D = 0$  wt%, ( $\circ$ ,  $\bullet$ )  $C_D = 1$  wt%, ( $\triangle$ ,  $\blacktriangle$ )  $C_D = 2$  wt% and ( $\square$ ,  $\blacksquare$ )  $C_D = 4$  wt%).

outlet temperature of 170°C. The mean diameter of the granules was  $\sim 45$   $\mu\text{m}$ . The tensile strength ( $\sigma_T$ ) of a single granule was measured by a commercial diametral compression testing machine (Model MCTE-200, Shimadzu Co. Ltd., Kyoto, Japan). The single granule was put on the polished plate of an ultrahard metal. The granule was compressed uniaxially by a 50- $\mu\text{m}$ -diameter circular diamond plate and crushed in diametral compression at a loading rate of 0.01 g/min. The relations between the load and displacement during loading were measured. For failure in tension along the diameter, the fracture  $\sigma_T$  of a granule was dependent on the load at fracture ( $P_f$ ) and the diameter of the granule ( $d_G$ ).  $\sigma_T$  was calculated from  $\sigma_T = 2.8P_f/(\pi d_G^2)$ . This relationship was derived by Hiramatsu and Oka<sup>13</sup> for the strength of a brittle, spherically shaped specimen tested in diametral compression.

For the compaction studies, spray-dried granules were packed in a cylindrical cell 2 cm in diameter or a rectangular cell with a 7 cm  $\times$  5 cm base and uniaxially prepressed at 10 MPa for 3 min. The compacts then were further consolidated by cold isostatic pressing (Model MCT-100, Mitsubishi Heavy Industries Ltd., Tokyo) at 20–800 MPa for 3 min. The thickness of each sample was  $\sim 5$  mm after isostatic pressing. The

green density was determined from the weight and dimensions of the specimens. Pore-size distribution and porosity ratio in the granules and green compacts were measured by mercury porosimetry (Poresizer Model 9310, Micromeritics Inc., Norcross, Ga.).

The green compacts then were sintered at 1650° or 1850°C in nitrogen gas at a pressure of 0.95 MPa for 4 h. The bulk density of the sintered bodies was determined by the Archimedes displacement method using distilled water. If the sintered bodies had a relative density  $< 90\%$  of theoretical and open porosity, the bulk density was determined by the measurement of sample dimensions.

Three-point bending strength was measured using 5.0 cm  $\times$  0.4 cm  $\times$  0.3 cm test bars diamond machined from sintered plates pressed at 200 MPa. Flexural strength tests were conducted by three-point loading at room temperature in air with a crosshead velocity of 0.1 mm/min. Span and loading

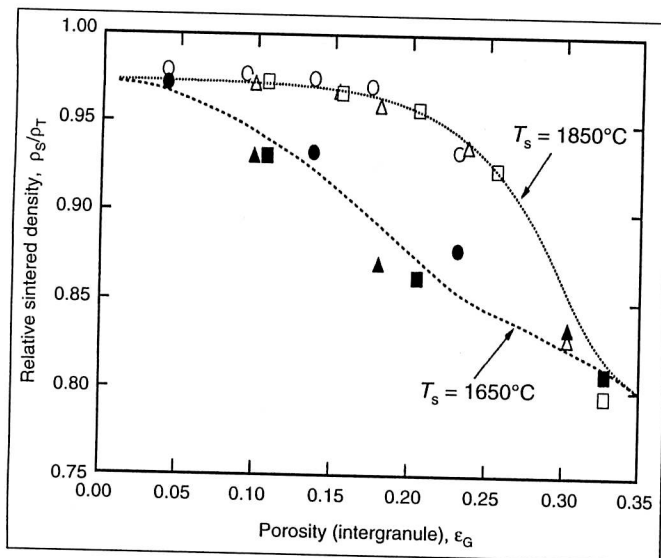
point diameter for the bending test were 3 cm and 5 mm.

### Suspension Behavior

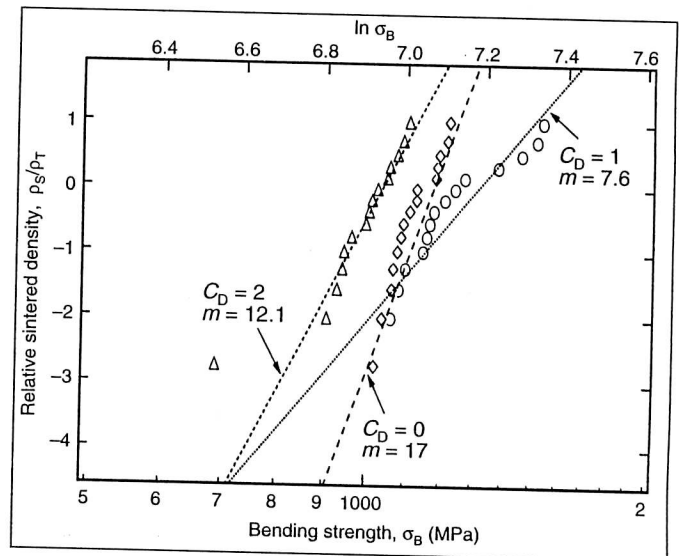
The viscosity and the mean aggregate diameter of each suspension with different amounts of dispersant were determined. The minimum viscosity and aggregate size existed at  $C_D = 2$  wt%. Excess additions of dispersant (e.g.,  $C_D = 4$  wt%) increased the viscosity and promoted powder agglomeration.

The structure and fracture strength of spray-dried granules varied by the amount of water-soluble polymeric dispersants used. Bimodal pore-size distributions always were observed by mercury porosimetry<sup>12</sup> in packed beds of granules without pressing. The larger peaks corresponded to intergranular pores and smaller peaks to intragranular pores. The mode of intragranular pore and intragranular pore volume decreased with decreased viscosity and mean size of the aggregates in suspension.

Effect of Dispersant Amount on Viscosity, Mean Diameter of Aggregates in Suspension before Spray Drying and Granule Strength				
	Dispersant amount, CD (wt%)			
	0	1	2	4
Viscosity (mPa·s)	329	18.6	17.8	35.3
Mean aggregate diameter ( $\mu\text{m}$ )		0.44	0.26	0.33
Intergranular pore size mode (nm)	144	69.1	40.4	50.9
Mean granule strength, $\sigma_T$ (kPa)	365	327	728	833
Weibull modulus, $m_G$	5.4	3.0	4.3	3.8



Relationship between porosity rate for intergranular space in compacts and relative density of sintered bodies ((○, ●)  $C_D = 1$  wt%, (△, ▲)  $C_D = 2$  wt% and (□, ■)  $C_D = 4$  wt%).



Distributions of three-point bending strength of sintered  $\text{Si}_3\text{N}_4$  ceramics at  $T_s = 1850^\circ\text{C}$  and  $p_c = 200$  MPa ((◇)  $C_D = 0$  wt%, (○)  $C_D = 1$  wt% and (□)  $C_D = 2$  wt%). Weibull distribution function was used.

The fracture  $\sigma_T$  of each spray-dried granule was determined by a diametral compression test and analyzed by a Weibull distribution. The mean strength of granules initially decreased with the addition of dispersant from  $C_D = 0$  wt% to  $C_D = 1$  wt% and increased with increased  $C_D$  from 1 wt% to 2 and 4 wt%. The Weibull modulus was the smallest at  $C_D = 1$  wt%.

### Consolidation Behavior

The consolidation behaviors of the green bodies of spray-dried granules prepared from suspensions with different concentrations of dispersant were examined by measuring changes in pore-size distribution in green compacts after isostatic pressing.<sup>12</sup> Peaks at large pore diameters corresponded to intergranular pores and peaks at small pore diameters corresponded to intragranular pores. The increase of isostatic pressure up to 200 MPa did not affect intragranular porosity. However, the average intergranular pore decreased. The interparticle pore-size distribution could be fitted by a Gaussian equation.

If we assume that the intragranular pore-size distribution did not change after isostatic pressing up to 200 MPa, then the intergranular volume ( $V_G$ ) in compacts corresponded to the total volume outside of the fitted curve.<sup>12</sup>

The intergranular porosity ( $\epsilon_G$ ) was calculated from  $V_G$  in green compacts. The relative density of the green bodies ( $\rho_G/\rho_T$ ) increased in proportion to the logarithm of the isostatic pressure. Slope and relative density of each granule with different amounts of dispersant were similar for all samples. On the other hand,  $\epsilon_G$  decreased with decreased granule strength and  $C_D$ . For instance,  $\epsilon_G$  at  $C_D = 1$  wt% and a mean granular strength of ~300 kPa was smaller than that at 2 or 4 wt%, and granules completely collapsed at 300–400 MPa.

On the contrary, at a  $C_D$  of 2 or 4 wt%—when the mean granular strength was >700 kPa—intergranular pores existed in green compacts at an isostatic pressure <800 MPa. Granules did not completely collapse during relatively low-pressure compaction, i.e.,  $p_c = 50$  MPa. Subsequent fracture was observed along intergranular pores. Some granules remained in the green compacts during relatively high isostatic pressure, i.e.,  $p_c = 200$  MPa. These granules were observed to collapse only at high isostatic pressure, i.e., 800 MPa.

### Sintering Behavior

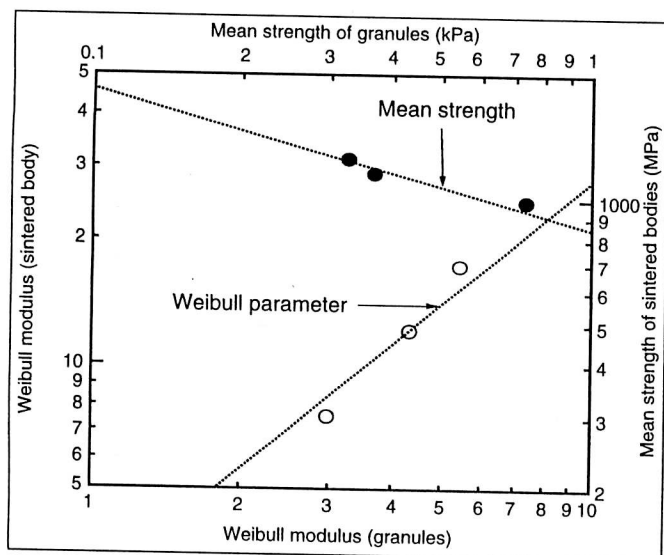
For  $C_D$  values of 2 and 4 wt%, the relative density of the sintered bodies depended on the isostatic pressure. The relative density of sintered bodies

decreased with increased concentration of dispersant for all pressure at  $1850^\circ\text{C}$ . When ultrahigh isostatic pressure (800 MPa) was used, almost complete densification of all the green bodies was obtained after sintering at  $1850^\circ\text{C}$ . The intergranular porosity in the green bodies almost completely collapsed by isostatic pressing at 800 MPa. On the other hand, in the cases where  $C_D$  was 0 or 1 wt% and an isostatic pressure of 20 MPa was used, almost complete densification of the green bodies was obtained after sintering at  $1850^\circ\text{C}$ .

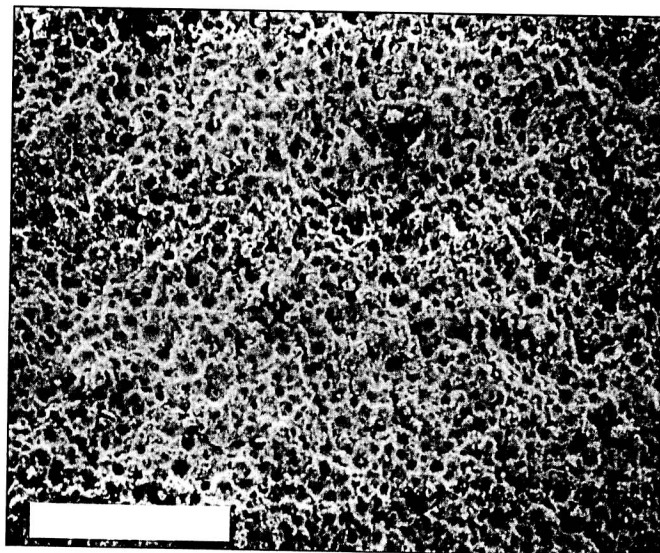
The relative sintered density was plotted vs  $\epsilon_G$ . Under similar sintering conditions, the density of sintered bodies depended only on  $\epsilon_G$ , and  $\epsilon_G$  increased with increased  $\sigma_T$  of the granules, because the granules did not collapse under normal compaction pressure. For densification of green compacts, the strength of granules should be designed as low as possible, such that the isostatic pressure could be decreased to ensure complete collapse of intergranular pores in the green compacts.

### Bending Strength

The bending-strength ( $\sigma_B$ ) distributions of sintered bodies were described by Weibull distribution functions. Isostatic pressures of 200 MPa and sintering temperature of  $1850^\circ\text{C}$  were used for



Relationship between (●) mean strength and (○) Weibull modulus of granules and of sintered bodies.



SEM micrograph of the fracture surface of a green body ( $C_D = 4$  wt% and  $p_c = 50$  MPa, bar = 0.50 mm).

sample preparation. The maximum mean  $\sigma_B$  occurred for samples where  $C_D = 1$  wt%. However, the Weibull modulus had its minimum value at  $C_D = 1$  wt%. In the case of  $C_D = 2$  wt%, which had the maximum mean  $\sigma_T$  for spray-dried granules, the mean  $\sigma_B$  had minimum values.

The Weibull modulus for  $\sigma_B$  distribution of sintered bodies had its minimum value at  $C_D = 1$  wt%, corresponding to a low Weibull modulus for granular strength.

An adequate correlation between mean strength and Weibull modulus of sintered bodies and that of granules was suggested. The high-strength granules could not be completely collapsed, and, therefore, they resulted in intergranular pores that formed between unfractured granules in the green bodies. We suggested that the low value of the Weibull modulus of granular strength was caused by the inhomogeneous structure and strength of the spray-dried granules.

To obtain the high reliability of sintered bodies, the uniform dispersion of aggregates and the uniform mixture of

sintering aids and dispersants in suspension were important. Furthermore, the mean  $\sigma_B$  decreased with increased granular strength. It was suggested that the size of intergranular pores increased in sintered bodies with increased strength of spray-dried granules. Therefore, the bending strength of the sintered bodies depended on granule strength.

## Dispersant Controls Strength

The strength and microstructure of spray-dried granules of  $\text{Si}_3\text{N}_4$  powders with  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  ultrafine powder sintering aids were controlled by the amounts of the water-soluble polymeric dispersants added. The intergranular pore volume and size between unfractured granules in green compacts increased with increased granule fracture strength. Under constant sintering conditions, the density of the sintered bodies depended only on intergranular porosity. As the strength of the granules increased, the cold isostatic pressure necessary to obtain almost complete densification of sintered bodies increased. The mean

bending strength of the sintered bodies decreased with increased fracture strength of the spray-dried granules. The Weibull modulus of bending strength distribution of sintered bodies decreased in proportion to decreased granular strength. The strength of spray-dried granules had to be designed as low as possible to obtain high reliability and strength and uniform densification of the  $\text{Si}_3\text{N}_4$  sintered bodies. ■

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The list of references to this article is available on the Internet, <http://www.ceramicbulletin.org> or by contacting the Editorial Assistant by mail addressed to Society headquarters or by Fax at 614-794-5822. Request Data Depository File No. 277.

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