Optimization of Granules and Slurries for Press Forming

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プレス成形用顆粒及びスラリーの最適設計

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The present paper deals with the determination of optimal conditions for preparing spray-dried granules and slurries, based on the characteristics of granules and supplied slurries. These characteristics were evaluated by the compression and stress-relaxation method, and by the centrifugal consolidation method, respectively. Spray drying of the flocculated slurry resulted in low-density granules with a spherical and solid morphology, which ensures a high compressibility. Another important factor governing the press forming is to adjust the amount of binder so as to improve the visco-elastic deformation of granules; this leads to a better homogeneity of the resulting compacts.

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1. Introduction

Large scale manufacturing of ceramics requires reproducible and economic processes, one of which is forming by uniaxial die pressing. In the compaction of ceramics by pressing, granules have to ensure an excellent compressibility, the property to attain a high density with a pressure as low as possible and an adequate uniformity required for the production of a defect-free green body. The granulation step of fine powders is most conveniently achieved by spray-drying. The spherical morphology and the smooth surface of spray-dried granules confer the unique characteristics for pressing. Many investigations have been performed to evaluate the mechanical and rheological properties of spray-dried granules and supplied slurries.^{1)–5)} These results, however, do not make it clear how the characteristics of granules influence the quality of pressed compacts with higher mechanical strength. This also means that a trial and error procedure has been generally needed to determine the optimal conditions for designing slurries which ensure the quality of final products.

The compression of granules generally proceeds via the plastic and/or visco-elastic deformation mechanisms. The images of compression process caused by these mechanisms are illustrated in Fig. 1. When granules which show plastic deformation have a distribution of their mechanical strength, the granules with the higher strength than a forming pressure would not break in a compact, resulting in formation of a fracture origin. Perfectly viscous granules, on the other hand, will form perfectly close packing without an applied pressure. This reasonably implies that the visco-elastic behavior should play an important role in the compaction process of granules.

In previous papers^{6),7)} a new evaluation technique has been developed for characterizing compressive behavior of spray-dried granules, using the conventional compression and stress-relaxation test. Experiments with spray-dried alumina granules prepared under the various conditions demonstrated that the visco-elastic deformation should characterize the compressive behavior of granules. A shape forming model has been also proposed with taking into account a shrinkage process of sprayed droplets in drying, reasonably implying the dependency of flocculation degree of slurry on granule morphology.⁸⁾ During the initial step of

Fig. 1. Comparison of plastic and viscous granules, and their images in products.

spray-drying, the dispersed particles in droplet are forced to form a network structure, the mechanical strength of which exerts a strong influence on the morphology of resulting granules. The mechanical properties of slurry governing the granule morphology can be characterized by applying the centrifugal consolidation method,^{9),10)} in which the strength of flocculate structure is readily examined by monitoring the transient behavior of the particle-network formation process.

The present paper describes the experimental results for an investigation of press forming process of alumina granules, the objective of which is to characterize the influence of mechanical properties and morphology of granules on the compression mechanism, and to identify the optimal conditions of supplied slurries for designing granules which ensure homogeneous products with high densities.

2. Experimental

2.1 Preparation of slurries and granules

Two types of slurry were prepared from commercial-grade α - Al_2O_3 powders (AL-160SG-3 with average particle

Table 1. Characteristics of Prepared Slurries

[Slurries-1]			
Sample	Dispersant conc. mass%	Binder	Viscosity mPa · s
G-1	0.5	polyvinyl alcohol	160
G-2	0.5	polyvinyl alcohol polyacrylates polyethylene glycol	815
G-3	0.5	polyacrylates polyethylene glycol	3440

[Slurries-2]		
Sample	HNO ₃ conc. / mol l ⁻¹	Slurry pH
G-P4	0.0706	4.0
G-P6	0.0158	6.6

size of 0.56 μm , Showa Denko) and distilled water by ball-milling for 8 h using alumina balls in an alumina bottle, in some cases, followed by addition of binder dissolved in the remaining water and an additional 2 h of milling. Solids content was 27 vol%. Polycarbonate ammonium was used for the preparation of slurry-1, in which material and blending proportion of binder system were controlled to vary the slurry characteristics. A solution of nitric acid was used to adjust pH values of slurry-2 for the control of flocculation degree. The slurries were degassed for 10 min by means of vacuum treatment and then subjected to steady-state viscosity measurements using a rotational viscometer (Visco-BL, Tokimec Inc.) at 298 K. Characteristics of the prepared slurries are summarized in Table 1.

The spray-dried granules with solid morphology and those with a single large pore or crater were prepared using a disc-type spray dryer (Shoei Ind. Co.) as described extensively elsewhere.⁶⁾⁻⁸⁾

2.2 Characterization of slurries

Mechanical properties of the supplied slurries were evaluated by the centrifugal consolidation method,⁹⁾ which can be usefully and readily employed to examine the effects of slurry characteristics on green-body and thus on spray-dried granules by monitoring the consolidation behavior of the slurry.^{6),9),10)} The prepared slurry was poured into centrifuge tubes (polyacrylate tubes with an inner diameter of 10 mm) to an initial height of approximately 90 mm, and then centrifuged (Model Centrifuge CT4D, Hitachi-Koki Co.) at centrifugal speeds between 500 and 3000 rpm, which result in corresponding centrifugal effect ranging from 35 to 1260 at the bottom of the tube. The distance from the center of rotation to the bottom of the tube was 125 mm. The experiments were performed by first maintaining the centrifugal speed of 500 rpm for 2 h, and then raising it by steps of 500 rpm up to the maximum of 3000 rpm. The centrifugal time was 30 min at each elevated speed. After centrifugation at each run, the tube was removed from the centrifuge and vertically aligned, and then the height of the consolidated cake was measured to estimate the average packing fraction. The centrifugal consolidation stress at each run was determined from the centrifugal force acting on the center of the formed cake.

2.3 Characterization of granules

Figure 2 shows the assembly of experimental apparatus used for observing compressive behavior of granules by applying compression and stress-relaxation test. The gran-

Fig. 2. Experimental apparatus used for observing compressive behavior of granules by applying the conventional compression and stress-relaxation method.

Fig. 3. Characteristics of the observed compression and stress-relaxation curve.

ules, sieved within a range of 45–65 μm and packed with an initial height of 2 mm, were pressed in a die (inner diameter: 16 mm) mounted in a standard mechanical testing machine (SDW-2000, Imada Co.) at crosshead speed of 0.1 mm/min. The surface of the granule bed in the die was lightly swept level with a small brush. It is essential that no packing occurs during this procedure. The compression and relaxation periods were 1 and 15 min, respectively. The compression-relaxation procedure was repeated until the final compression pressure of 90 MPa. To gain an insight into the compression mechanism, it is essential to analyze the transient behavior of stress-relaxation process at each compression level. It is feasible to evaluate the increase in compression level by applying the characteristic values defined in Fig. 3, which shows a compression-relaxation curve typically observed at each step. At the moment when the compression is stopped, one can observe the reduction of compressive stress stemming from the plastic deformation (characterized by the value $(P_p - P_r)/P_p$). The compressive stress then decreases according to the visco-elastic deformation process $((P_r - P_e)/P_p)$ characterized by relaxation time, and reaches final residual elastic stress (P_e/P_p) .

The morphology of the spray-dried granules was observed using a liquid immersion technique (immersion liquid: α -bromonaphthalene) under an optical microscope.¹¹⁾

Densities of granules were obtained from the specific pore volume determined by Hg penetration porosimetry.

2.4 Measurements of the strength of sintered bodies

The granules were first compacted uniaxially at 25 MPa in a rectangular die (50×60 mm) and then isostatically at 100 MPa, followed by firing at 1873 K for 3 h in air according to the predetermined firing program. Four-point bending strength of the specimens thus obtained was determined at room temperature with a testing machine (Autograph AG-25TB, Shimadzu Co.) in conformity to JIS R-1601 (average sample dimensions: 40×3×4 mm³, span: 30 mm, crosshead speed: 0.5 mm/min).

Densities of prepared compacts were obtained from the specific pore volume determined by Hg penetration porosimetry, whereas those of sintered bodies were measured by the Archimedes method using water as the immersion medium.

3. Results and discussion

3.1 Characteristics of spray-dried granules

Figure 4 shows typical granules observed using a liquid immersion technique. Most granules are roughly spherical. The granules formed from slurries with lower viscosity or lower pH value contain large craters.

Fig. 4. Typical granules prepared in the spray dryer: (a) 27 vol% solids, pH 4; (b) 27 vol% solids, pH 6.7.

Figure 5 shows the observed stress curves for several granules, where the time changes in compressive stress are plotted as a function of the corresponding packing fraction of the compact. During the compression of low levels, rearrangement of granules occurs such that the voids between them are filled. Further increase in compression level tends to increase the residual stress, resulting from fracture or deformation of granules. The starting point of compressive stress and corresponding initial packing fraction shows fluidity of granules, since no packing occurred during the procedure of cross-head adjustment. These stress curves give us much more information on the deformation mechanism of packed granules.^{6,7} We here focus on the stress-relaxation process stemming from visco-elastic deformation defined in Fig. 3. Figure 6 shows the transient behavior of visco-elastic deformation, plotted as a function of packing fraction. Granules without binder (G-P4 and G-P6) have lower visco-elastic deformation than those containing binder, reasonably suggesting the strong dependency of compressibility on binder. As the compression proceeds (packing fraction > 0.37), the relaxation stress of granules G-3 becomes larger than that of G-1 or G-2 at any compression

Fig. 5. A series of data observed for sample granules prepared from slurry-1, representing time changes in compressive stress plotted as a function of the corresponding packing fraction of the compact.

Fig. 6. Transient behavior of relaxation stress stemming from visco-elastic deformation observed at each compression level.

level, thus reaching higher packing fraction of the residual compact. The detailed analysis of the compressive behavior before and after the yield point and on the transient behaviors of stress-relaxation process characterized plastic deformation and/or residual elastic stress is described elsewhere.⁸⁾

3.2 Bending strength and granule morphology

Bending strengths of sample specimens are plotted as a function of density of sintered body in Fig. 7, where the granule morphology is also described. The data are the averages of fifteen determinations, standard deviations of which are shown as error bars. Densities of granules, compacts, and sintered bodies are also summarized in Table 2, together with maximum values of the visco-elastic deformation measured from the stress relaxation curves.

For granules G-1, 2, and 3, the bending strength increases with an increase in the density of sintered body. These sintered bodies are fabricated from the compacts with high density as shown in Table 2. In the cases for granules without binder, it should be noted that one can clearly recognize a difference between bending strengths of the sintered bodies from granules G-P4 and P6 in spite of little difference in the density of sintered body. This result suggests that spherical and solid morphology should promote the bending strength of sintered body.

Figure 8 shows an effect of changes in density caused by compaction on the bending strength, where the abscissa denotes a ratio of the difference in densities between compact and granule to the granule density. The bending strength should be enhanced by the increase of the difference in densities between compact and granule. Clearly, the density of compacts from granules G-P4, which results in the sintered body with the lower bending strength, is almost the same as that of granules. The results for granules con-

taining binder also demonstrate that the bending strength increases with an increase in the difference between densities of compacts and granules. The density of compact from G-3 is slightly higher than that from G-P6, irrespective of the same morphology, probably resulting from the difference in the stress-relaxation stemming from the visco-elastic deformation. Table 2 also demonstrates that the higher density of granules (G-1 and G-P4) tends to suppress their compressibility, thereby lowering the bending strength.

Spray-dried granules should have a distribution of density, suggesting that the compacts, which have almost the same density as their granules, contain granules not breaking and/or deforming throughout a press forming process. These compacts are essentially inhomogeneous, leading to the reduction of the bending strength. Granules with the lower density should break and/or deform during the press forming, thereby resulting in the homogeneous compacts. Granules with low density have the morphology of spherical and solid as demonstrated in the previous paper.⁸⁾ Thus it is concluded, that the sintered body with the higher bending strength should be fabricated from spherical and solid granules which show the larger stress relaxation stemming from the visco-elastic deformation, in other words, which have the lower granule density and the larger difference in density between granules and compacts.

3.3 Control of granule morphology

It is of importance to establish the meaningful slurry formulation which ensures the spherical and homogeneous morphology of the resulting granules. In previous papers,^{8),12)} we demonstrated that the structure of spray-dried granules strongly depends on the degree of flocculation in the prepared slurry. Granules prepared from dispersed slurry are irregularly shaped and the majority of them are hollow, while flocculated slurry results in essentially spherical and solid granules. It has been also found that the size of flocculate measured by X-ray sedimentation method reasonably correlates to the granule morphology instead of the apparent viscosity which has been generally used as a characteristic index for the flocculation level of the slurry.^{8),12)} Since in the X-ray sedimentation method the concentration of the slurry is reduced to approximately one-tenth of the original and there are no effects of shear stress stemming from the surrounding flow on the flocculate structure during measurement, the size of flocculate can be used

Fig. 7. Four-point bending strength as a function of density of sintered body.

Table 2. Characteristics of Granules, Compacts, and Sintered Bodies

Sample	Maximum value of visco-elastic deformation	Relative density of granule	Packing density of compact	Density of sintered body g cm ⁻³	Bending strength MPa
G-1	0.647	0.518	0.533	3.87	276
G-2	0.693	0.501	0.567	3.89	395
G-3	0.647	0.503	0.596	3.92	418
G-P4	0.515	0.563	0.565	3.90	297
G-P6	0.424	0.508	0.558	3.91	378

Fig. 8. Effect of changes in density caused by compaction on the bending strength.

Fig. 9. Transient behavior of centrifugal consolidation process, representing a relation of centrifugal consolidation stress to packing fraction, which leads to the optimal conditions for preparing slurries applied for spray-dried granules.

as an index to represent the strength of flocculate.

The observed centrifugal consolidation curves are shown in Fig. 9 as a relation of the packing fraction to the centrifugal consolidation stress. The flocculation degree of slurry reasonably correlates with the final packing fraction of the sediment obtained at centrifugation. These results suggest that the slurry which results in spherical and solid granules with lower density, has the lower packing fraction finally achieved. These slurries are essentially strongly-flocculated, suggesting the optimal conditions for the preparation of slurry. On the other hand, the slurry giving higher final packing fraction results in hollow granules with higher density. Hence it is concluded that dispersant should be adjusted so as to prepare the slurry with higher viscosity and lower compressibility.

The shape forming process of spray-dried granules can be interpreted as a process where the slurry system is allowed to be highly concentrated, dehydrated, and then dried.⁹⁾ In the previous paper⁸⁾ we proposed a shape forming process of granules by taking into account a shrinkage process of sprayed droplets. During the initial step of drying, the size of droplets decreases as water is removed, resulting in the formation of a granule shell where evaporation occurs. Water contained in the internal void moves to evaporate, accompanying the transport of particles toward the shell. In the cases where particles are mobile in a droplet, which is indicated by a weak flocculation, the particles pack to higher density near the shell. One side of the granule is allowed to collapse inward because of the pressure difference between the internal vacancy and surroundings. In the cases, on the other hand, where particles are immobile against the migrating water because of a strongly flocculated structure, units of flocculate play an important role in the granule formation process. This process results in a relatively high void fraction near the surface because flocculates do not move significantly. When the strength of flocculates is relatively

high, flocculates should not influence the shrinkage of granules, resulting in solid granules with high void fraction. Similar models have been proposed by several researchers on the basis of correlations between slurry rheology and granule characteristics.^{1),5)}

4. Conclusions

In order to obtain the optimal conditions for press forming process, the influence of mechanical properties of granules and prepared slurry on the bending strength of the sintered body has been investigated systematically.

Low-density granules with spherical and homogeneous morphology ensure the high compressibility, finally leading to the sintered body with high bending strength. The granule shaping model reasonably indicated the main factor governing these mechanical properties to be the flocculated structure in the prepared slurry. The centrifugal consolidation method demonstrated its availability for characterizing the flocculation level in the slurry, thus leading to the optimal conditions that the slurry should be prepared by adjusting the dispersant concentration so as to lower both the apparent viscosity and the packing fraction finally achieved.

The homogeneity of a compact strongly depends on the visco-elasticity of granules. The homogeneous compacts should be fabricated from granules containing binders adjusted so as to improve the visco-elastic deformation. The compression mechanism of granules should be reasonably characterized by applying the compression and stress-relaxation test, thereby leading to the optimal conditions for designing spray-dried granules.

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