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Influence of Slurry Flocculation on the Character and Compaction of Spray-Dried Silicon Nitride Granules

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The effect of slurry flocculation on the characteristics of silicon nitride granules prepared by the spray drying process is investigated. The flocculation state of an aqueous silicon nitride slurry is controlled by adding nitric acid and evaluated as a function of pH. Dense and hard silicon nitride granules result from a well-dispersed slurry having a high pH (e.g., 10.8). These hard granules retain their shape in green compacts and form detrimental defects. Lowering the pH of the slurry to a certain value (e.g., pH 7.9) results in slurry flocculation. Granules prepared from this flocculated slurry have low density and low diametral compression strength and contribute to the elimination of large pores in green compacts.

I. Introduction

Elimination of defects is a primary concern for advanced ceramics utilized in structural applications. While various kinds of defects such as inclusions, exaggerated grains, and cracks exist, large pores are the most common defects in sintered ceramics.[1–3] We and other researchers have found that the behavior of pores in the sintering process is very dependent on their size.[4–9] The difficulty in removing large pores during liquid-phase sintering is understandable when we consider the capillary force acting on the liquid; liquid is pulled into small pores since its thermodynamic stability is increased with this process if it wets the surfaces of the particles. The origin of these large pores is mostly related to defects in granules such as pores and dimples and void spaces between granules.[10] In order to manufacture ceramics without large pores, it is vital to control the structure and mechanical characteristics of granules during the forming process.

In the preparation of favorable granules by spray drying, it is crucial to understand the effect of the slurry flocculation state on the structure and characteristics of granules. It is believed that the raw powder has to be well dispersed in a slurry to enhance milling efficiency. However, highly dispersed fine particles possibly aggregate during the drying process and form hard granules. Kamiya *et al.*[11,12] have reported that the hard aggregation of fine silica powder causes low compact density, less than 40% of theoretical density obtained using a cold isostatic press operating at 0.3 GPa.

The purpose of the present study is to experimentally clarify the influence of the dispersion state of a milled slurry on the characteristics of spray-dried granules and the resultant green bodies using a commercially available Si_3N_4 powder with oxide sintering aids.

II. Experimental Procedure

Commercially available α-Si_3N_4 powder (Ube SN-C0A) was used in this study. It nominally contains 5 wt% Al_2O_3 and 5 wt% Y_2O_3 as sintering additives. The specific surface area of the starting powder was determined to be 10.5 m^2/g by single-point BET analysis (Model SA-1000, Shibata, Japan). The powder and a deflocculant (2,2′,2″-nitrilotriethanol, 1 wt%) were ball-milled in a plastic jar for 40 h in distilled water using Si_3N_4 ball media. The concentration of powder in the slurry was 40 vol%. These conditions were experimentally optimized to obtain an adequate specific surface area of the powder (around 15 m^2/g) for sintering and to minimize the weight loss of Si_3N_4 ball media during milling. The particle size distribution of the milled powder was measured with a Microtrac particle size analyzer (Model SPA-7995-30, Nikkiso, Japan). The milled slurry was then mixed with distilled water to reduce the solids concentration to 30 vol% and passed through a sieve (500 mesh) to remove foreign objects. The starting pH (around 10.8) of the milled slurry was adjusted to 7.9–10.0 by slowly adding a HNO_3–H_2O solution (0.13 mol/L) with continuous stirring at room temperature. No organic binder was employed in any case. The final solids concentrations of the slurries were adjusted to 11 vol% by adding water in all cases to make the apparent viscosity suitable for spray drying. The flocculation state of a slurry was evaluated from its viscosity, measured with a viscometer (Quartz Rheometer, QRT-1000, Tokyo

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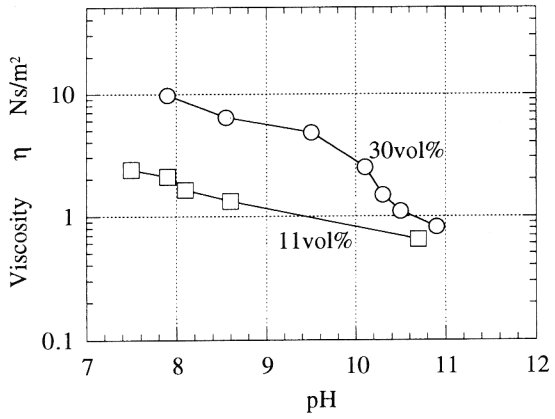

Fig. 1. Viscosity of flocculated slurry measured at a shear rate of 220 s^{-1} as a function of pH.

Dempakiki, Japan) at a shear rate of 220 s^{-1}. A spray dryer (Model COC-16, Ohkawara-kakohki Co., Japan, internal diameter 1.6 m) was operated with an inlet air temperature of 150°C and an outlet air temperature of 70°C. A rotary atomizer was rotated at 8000 rpm with a slurry feeding rate of about 100 g/min. There was no wall sticking since all internal walls were covered with fluorocarbon polymer sheets. The spray-dried granules were screened (100 mesh) and characterized. These granules were then mold pressed into pellets at 30 MPa and subsequently cold isostatically pressed at 150 MPa to form green compacts

The structure of the granules was examined in transparent mode using an immersion liquid (refractive index, 2.05) under an optical microscope.[13,14] The morphology of the granules and green compacts was also investigated by SEM (JSM-T300, JEOL, Japan). Mercury porosimetry (MOD 220, Carlo Erba, Italy) was employed to determine the porosity of the granules. The compressive strengths of the granules were measured with a micro compression testing machine (Model MCTE200, Shimazu Co., Kyoto, Japan) and analyzed by assuming elastic deformation of spherical particles.

III. Results

The increase in slurry viscosity with the addition of nitric acid and the resultant decrease in pH are plotted in Fig. 1. The final solids concentration was adjusted to 30 and 11 vol% by adding water after the titration, for the actual solids concentration in a slurry changed during the titration and affected the viscosity measurements. For a solids concentration of 30 vol%, the viscosity of the slurry increased from its initial value (around 0.8 $N \cdot s/m^2$) to nearly an order of magnitude greater at pH 7.9. The viscosity increased less markedly for the slurry with a solids concentration of 11 vol% than for that with a solids concentration of 30 vol% and reached 2.5 $N \cdot s/m^2$ at pH 7.5. A solids concentration of 11 vol% was adopted in this study because a slurry pump employed in the spray dryer restricted the range of slurry viscosity to below 5 $N \cdot s/m^2$.

The majority of granules obtained by spray drying had average diameters ranging from 45 to 65 μm. The granule size distribution was wide (<25 to 150 μm) and did not depend on the flocculated state of the slurry. Figure 2 shows the structure of granules prepared from (a) dispersed (pH 10.8) and (b) flocculated (pH 7.9) slurries. The granules prepared from the dispersed slurry are irregularly shaped and a majority of them are dimpled. In contrast, the granules prepared from the flocculated slurry are essentially spherical and no dimples are observed. Comparative darkness of images of granules prepared from the flocculated slurry suggests a large pore distribution in granules. Since the transparency of light in the liquid immersion technique is strongly dependent on the change of refractive index between the liquid medium and the particles, a low immersion state in granules with large pores causes dark images.

Figures 3 and 4 show the morphology of granules observed by SEM. The surfaces of granules prepared from the dispersed slurry appear to be smooth and dense. In contrast, those fabricated from the flocculated slurry are rough and involve relatively large clusters consisting of several particles. The sizes of these clusters are 0.5 to 2 μm, as shown in Fig. 4.

Figure 5 shows the pore size distribution in granules measured by mercury porosimetry. Pores larger than 10^4 Å were found. They were assumed to correspond to the space between granules and were omitted in this figure. The dotted line also indicates the milled powder particle size distribution. The particle size is about 10 times larger than the pore size and the average particle size is around 0.4 μm. The average pore size increases with decreasing pH of the slurry: 350 Å at pH 10.8 to 980 Å at pH 7.9. The pore size distribution also varies with the pH of the slurry and becomes sharper with decreasing pH. This result is consistent with the observed morphology; i.e., dense granules result from the dispersed slurry. The data obtained from mercury porosimetry were analyzed to determine the density of the granules. The following equation was used to obtain a granule density (ρ_g, g/cm^3) from the calculated cumulative pore volume (V_p, cm^3/g) and the theoretical density of the material (ρ_m, 3.25 g/cm^3):

$$\rho_g = \frac{1}{V_p + \frac{1}{\rho_m}} \quad (g/cm^3) \tag{1}$$

Figure 6 shows the densities of granules and compacts formed at 150 MPa as a function of pH of the slurry. The granule density changes with the pH of the slurry, whereas the density of green compacts molded and cold isostatically pressured is approximately constant for all granules, around 1.77 g/cm^3. At high pH, the density of the granules is approximately equal to that of the compacts. At low pH, the density of the compacts is significantly higher than that of the granules.

Figure 7 shows the fracture surface of green compacts formed with different granules. In the compact formed with granules prepared from a well-dispersed slurry, the traces of granules are clearly seen. Some cracks around the remaining granules and pores at the boundaries of the granules are also observed. No traces of granules are found and the surface is smooth in the compact formed with granules from a flocculated slurry. This homogeneity caused by the weak structure of granules may provide a homogeneous structure of sintered ceramics.

Figure 8 shows a comparison of the compressive strength of granules prepared from dispersed and flocculated slurries. The following equation was employed to calculate the compressive strength of the granules; granule failure occurs with the maximum tensile stress which appears in the center of the granule at the maximum compressive load:[15]

$$\sigma = \frac{2.8P_{max}}{(\pi d_G^2)} \quad (pascals) \tag{2}$$

where σ is the tensile stress (pascals), P_{max} is the maximum compressive load (newtons), and d_G is the granule diameter (meters). σ is plotted as the diametral compressive strength of granules in Fig. 8. The number of samples was 30 in each experiment. The probability of fracture corresponding to the compressive strength of each sample was defined by the median ranking method. A Weibull distribution with two parameters was adopted for the experimental data using the maximum likelihood method. It is evident that the granules prepared from the flocculated slurry have lower compressive strength. This result is consistent with the other results explained above. It must be noted that the effect of dimples and the irregularity of shape was ignored in the calculation of compressive strength. This does not alter the general trend of the results. The irregularity of the shape leads to the stress concentration and reduces the compressive strength of granules. If the granules prepared

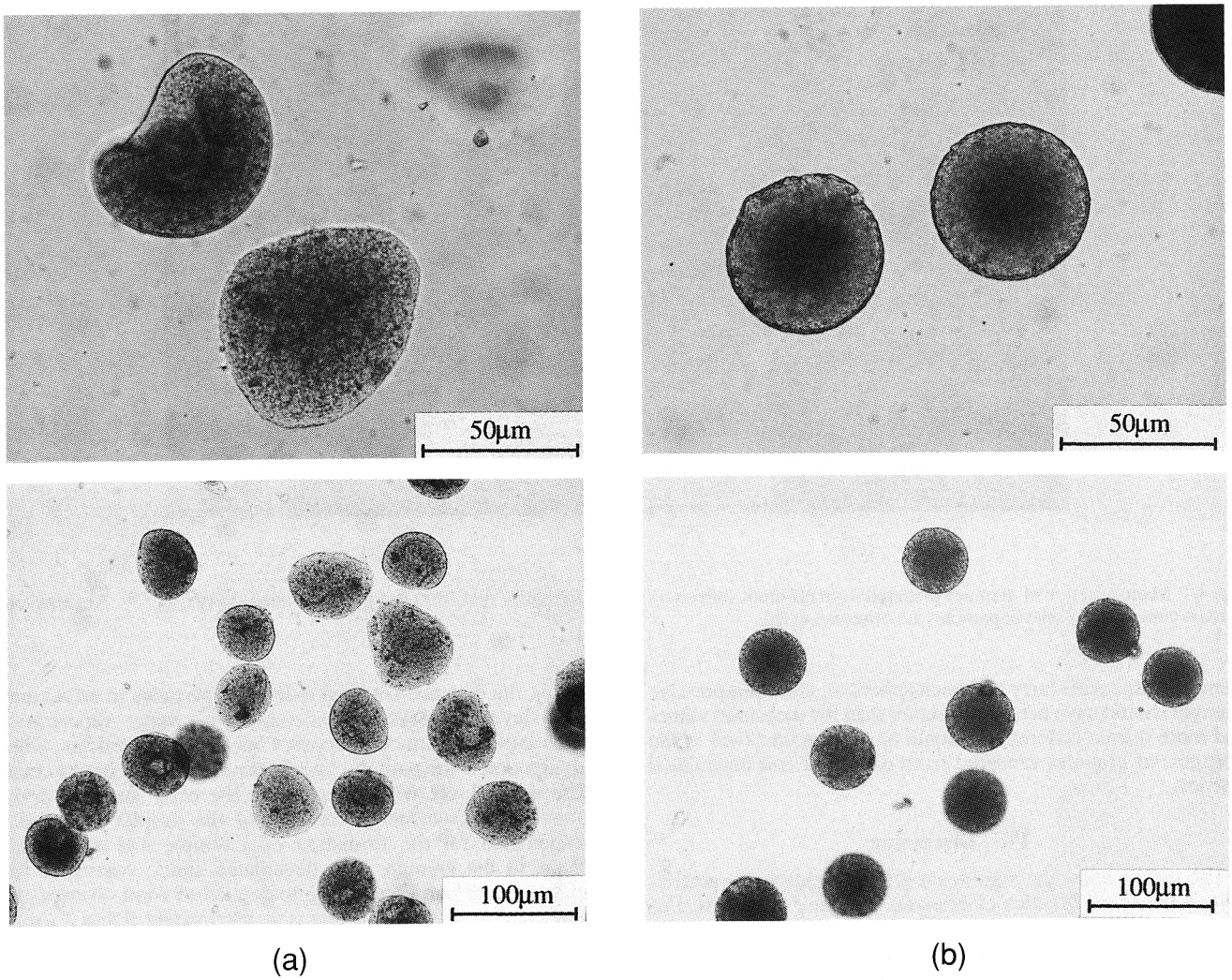

Fig. 2. Optical microscope photographs of powder prepared from (a) dispersed slurry (pH 10.8) and (b) flocculated slurry (pH 7.9) by liquid immersion technique.

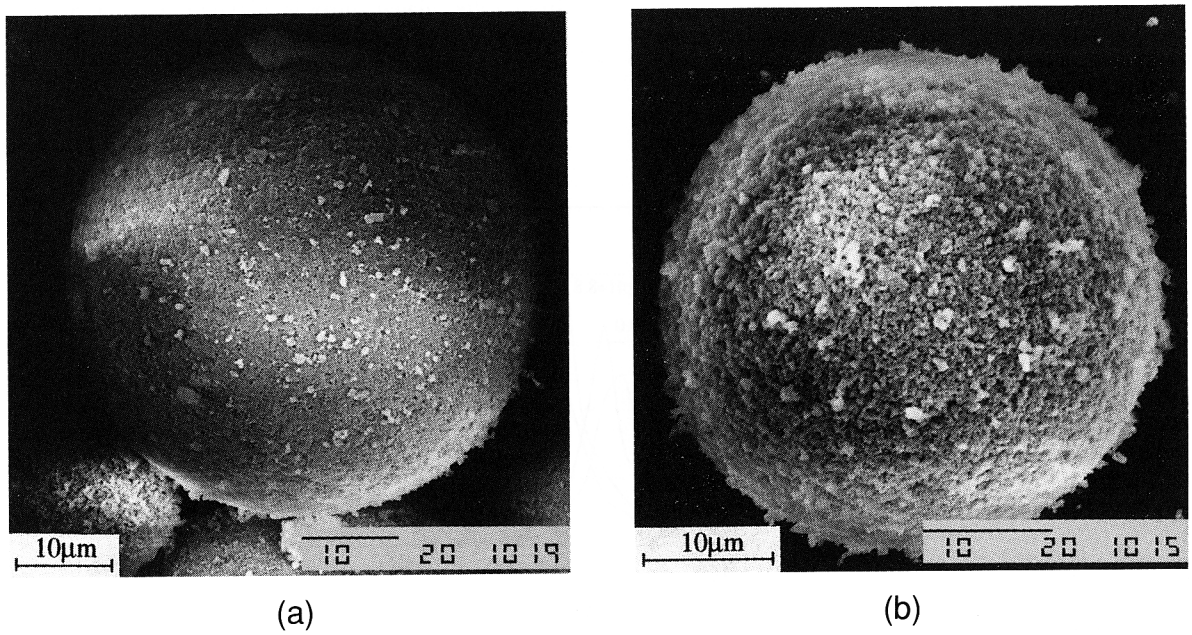

Fig. 3. SEM photographs of powder prepared from (a) dispersed slurry (pH 10.8) and (b) flocculated slurry (pH 7.9).

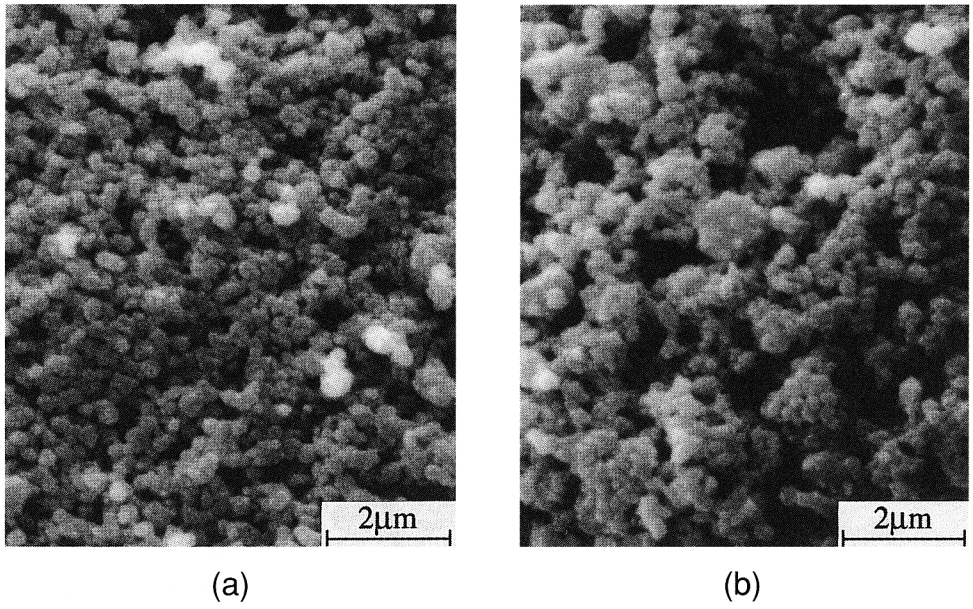

Fig. 4. Microstructure of granules prepared from different slurries: (a) dispersed slurry (pH 10.8) and (b) flocculated slurry (pH 7.9). Agglomerated clusters consisting of several particles are observed in (b).

from the dispersed slurry had been spherical, their compressive strength should have been even higher than the measured values and more drastic differences should have been observed in the strengths of granules prepared from dispersed and flocculated slurries.

IV. Discussion

The results show the significant effect of slurry characteristics on the characteristics of granules and their compacts. For understanding the effect of slurry dispersion on the characteristics of granules, it is necessary to consider the development of the powder packing structure during the spray drying process. Lukasiewicz reviewed fundamental techniques of spray drying in detail including mechanisms of granule formation and binder migration.[16] In the present study, the drying process of droplets seems to be as follows. When the droplets are blown into a spray dryer, vaporization of water occurs on the droplet surfaces. This vaporization causes a gradient of solids concentration in the droplets, and as a result internal water moves to the surface. The volume of a droplet decreases with the vaporization of water and the shrinkage of droplets occurs. At a certain time during this shrinkage, the accumulated and solidified layer appears on the droplet surface and advances into the droplet.

Two cases are considered to understand the effect of dispersion on the characteristics of granules. In a well-dispersed slurry, the distance between individual particles in an accumulated layer decreases considerably with water vaporization. High capillary attraction appears between the particles, which agglomerates the particles and forms a dense and hard granule. The dense layer which appears in the early stage of drying obstructs the uniform shrinkage of the droplet also and is responsible for the formation of a dimple and an irregular shape in the granule. In a flocculated slurry, several to tens of individual particles are agglomerated to form clusters. The average size of these clusters is approximately 0.5 to 2 μm, as shown in Fig. 4. A relatively large space is retained between them during drying and reduces the structural strength of the solidified layer and a final granule. This weak structure of the accumulated layer contributes to uniform shrinkage, which is required for the formation of a spherical granule.

Measurement of density provides instructive information on the characteristics of granules and green compacts. The average density of green compacts in this experiment is almost constant, 1.77 g/cm^3 in all cases. The density of granules fabricated from a flocculated slurry is markedly low compared to that of compacts, as shown in Fig. 6. In contrast, the density of granules prepared from a dispersed slurry is almost the same as that of compacts. This shows that the granules from a flocculated slurry densify and break during the forming process while the granules from a dispersed slurry only deform. The densification

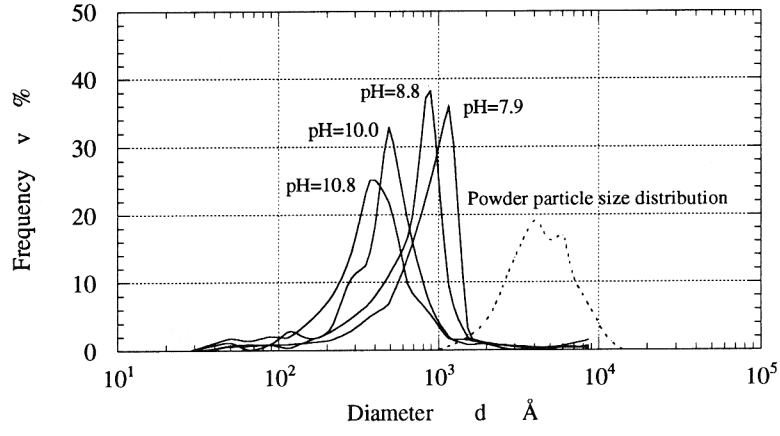

Fig. 5. Pore size distribution in silicon nitride granules prepared from flocculated slurries at various pHs. Dotted line indicates the milled powder particle size distribution.

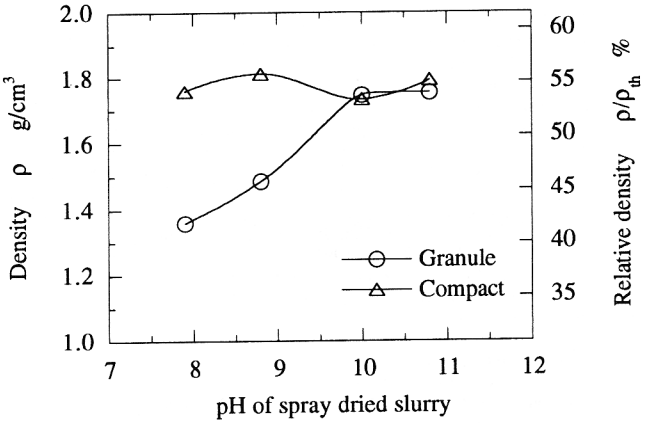

Fig. 6. Change in density of granules and green compacts with pH of spray-dried slurry.

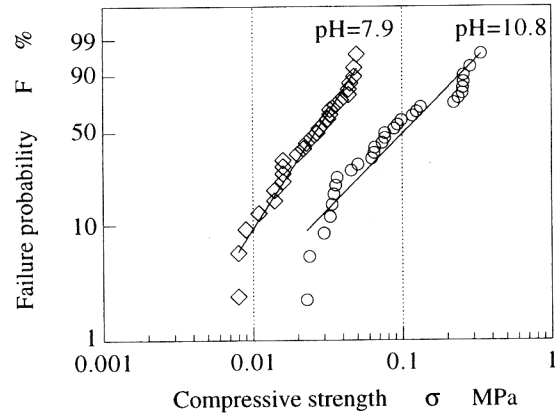

Fig. 8. Comparison of compressive strength of silicon nitride granules prepared from different slurries: dispersed (pH 10.8) and flocculated (pH 7.9).

of granules in compaction contributes to form a uniform compact and to reduce the marked defects in compacts as shown in Fig. 7. It is a notable fact that keeping the granule density well below the compact density causes the breakage of granules during forming and eliminates large defects in compacts.

The pH and ζ-potential control the slurry flocculation through their dominant effects on the electrostatic repulsion between the particles.[17] It is experimentally known that a ζ-potential over ±20 mV provides adequate electrostatic repulsion to disperse the particles in a slurry. Oda *et al.*[18,19] investigated the ζ-potential behavior of α-Si_3N_4, α-Al_2O_3, and Y_2O_3 and determined their isoelectric points to be pH 4.9, 8.3, and 9.6, respectively; however, the actual value of pH varies considerably with the experimental conditions such as purity, solution medium, solids concentration, and the method of measurement. Cesarano *et al.*,[20,21] for example, reported that the point of zero charge for α-Al_2O_3 is at pH 8.7. Bergström *et al.*[22] also measured the electrophoretic mobility of various Si_3N_4 powders after prolonged aging of an aqueous slurry and found a rather high pH (6.8) for the isoelectric points. Around these isoelectric points, weak electrostatic repulsion causes the agglomeration of particles resulting in flocculation of the slurry. Oda *et al.*[18] measured the pH dependence of the ζ-potential of Si_3N_4 and found a gradual decrease of the ζ-potential from 0 to −20 mV as the pH changed from 4.9 to 9.0. The ζ-potential of Si_3N_4 between pH 9.0 and 11.0 is almost constant and is approximately −23 mV. These studies show that the electrostatic repulsion between the negatively charged surface sites of Si_3N_4 provides good dispersion around a pH of 10.8 in the present study. The flocculation of an aqueous Si_3N_4 slurry at low pH is clearly due to the reduction of the ζ-potential to the isoelectric point of Si_3N_4.

These ζ-potential behaviors of powders also provide useful guidelines for eliminating the segregation of additives. Several studies have been reported for improved compositional homogeneity of green compacts although most of them are restricted to colloidal processing.[23–26] From the ζ-potential behavior, it is expected that the agglomeration of additives occurs near their isoelectric points and hence a pH of 8.5 to 10 is insufficient for developing enough electrostatic repulsion among particles in a slurry that includes Al_2O_3 and Y_2O_3. In contrast, the opposite electric charges of Si_3N_4 and the additives around a pH of 7.7 causes an attraction between them and seems appropriate for homogeneous distribution of additives with Si_3N_4 particles. A distribution analysis of additives in green compacts with an

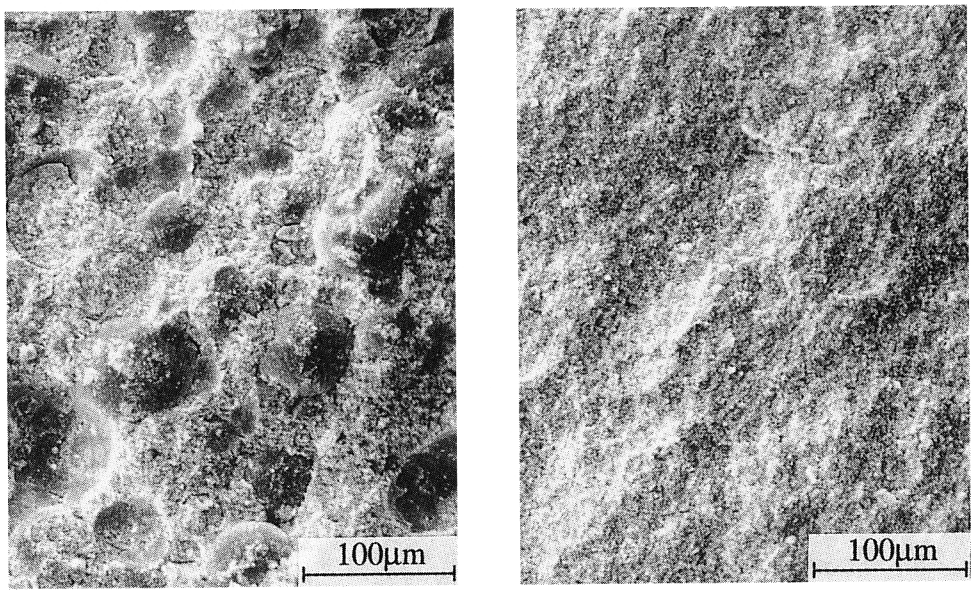

Fig. 7. Fracture surface of compacts. Granules were prepared from different slurries: (a) dispersed slurry (pH 10.8) and (b) flocculated slurry (pH 7.9).

Eelectron Probe Micro Analyzer is in progress to confirm the above discussion.

In the future, a detailed analysis of the additive distribution in granules in terms of ζ-potential and the flocculation mechanism will be done and it may lead to fine tuning of the granule preparation process. Together with a structural analysis of ceramics during and after sintering, this approach will provide a good understanding of liquid-phase sintering of ceramics and will contribute to the development of the optimum manufacturing process needed for producing highly homogeneous and reliable ceramics.

V. Conclusion

The flocculation of a spray-dried slurry considerably affects the structure and properties of the prepared silicon nitride granules. It is possible to control the flocculated state of a milled slurry by adjusting the pH—by adding HNO_3–H_2O solution to the slurry. The granules prepared from a well-dispersed slurry have a high density and a high diametral compression strength and leave a relic spray-dried agglomerate structure as defects in compacts. Controlling the pH of a slurry to 7.9 reduces the density of granules and the diametral compression strength. Compacts formed with the latter granules include no defects such as traces of granules after cold isostatic pressuring and may be the cause of improved mechanical properties after sintering.

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