Comparison of alumina granules prepared by spray freeze granulation drying and spray drying

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Alumina granules were fabricated by using the spray freeze granulation drying (SFGD) and spray drying (SD) processes, and the granule properties, such as the granule size distribution, packing density, angle of repose, and compression strength, were examined. In addition, powder compacted bodies were made from the SFGD and SD granules, and the corresponding densities and defects were evaluated. Furthermore, the compacted bodies were sintered, and their densities and strength were evaluated. It was found that the properties of SFGD granules were affected by the solid content of the slurry, because the slurry droplets were frozen with water to fabricate these granules. The sintered body fabricated from SFGD granules exhibited a higher strength compared to that from the SD granules, as weak and homogeneous granules were fabricated using SFGD.

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1. Introduction

In the ceramics production process, granulation is often performed to fabricate granules from raw powders to improve the flowability or packing density. The spray drying (SD) method is a widely used granulation method, in which ceramic slurry droplets are sprayed into hot air and dried to make the granules, as shown in the upper part of Fig. 1. The granules obtained using this method often have a hard shell and inner hollow structure, as the raw powders and/or binders move to the granule surface along with the movement of the solvents (water or alcohols) during drying. The presence of such a shell and hollow structure lead to insufficient densification, defect formation, and strength degradation of the sintered ceramics.¹³

Another technique to fabricate granules is the spray freeze granulation drying (SFGD) method.¹² As shown in the lower part of Fig. 1, the SFGD method involves two steps, namely, spray freeze granulation and drying. In the first step, the sprayed slurry droplets are cooled to make frozen granules, and in the second step, the frozen granules are dried under a vacuum condition (or “freeze dried”). In this method, the droplets are frozen with water to ensure that ice crystals are contained in the granules. Because the ice crystals are sublimated during drying, traces of the ice crystals remain as pores in the granules. Several researchers have reported upon the structure of such granules.³–⁸ However, the SFGD method involves problems such as difficulty in handling the frozen granules and the long time required for freeze-drying; thus, this approach has not been widely applied.

Nevertheless, it has been suggested that the use of SFGD granules could reduce the defects in structural ceramics, leading to improved strength.⁹,¹⁰ In addition, another study indicated that the strengths of the sintered bodies fabricated from SD and SFGD granules depend on
the granule density and cold isostatically pressed (CIP) pressure. Recently, some authors reported that an alumina sintered body fabricated from SFGD granules exhibited a higher density than that of the body obtained from SD granules. However, the relation among the granule fabrication, granule properties and characteristics of compacted/sintered bodies remains largely unclear.

To examine the relationship, in this work, SFGD alumina granules were fabricated from slurries with different solid contents, and their properties, such as the granule shape, structure, packing density, angle of repose, and compressive strength, were evaluated. Subsequently, densities of the powder compacted and sintered bodies fabricated from the granules were measured. These results were compared to the corresponding values for the bodies obtained from SD granules and discussed.

2. Experimental

Alumina raw powder, AES11 (mean powder size 0.4 μm) by Sumitomo Chemical Co., Ltd. was used. The slurry was made from the powder with water and dispersant by ball milling. Then, a binder (polyvinyl alcohol, PVA) of 1 mass % based on the weight of alumina was added. Additional water was introduced to obtain slurries with solid contents of 35, 40, and 45 vol %.

For the SFGD process, the slurry was sprayed toward liquid nitrogen by using a two-fluid nozzle (Fig. 2). The diameter of the spray nozzle, spray gas pressure, slurry feed rate, and distance from the nozzle to liquid nitrogen surface were 0.7 mm, 50 kPa, 10 mL/min., and 0.3 m, respectively. The frozen granules obtained using this procedure were dried under a vacuum condition, and dried granules were obtained. Subsequently, the granules were passed through a 106μm mesh to remove the coarse agglomerate. Hereinafter, the SFGD granules are denoted as 35-F, 40-F, and 45-F, with the number to the solid contents of the slurries.

For comparison, the spray-dried granules were fabricated from 35 vol % slurry by using the same nozzle at the same spray gas pressure and slurry feed rate. These granules are denoted as 35-SD. Commercially available AES11 spray-dried granules, denoted as C-SD, were also used for comparison. The granules were fabricated by rotary disk spraying, and the content of the alumina powder in the slurry was unknown. The material contained approximately 4 wt % binder, as determined by thermogravimetry.

The shapes and structures of the granules were observed by scanning electron microscopy (SEM). The granule size distribution was measured by using a laser diffraction particle size analyzer in the dry condition. The packing density and angle of repose of the granules were evaluated. In addition, the compressive strength of the individual granules was measured by using a micro-compression tester (Shimadzu Corp.).

The strength, σ, was calculated using the following equation:

\[ \sigma = \frac{2.8P}{\pi d^2} \]  

where \( P \) is the load to fracture, and \( d \) is the diameter of the granule. The granules ranging from 70–100μm in diameter were provided for this measurement.

Compacted bodies with a diameter of 20 mm and height of 10 mm were fabricated from the granules under a uniaxial press of 50 MPa. The density of the compacts was measured, and the defects were examined by infrared transmission microscopy. The compacted bodies were sintered at 1600°C for 2 h, and the density of the sintered body was determined. Furthermore, sintered bodies with dimensions of 25 × 25 × 4 mm were fabricated using a CIP body (CIP pressure: 50 MPa) to measure the strength. Rectangular specimens with dimensions of 20 × 1.8 × 4 mm were cut from the sintered bodies and subjected to a three-point bending test (under span: 16 mm).

3. Results and discussion

Figure 3 shows the SEM micrographs of the 35-F, 35-SD, and C-SD granules. Many pores were observed on the
surface of the 35-F granules, which corresponded to the traces of the ice crystals formed by freezing. A similar structure was observed in the case of the 40-F and 45-F granules. Dimples were often observed on the surface of the 35-SD and C-SD granules, notably so in the case of the C-SD granules. The presence of pores in the SFGD granules and dimples in the SD granules was consistent with the findings of previous reports.2)–5),8)

Figures 4(a) and 4(b) show the size distribution of the SFGD and SD granules, respectively. The SFGD granules exhibited a major peak at approximately 30–50 μm. For granules made from a slurry with a higher solid content, the granule size increased and volume of finer granules reduced. The 35-SD granules exhibited a peak at approximately 20 μm, and the granules had a broad distribution on the smaller side. The C-SD granule exhibited a peak at approximately 80 μm, and the volume of fine granules was small. This was a typical distribution characteristic for granules fabricated by rotary disk spraying.

The SFGD and 35-SD granules were sprayed under the same nozzle condition, and therefore, the initial droplet size distribution should ideally have been similar. The SFGD granules did not exhibit a reduced size, as the slurry droplets were frozen with water. On the contrary, the 35-SD granules exhibited a reduced size owing to the occurrence of drying shrinkage. Therefore, the 35-SD granules contained finer granules and exhibited a peak at finer side to SFGD granules.

Figure 5 shows the packing density of the granules. The packing density of the SFGD granules was 0.78, 0.94 and 1.06 × 10^3 kg m⁻³ for the 35-F, 40-F and 45-F granules, indicating that a higher solid content of the slurry led to a higher packing density. The 35-SD granules exhibited a packing density 1.22 × 10^3 kg m⁻³, which is higher than that for the 35-F, likely because of the higher powder fraction in the granules induced by the drying shrinkage and a larger volume of finer granules. The packing density of the C-SD granules was 1.16 × 10^3 kg m⁻³.

Figure 6 shows the angle of repose of the granules. The angle of the SFGD granules was 39, 36, and 29° for 35-F, 40-F and 45-F, respectively, indicating that a higher solid content of the slurry corresponded to a lower angle. The angle for the 35-SD granules, 50°, was higher than that for the 35-F. The angle for the C-SD granules was 30°. These results were affected by the size distribution and packing density of the granules, as the angle of repose generally increases as the volume of fine granules increases.

Figure 7 shows the average compression strengths of the granules, along with the maximum and minimum strengths. The average strength of the SFGD granules was 0.5, 0.9 and 1.4 MPa for the 35-F, 40-F and 45-F granules, indicating that the strength increased with an increase in the solid content of the slurry. The difference in the maximum and minimum strengths was small in the case of the SFGD granules, with the maximum difference being 1.8 times for the 45-F. The SD granules exhibited higher

![Fig. 4. Granule size distribution for (a) SFGD and (b) SD granules.](image1)

![Fig. 5. Packing density of granules.](image2)

![Fig. 6. Angle of repose of granules.](image3)

![Fig. 7. Compression strength of granules.](image4)
strengths, specifically, 1.6 and 2.1 MPa for 35-SD and C-SD, respectively, compared to that of the SFGD granules. The difference in the maximum and minimum strengths for the SD granules was large, specifically, 3.3 and 3.9 times for 35-SD and C-SD, respectively.

These results indicate that the SFGD process produced weak and homogeneous granules, likely because of the existence of pores pertaining to the traces of the ice crystals. In contrast, the SD granules were hard and inhomogeneous. The higher strength was likely because of the higher powder fraction in granules and the formation of a hard shell. The inhomogeneity of the strength is assumed to be because of the inhomogeneous formation of the shell. In particular, the difference in the drying condition for each granule might affect the formation of the shell.

Figure 8 shows the densities of the compacted and sintered bodies fabricated using the granules. The densities of the compacted bodies from SFGD granules were 2.19, 2.20 and $2.21 \times 10^3$ kg m$^{-3}$ for 35-F, 40-F and 45-F, respectively, indicating that the density increases with an increase in the solid content of the slurry. The compacted bodies from the SD granules exhibited higher densities of 2.27 and $2.23 \times 10^3$ kg m$^{-3}$ for 35-SD and C-SD, respectively, compared to those for the SFGD granules. The sintered bodies from the SFGD granules exhibited a density of $3.94-3.95 \times 10^3$ kg m$^{-3}$, with the highest density pertaining to the 40-F granules. The sintered bodies obtained using the SD granules exhibited lower densities, 3.90 and 3.85 for 35-SD and C-SD, respectively, compared to those for the SFGD granules. Thus, the trend of the density was reversed after sintering, i.e., the powder compacted bodies from the SFGD granules had a lower density; however, the sintered bodies had a higher density, compared to those from the SD granules.

This result can be discussed considering the properties of the granules. Because the SFGD granules had a lower packing density, it was difficult to improve the density of the powder compacted body. However, owing to the higher homogeneity of the granules, a homogeneous compacted body could be obtained. Such a body was sintered with less defect formation, and the sintered body thus had a higher density. The densest sintered body corresponded to the 40-F granules likely because this case involved the optimal balance between the packing density and the homogeneity. Next, the assumption that the sintered density and strength are proportional is considered. In the previous work, 3 wt% binder in zirconia was employed, whereas in this work, 1 wt% binder was contained in alumina. Therefore, the amount of the binder in the previous work was almost four times more in volume than that in this work. Therefore, the previous granules were harder than those obtained in this work, and a higher pressure was required to obtain a compacted body with fewer defects. This aspect is likely why the strength peak appeared at 30 vol% in the previous work, and the density peak appeared at 40 vol% in this work. In contrast, the SD granules had a higher packing density, which led to a higher compact density. However, it contained stronger (harder) granules, which were difficult to collapse by a uniaxial press; therefore, these defects remained around the stronger granules even after sintering, thereby making it difficult to improve the density.

To confirm this phenomenon, the defects in the compacted body were examined. Figure 9 shows the infrared micrographs of the powder compacted bodies, in which the black spots correspond to the defects. The compacted body obtained using the 35-SD and C-SD granules exhibited several defects compared to that in the 35-F compacted body, which is consistent with the foregoing discussion.

Figure 10 shows the average strength of the sintered bodies, along with the maximum and minimum strengths. The highest strength (480 MPa) corresponded to 35-F, and the strengths for 35-SD and C-SD were 446 and 381 MPa, respectively. This result corresponds well with the density

![Fig. 8. Densities of the compacted and sintered bodies fabricated from the granules.](image)

![Fig. 9. Infrared transmission microscopy of compacted bodies.](image)
It is thus indicated that a sintered body with a higher density, fewer defects and higher strength can be obtained from the SFGD granules.

Furthermore, the results obtained in this work were compared to those reported in a previous work. In the previous work, at a lower CIP pressure (100 MPa), the strength of the CIPed and sintered body from the SFGD granules was higher than that from the SD granule. This finding is consistent with that obtained in this study (CIP Pressure: 50 MPa). Furthermore, at a higher CIP pressure (300 MPa), the strength pertaining to the SD granules increased. Although the strength of a body CIPed and sintered at a higher pressure was not determined in this work, it is likely that a similar behavior may be observed.

4. Conclusions

In this study, the properties of alumina granules fabricated by SFGD and SD were compared. It was observed that the properties of the SFGD granules were affected by the solid content of the slurry, and granules with a larger size, higher packing density, lower angle of repose, and higher compression strength could be obtained from the slurry with a higher solid content. The density of the compacted body made from a slurry with higher solid content (45 vol%) was higher; however, the density of the sintered body was the highest in the case of the slurry with a moderate solid content (40 vol%).

Compared to the SFGD granules, the SD granules exhibited a smaller size, higher packing density, higher angle of repose, and higher compression strength. Although the packing density was higher for such granules, the sintered density became lower. The strength of the sintered body obtained using the SD granules was lower than that from the SFGD granules. Many defects were observed in the compact body obtained using the SD granules, which could lead to a lower sintered density and strength. Therefore, the SFGD granules are considered to be more suitable to fabricate a sintered body with a higher strength.

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