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Optimization of Suspension Characteristics for Shaping Processes

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Abstract

This paper deals with the relationships between suspension characteristics and the structure of green bodies in shaping processes. The slip casting process with aqueous alumina slurry and the uni-axial pressing process of spray-dried granules prepared with aqueous silicon nitride slurry were selected. In the slip casting process, it was clear that the measurement of sedimentation behavior in a centrifugal field and the aggregate particle size analysis were promising methods to determine the optimum characteristics of a suspension for slip casting. In the spray drying and uni-axial pressing process, the compressive strength of granules was measured by a microcompression testing machine, and the porosity of granules was measured by a mercury porosimeter. Both values were applied to analyze the effect of the slurry on the granules' properties. Futhermore, it was suggested that the characterized results were promising to determine the optimum characteristics of spray-dried granules for uni-axial pressing. © 1996 Elsevier Science Limited.

1 Introduction

It is a key technology to control the microstructure of green bodies in advanced ceramics, especially in structural ceramics to eliminate the defects in sintered bodies which lead to lower reliability. Many defects originate from the production process before sintering. For instance, large pores are the most common defects in sintered ceramics[1-3] and they are mostly related to defects in granules such as pores, dimples and void spaces between granules.[4] As the defects in the green bodies grow in the sintering process, the microstructure should be controlled in the green bodies to minimize the size of defects as well as to achieve a uniform and dense microstructure.[5]

In shaping processes such as slip casting and uni-axial pressing of spray dried granules, the starting step is to prepare a slurry. In the slip casting process, the microstructure of green bodies changes with suspension characteristics.[6] On the other hand, in uni-axial pressing, the characteristics of spray-dried granules are changed with the suspension characteristics.[7,8] As the structure of green compact is affected by the granules' characteristics, it is clear that the suspension characteristics have a large effect on the microstructure of green compact.[7,8] Therefore, the key technology for both shaping processes is to make clear the relationships between suspension characteristics and the microstructure of green bodies.

The suspension characteristics have been measured by several methods which include viscometer, zeta-potential analyzer and gravity settling behavior. However, these methods are not adequate to determine the optimum characteristics of a suspension for shaping processes.[6,7,8] Therefore, this paper deals with characterizing methods to relate suspension characteristics to the microstructure of green bodies.

In the slip casting process, new measuring methods will be proposed, which are promising to determine the optimum conditions of suspension characteristics for slip casting. Additionally, in the case of spray drying and uni-axial pressing processes, a new method will be proposed to characterize the relationships between slurry preparation conditions and the characteristics of spray-dried granules as well as the relationships between the granules' characteristics and the microstructure of green compacts.

2 Experimental Procedure

2.1 Slip casting experiment

Table 1 shows the slurry preparation conditions. Commercially available low-soda alumina powder (Al-160SG-4, Showa Denko, Japan) was used as

Table 1. Slurry preparation conditions

	Slip casting	*Spray drying/pressing*
Powder material	Low-soda alumina	Silicon nitride
Particle true density ρ_t (g/cm^3)	3.94	3.19
BET specific surface area (m^2/g)	6.0	10.7
Average particle size (μm)	0.6	0.8
Dispersant	Polyacrylic acid ammonium salt	Maleic anhydride derivative
Solvent	Ion-exchange distilled water	Ion-exchange distilled water
Solid concentration (vol%)	42	34
Mixing time (h)	1	24

test material, and polyacrylic acid ammonium salt (A-30SL, Tooa Gousei Kagaku Kougyo Co., Japan) was selected as dispersant. Figure 1 shows the flow chart of the slip casting process. The apparent viscosity of the prepared slurry was measured by viscometer (BL type, Toki Sangyou Co., Japan) at a shear rate of $1{\cdot}29\ s^{-1}$. An X-ray particle size analyzer based on the sedimentation method (Sedigraph 5100, Micromeritics Instruments Corp.) was also applied to characterize the aggregate size distribution of the suspension which was measured by diluting the slurry down to 7 wt% of alumina concentration. In addition, the settling behavior of the suspension was measured in a centrifugal field by Sedimenputer SPT-C (Hosokawa Micron Corp., Japan).

The measuring principle of the apparatus[9] is shown in Fig. 2. The homogeneous suspension including a sample powder is poured into a cell and this is set on a rotor, the balance of the rotor being established before the measurement. The rotor is set in motion, the particles settle in the centrifugal field and the center of gravity of the cell is shifted from its initial position. The degree of suspension sedimentation is given as the voltage which represents the cumulative deviation of the center of gravity from the initial position, and plotted against the processing time of the apparatus.

Green bodies were fabricated with a gypsum mold, and the microstructure of green body was measured by a mercury porosimeter (Pore Sizer 9220, Micromeritics Instruments Corp.).

2.2 Spray drying and uni-axial pressing experiment

Table 1 shows the slurry preparation conditions. Commercially available silicon nitride powder (SN-E10, Ube Industries Ltd., Japan) and maleic anhydride derivative dispersant (AKM0531, Nippon Oil & Fats Co., Japan) were used in the experiment. Figure 3 shows the flow chart of the spray drying and uni-axial pressing process.The apparent viscosity of the prepared slurry was measured by the viscometer under the same conditions as for aqueous alumina slurry.

Then, granules were fabricated by a disc-type spray dryer (model: CL-8, Ohkawara-Kakohki Co., Japan). The dryer was operated with an inlet air temperature of 150°C and an outlet air temperature of 90°C. A rotary atomizer rotating at 15,000 rpm was employed for atomization. Spray-dried granules were screened (250 μm) and characterized. A mercury porosimeter was employed to determine the open porosity of granules. The compressive strength of granules was measured by a microcompression testing machine (model: PCT-200, Shimazu Co., Japan).

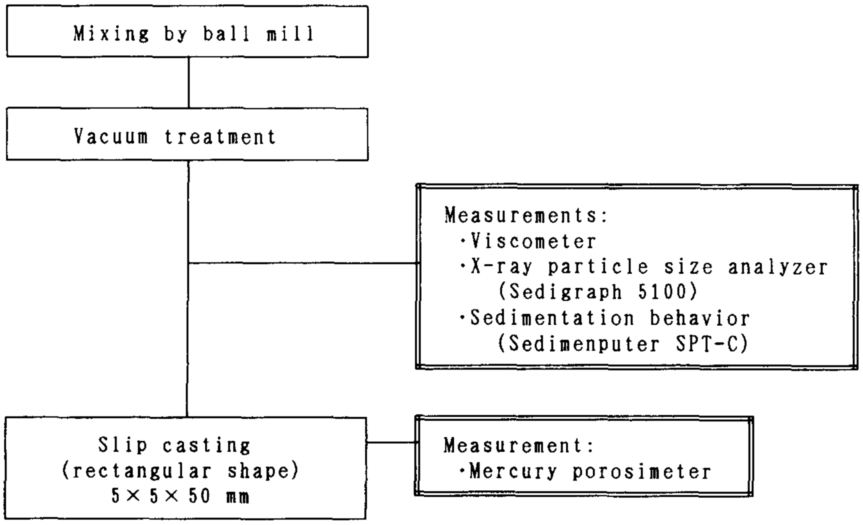

Fig. 1. Flow chart of slip casting process.

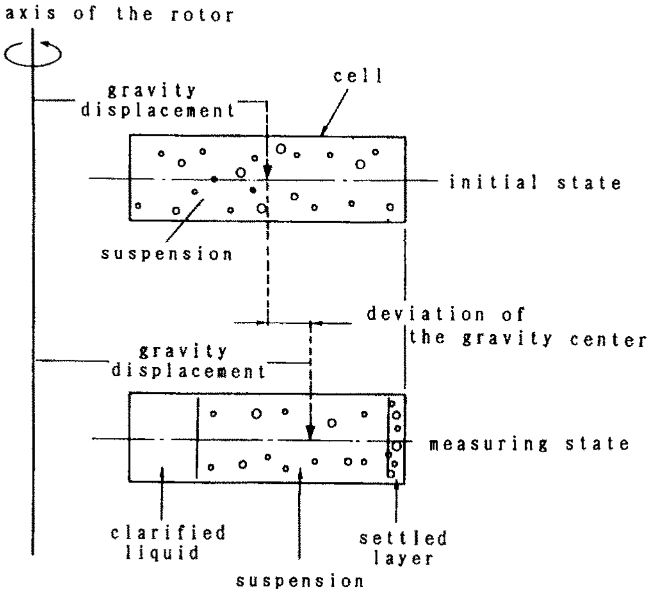

Fig. 2. Principle of the measurement of suspension settling behavior in centrifugal field.

A quantity of granules were poured into a cylindrical mold of 20 mm internal diameter and pressed uni-axially for 10 min. Then, the structure was analyzed by the mercury porosimeter.

3 Results

3.1 Slip casting process

Figure 4 shows the change of apparent viscosity of the slurry against the concentration of dispersant (C_D) which was defined as weight for 100 g alumina. The viscosity decreased against dispersant content up to C_D=0·3 and increased slightly with dispersant content from C_D=0·3 to 1·5. On the other hand, Fig. 5 shows the pore size distribution of green body by slip casting. It indicates that the pore volume and size decreased against the dispersant content, and that the apparent viscosity is not able to explain the change of structure of green body with dispersant content.

Figure 6 shows the degree of suspension sedimentation in a centrifugal field with time. It is proved that the equilibrium value of the suspension sedimentation curve increases as the dispersant concentration increases, and that the tendency shows good agreement with the change of green body structure as shown in Fig. 5.

The aggregate size distribution of suspension changed with the dispersant concentration as shown in Fig. 7. From this figure, it is found that the suspension becomes well-dispersed as the dispersant concentration increases up to C_D = 0·3, and that it becomes flocculated from C_D = 0·3 to 1·5. This explains how the apparent viscosity became small up to C_D = 0·3, and increased from C_D = 0·3 as shown in Fig. 4.

However, the very interesting thing is that the change of suspension sedimentation curve with dispersant showed a different tendency from that of the apparent viscosity with the dispersant. It suggests that the measurement of the sedimentation behavior of a suspension in a centrifugal field is a promising method to determine the optimum conditions of suspension characteristics for slip casting. It will be discussed with the aggregate particle size as shown in Fig. 7.

3.2 Spray drying and uni-axial pressing experiment

Figure 8 indicates the change of the apparent viscosity of aqueous silicon nitride slurry against dispersant concentration (C_D). The apparent viscosity decreased with dispersant content, and then kept an almost constant value from C_D = 0·1 to 1·5. Spray-dried granules were characterized by the porosity and the compressive strength. Figure 9 is the relationships between the porosity of granules

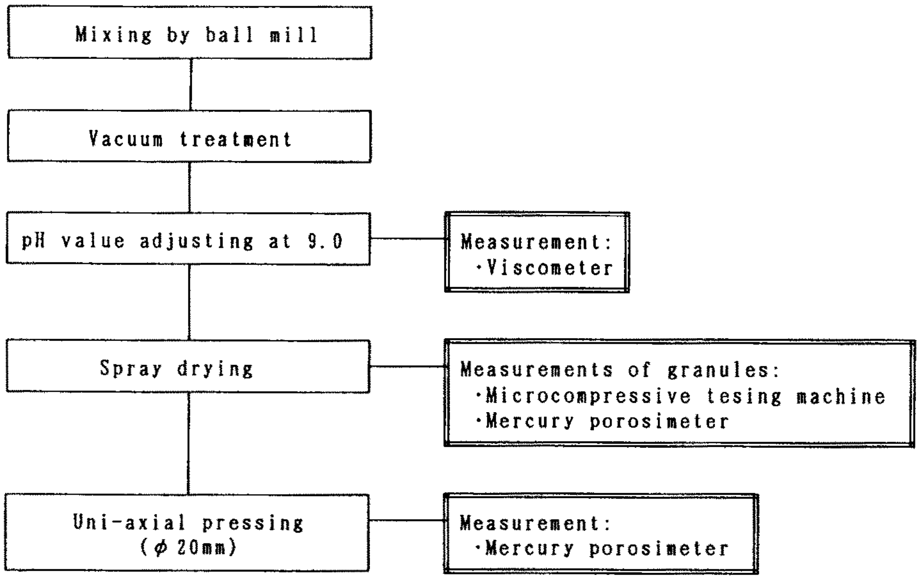

Fig. 3. Flow chart of spray drying and uni-axial pressing process.

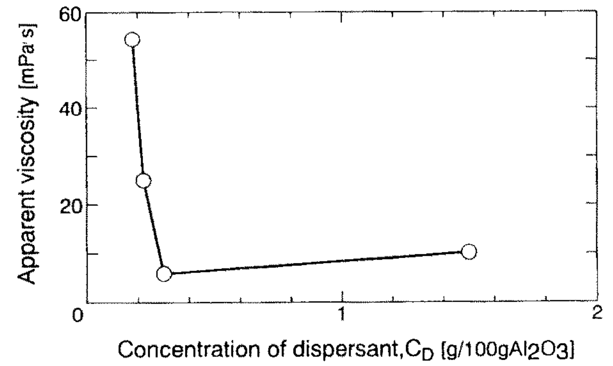

Fig. 4. The charge of apparent viscosity of aqueous alumina slurry against concentration of dispersant.

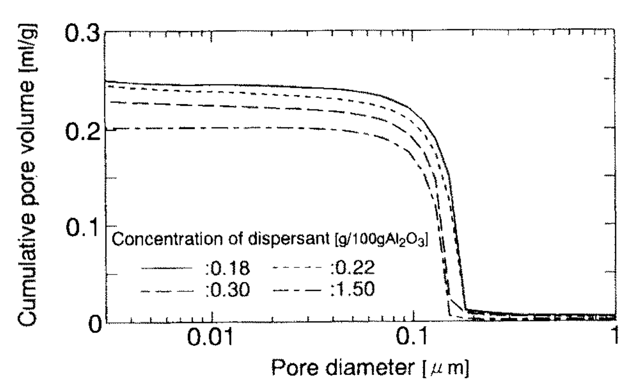

Fig. 5. Pore size distribution of green body fabricated by slip casting.

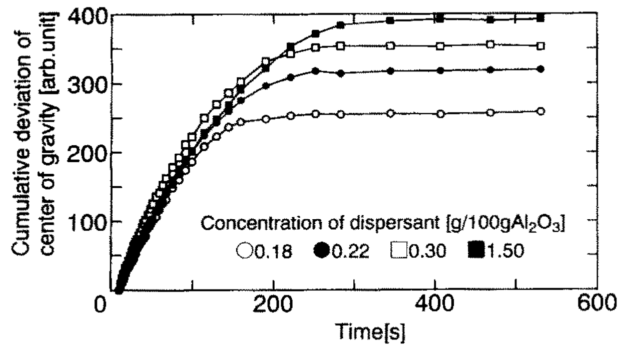

Fig. 6. Settling process of suspension in centrifugal field.

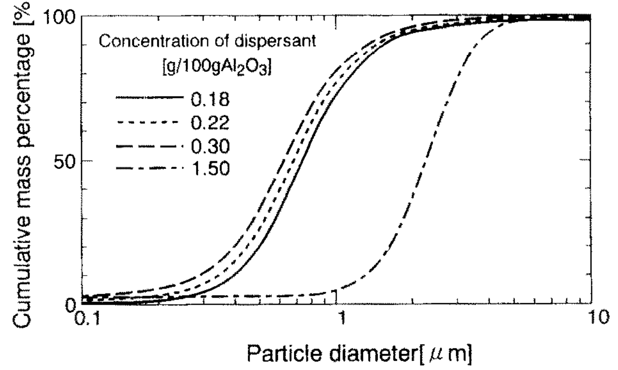

Fig. 7. Aggregate particle size distribution by X-ray particle size analyzer.

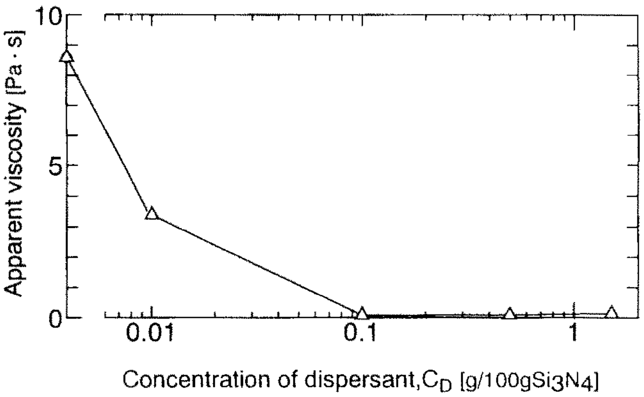

Fig. 8. The change of apparent viscosity of aqueous sillicon nitride slurry against concentration of dispersant.

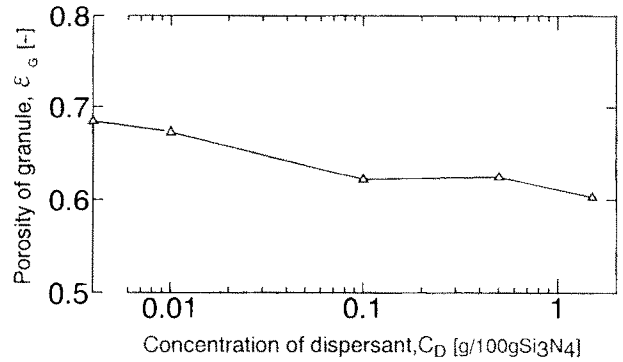

Fig. 9. Change of porosity ε_G of spray-dried granule against concentration of dispersant.

and the dispersant concentration. The porosity of granules was calculated from the cumulative pore volume (V_G) except for the range of over 10^3 nm pore diameter which indicated inter-granular pore volume. The following equation was applied to calculate the inter-particle porosity ε_G of granules:

$$\varepsilon_G = \frac{V_G}{V_G + 1/\rho_t} \qquad (1)$$

Figure 10 shows the change of compressive strength of granules with the dispersant concentration. The compressive strengths were calculated from compressive load by Hiramatsu's equation.[10]

$$\sigma_G = 2{\cdot}8P_f/(\pi d_G^2) \qquad (2)$$

where σ_G is the compressive strength, P_f is the maximum compressive load, and d_G is the granule diameter. It has been applied to calculate compressive strength of a brittle spherical specimen from the maximum load of uni-axial compression. The number of samples was about 20. The Weibull distribution with two parameters was adopted for the experimental data. The compressive strength of 50% fracture probability was used as a representative value.

It is discussed from Figs 8 and 9 that the apparent viscosity and the porosity decrease as the dispersant content increases up to $C_D = 0{\cdot}1$, and no correlation exists between both values from $C_D = 0{\cdot}1$ to $1{\cdot}5$. On the other hand, the compressive

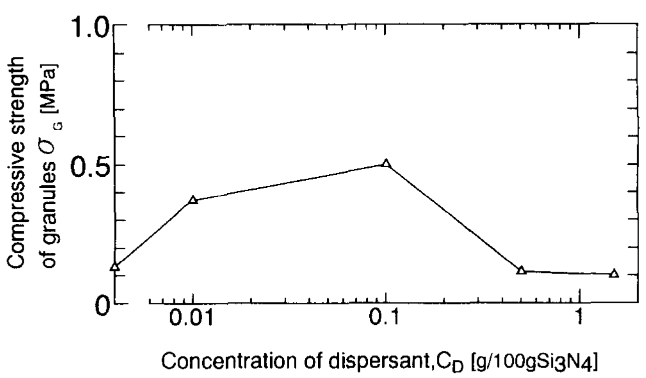

Fig. 10. Change of compressive strength σ_G of spray dried granules against concentration of dispersant.

strength of granules increased as the apparent viscosity decreased up to $C_D = 0\cdot 1$ as shown in Figs 8 and 10. However, there was no correlation between the compressive strength and the apparent viscosity from $C_D = 0\cdot 1$ to $1\cdot 5$. Comparing the results between the apparent viscosity and granule characteristics suggests that the measurement of apparent viscosity is insufficient to relate suspension characteristics to the granule characteristics and that another characterizing method should be found.

As a first step, a new characterizing method was proposed as shown in Fig. 11. This relates the compressive strength σ_G to the porosity ϵ_G of a single granule as a parameter of dispersant concentration of the slurry. Such a figure has been applied to analyze the compressive strength of a powder bed in powder mechanics.[11] It is clear from the figure that the compressive strength and the porosity of granules have a complex dependence on dispersant concentration which is classified into the following three steps: The first step exists in the region from $C_D = 0$ to $0\cdot 1$, where the compressive strength increases as the porosity decreases. The second step exists in the region from $C_D = 0\cdot 1$ to $0\cdot 5$, where only compressive strength drastically becomes small in the condition of almost constant value of the porosity. In the third step over $C_D = 0\cdot 5$, both compressive strength and porosity become small with the dispersant concentration.

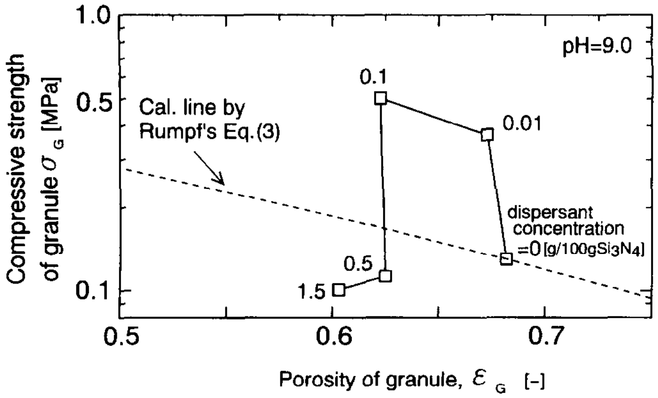

Fig. 11. Relationships between compressive strength and porosity of granules as a parameter of dispersant concentration.

4 Discussion

4.1 Characterizing methods of suspension for slip casting

It is clear from Figs 4 and 7 that the suspensions become well-dispersed up to $C_D = 0\cdot 3$. Therefore, the change of microstructure of green bodies up to $C_D = 0\cdot 3$ in Fig. 5 is explained by the model proposed by Arakawa *et al.*[6] indicating that the well-dispersed particles are more easily packed onto the surface of the mold. The same tendency is also found from Fig. 6, explaining that the degree of suspension sedimentation becomes large as the suspension becomes well-dispersed. However, the slurry of $C_D = 1\cdot 5$ is more packed than that of the best-dispersed suspension of $C_D = 0\cdot 3$, as shown in Fig. 5. Such phenomena are beyond the model, and further analysis should be conducted as follows:

In slip casting, the packing structure of particles on the mold changes with the movement of water from the packed bed into the gypsum mold. In the best-dispersed slurry, particles form a stabilized structure onto the surface of the mold until the dewatering is finished. On the other hand, the slurry of $C_D = 1\cdot 5$ is composed of flocculated particles as shown in Fig. 7, and the apparent viscosity at the start of slip casting is little higher than the best-dispersed slurry as shown in Fig. 4. However, the strength between flocculated particles is small enough to break its structure by hydrodynamic forces caused by the movement of water from the packed bed into gypsum mold. Such analyses are derived from the sedimentation curves in Fig. 6 and the aggregate particle size in Fig. 7. Therefore, it is proved that the green body of $C_D = 1\cdot 5$ is more dense than that of $C_D = 0\cdot 3$. Besides, it is understandable that the measurement of suspension sedimentation behavior in a centrifugal field and the X-ray particle size analyzer are promising methods to analyze the optimum conditions of suspension characteristics for slip casting.

4.2 Characterizing methods of spray dried granules

Figure 11 shows that the compressive strength of a single granule is determined by the coordination number of the primary particles generally given by the porosity, and the adhesive force between primary particles.[11] Rumpf[12] proposed the equation which relates the adhesive force between primary particles (H_P) to the compressive strength of powder bed (σ) on the assumption that the particle diameter (d_P) is uniform and the coordination number (k) is given by π/ε in the range of $\varepsilon = 0{\cdot}26\sim0{\cdot}7$. It is expressed by the following equation:

$$\sigma = \frac{1-\varepsilon}{\varepsilon}\frac{H_p}{d_p^2} \qquad (3)$$

While the adhesive force (H_P) between primary particles stays constant independent of slurry preparation conditions, the compressive strength of a single granule is given by the function of porosity expressed by eqn (3). The dotted line in Fig. 11 indicates the result calculated in the conditions that adhesive force keeps the value at $C_D = 0$ of pH 9·0. The difference between the dotted line and the measured line indicates the amount of compressive strength given by the change of adhesive force between primary particles.[11] It is clear that the adhesive force changed by slurry preparation conditions has a large effect on the value of compressive strength of the granule.

Figure 12 shows the pore size distribution of green compacts fabricated by pressing the spray-dried granules uni-axially in a cylindrical mold. The compressive stress was set at 98 MPa. The green compact fabricated by the slurry of $C_D = 0{\cdot}5$ had smaller pore size and cumulative pore volume than those of the green compact fabricated by the slurry of $C_D = 0{\cdot}1$. On the other hand, the apparent viscosity values of both slurries were almost the same as shown in Fig. 8. This means that the suspension characteristics cannot be directly related to the microstructure of the green compact, but should be discussed considering the characteristics of granules.

It is clear from Fig. 11 that the granules of $C_D = 0{\cdot}1$ have higher compressive strength than those of $C_D = 0{\cdot}5$, although they have the same porosity, thus the granules of $C_D = 0{\cdot}5$ tend to break compared to those of $C_D = 0{\cdot}1$. Such analysis explains the difference between the pore size distribution of the green compact fabricated by the granules of $C_D = 0{\cdot}1$ and that of $C_D = 0{\cdot}5$ as shown in Fig. 12. It suggests that the characterizing method of granules as shown in Fig. 11 is valuable to relate the characteristics of granules to the microstructure of the green compact as well as to characterize the effect of slurry preparation conditions on the characteristics of granules.

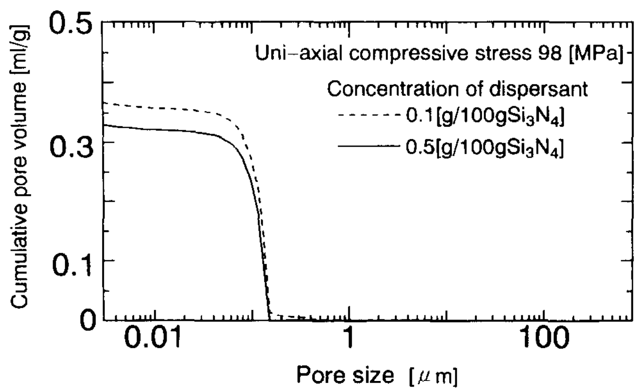

Fig. 12. Comparison of pore size distribution of green compacts prepared from different slurry.

5 Conclusions

The following conclusions are drawn in the relationships between suspension characteristics and the microstructure of green bodies in shaping processes:

(1) In the slip casting process, it is clear that the measurement of suspension sedimentation behavior in a centrifugal field and aggregate particle size analysis were promising methods for optimizing suspensions for slip casting.

(2) In the spray drying and uni-axial pressing process, it was found that the proposed method was valuable to characterize the effect of slurry preparation conditions on the characteristics of granules as well as the relationships between the granule characteristics and the microstructure of green compacts.

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