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The Effect of Granule Morphology and Composition on the Compaction Behavior and Mechanical Properties of 92% Alumina Spray Dried Granules

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Abstract

The compaction behavior and flexural strength of green compacts produced from four different types of 92% alumina spray dried granules were studied. Three of the granule types were produced in-house while the fourth is commercially-available. In addition, the decomposition behavior of the granules was studied by TGA in order to help explain the observed results. The morphology of the granules was observed using microscopy. Examination of the three granules produced in-house showed that they have several undesirable features; agglomeration, hollow granules and non-spherical granules. The morphology of the commercial granules showed them to be unagglomerated and spherical. The in-house granules with undesirable morphological features had a lower tap-density than the commercial granules. Bend bars were produced to a controlled green density of 2.20 g/cm^3. The flexural strength of the green bars was measured in 4 point bending. It was found that the average flexural strength of bar produced with in-house granules was 4 MPa. The bars produced with the commercial granules had an average flexural strength of 1.19 MPa. The compaction behavior of the granules was studied from 25-300 MPa. It was found that the in-house granules consistently had a higher yield pressure than the commercial granules, resulting in the need for higher pressure to achieve the same green density. The TGA results found that the in-house granules have a higher percentage of volatile components in the form of polymeric additives such as dispersant, binder and lubricant, than the commercial granules. The excess polymeric additives, particularly binder, can explain the observed increase in flexural strength of the in-house vs. commercial granules.

Key words: Alumina, Flexural strength, Density

Introduction

The use of spray dried granules for die pressing is advantageous for the production of advanced ceramic products. Several factors affecting granule compaction during die pressing include the applied pressure, granule flow-ability, and the friction between granules and the die wall. Good flow-ability, as determined by a low repose angle, provides uniform die fill. The addition of lubricants reduces inter/intra particle friction and the friction between granules and the die wall. Both of these increase the compact density.[1, 2] Granule morphology e.g. granule shape, particle size and distribution, are factors that influence the granule flow-ability, and are critical to control in order to achieve good compaction. These factors determine how the granules will initially fill the die as well as rearrange during the compaction process. Granules with irregular or dimpled shapes tend to have a lower fill and subsequent compacted density, compared to uniformly spherical granules. Good compaction does not have to lead to a good mechanical strength in green samples since there are other factors besides granule morphology e.g. the type and content of polymeric additives used in the granules. This research was conducted to study the influence of granule morphology/ characteristics on the flexural strength of compacted 92% alumina. Four different granule morphologies were examined. Three of the granule types were produced in-house while the fourth is commercially available. Due to the proprietary nature of the polymeric additives used in the commercial granules, a TGA analysis was conducted to study the decomposition of these granules, in an effort to discern information about the additives. An understanding of granule morphology, the polymeric additives used in the alumina granules, the granule

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compaction behavior, and the mechanical properties of the granules after compaction will lead to proper granule design and selection for use in die pressing.

Materials and Experimental Procedures

Material Preparation

Four different alumina granules were used for the experiments. Granules numbered 1, 2, and 3 were produced in-house and granule number 4 was a commercially available granule supplied from Y.S. Company (Japan). The in-house granules were produced from a slip prepared by wet ball milling. The formulation of the solids in the slip was 92% Alumina, 8 wt% sintering aids, and 8 wt% polymeric additives including binder, plasticizer, lubricant, and dispersant and was kept constant for granules 1, 2 and 3. The amount of water used for the slips of granules 1, 2, and 3 were 77, 77, and 82 wt%, respectively. These additions are based on the weight percent of the solids. A 33 vol% volume charge of alumina grinding media was used in the ball mill. After the milling process, the three slips were spray dried to form granules using a two-fluid nozzle, which uses compressed air to atomize the feed slurry in the spray dry chamber. The spray drying conditions are shown in Table 1. The granule morphology was observed using a 50x magnification optical microscope (Zeiss, Germany). Granule 1, the in-house granule, and the commercial granule 4, were chosen for thermogravimetric analysis (TGA). The granules were heated in air at a rate of 10°C/min. The maximum temperature was 800°C.

Table 1. In-house granule spray drying conditions

Granule No.	Spray drying condition				
	Inlet temperature (°C)	Outlet temperature (°C)	Chamber exhaust fan speed (rpm)	Compressed air pressure (psi)	Slurry feed (ml/min)
1	260	115	27	5	600
2	250	110	30	4	550
3	250	113	28	5	550

Pressing Process

All four granule types were uniaxially die pressed into bar shaped samples. The pressure was applied twice with a ten second hold time for each press. In the first experiment, the green density of the bars was controlled to be 2.20±0.02 g/cm^3. The compacted bars were polished using sand paper to obtain the final dimensions of 6.4 x 4.0 x 34.1 mm. In the second experiment, the press pressure was varied from 25 to 300 MPa to obtain compacted bars with various green densities. The bars were polished to obtain the final dimensions of 5.7 x 4.0 x 34.1 mm.

Flexural Strength Test

Four point bending was performed on the compacted bars using a Universal Testing Machine (Instron). The loading rate was fixed at 0.05 mm/min. The flexural strength (σ) was calculated using equation 1 [3], where "F" is the flexural load (unit N), "a" is the length from the supporting pin to the load pin (unit mm), "b" is the specimen width (unit mm), and "d" is the specimen thickness (unit mm).

$$\sigma = \frac{3Fa}{bd^2} \qquad (1)$$

Results and Discussion

Granule Morphology

The relevant properties and morphologies of the granules are shown in Table 2 and Figure 1, respectively. It is seen that granules 1, 2, and 3 have several undesirable features; agglomeration, hollow granules and non-spherical granules. Granule 4 was unagglomerated and spherical. TGA results comparing the in-house granule and the commercial granule are shown in Figure 2. The figure shows that the in-house granule has more weight loss than the commercial granule in the temperature of 200 to 700°C, which from the literature corresponds to the removal of the polymeric additives. A classification of the polymer additives can be made by observing similar TGA results from the literature.[4, 5] The binder, polyvinyl alcohol, is rapidly removed in the temperature range between 300 and 600°C. The dispersant, ammonium polyacrylate, is removed in the range between 100 and 400°C. The lubricant is removed in the range between 100 and 400°C as well. As can be seen in Figure 2., the weight loss curves of the in-house and commercial granule have the same general shape implying the use of similar polymeric additives. The in house granules have a higher content of lubricant, dispersant, and binder than the commercial granule, resulting in more weight loss. The TGA results could not be used to determine the content of individual additives separately. Further experiments would be required.

Table 2. Granule specifications

Granule No.	**Granule property**	
	Tap density (g/cm^3)	Particle size D[4,3] (micron)
1	1.11	41.64
2	1.13	46.27
3	1.03	55.27
4	1.30	36.71

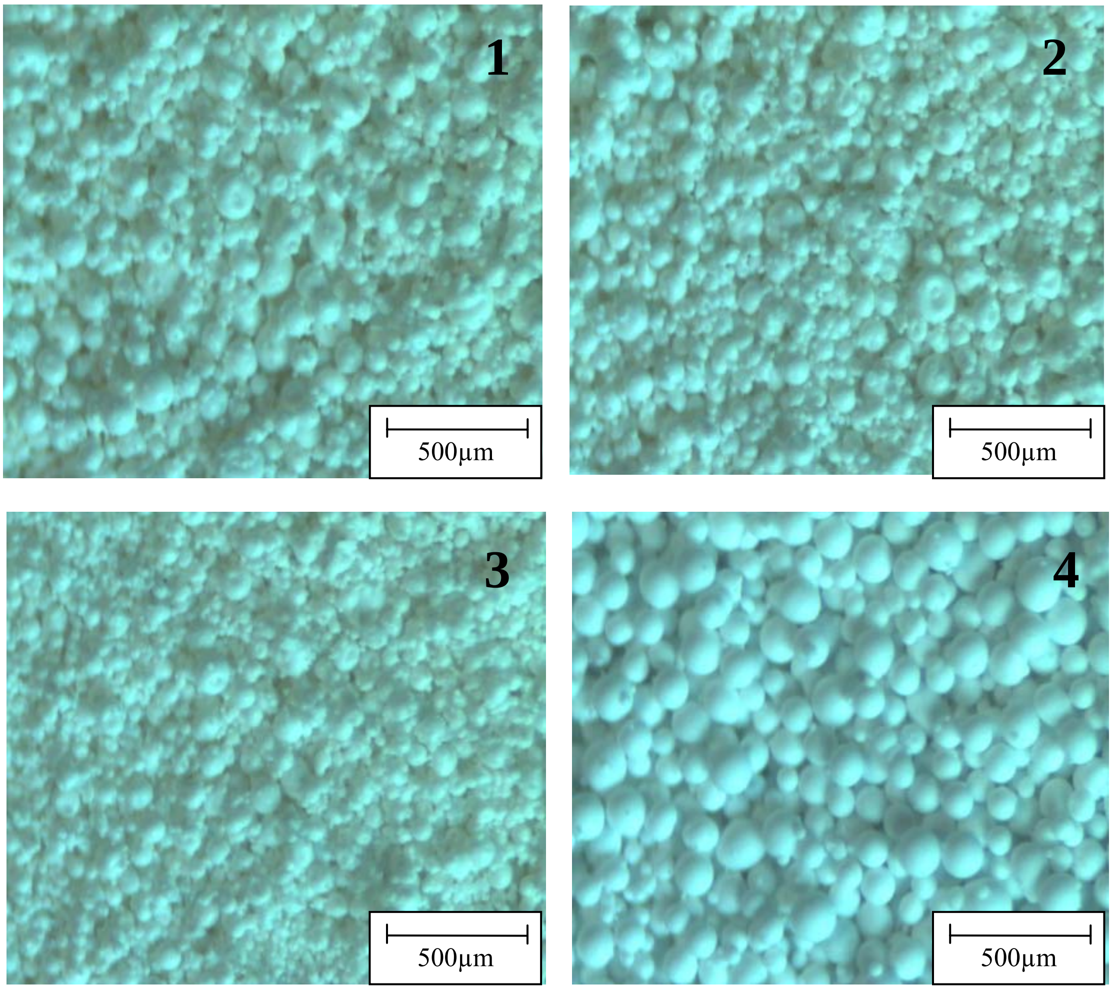

Figure 1. The morphology of the in-house granules 1, 2, and 3, and the commercial granule 4.

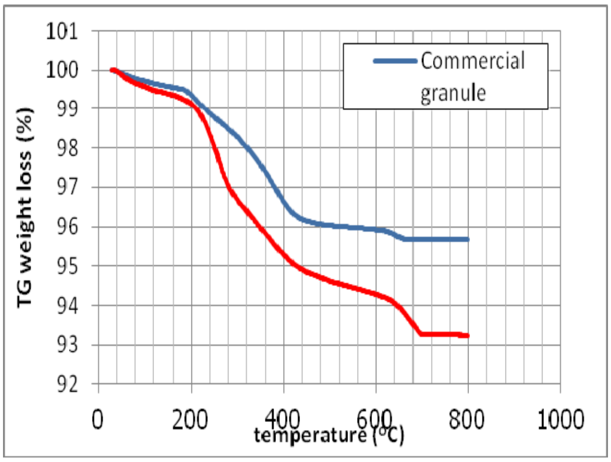

Figure 2. The TGA result of the in-house granule 1, and the commercial granule 4.

It has been noted that well dispersed slurries tend to produce hollow granules because of the higher mobility of the primary particles.[6] The finely dispersed powders are moved from the droplet interior to the droplet surface by the capillary induced liquid flow during spray drying. The hollow granules have a lower average density and a lower packing density, which likely explains why granules 1, 2, and 3 have lower tap densities than granule 4.

Granule Compaction

For samples pressed to a controlled green density of 2.20±0.02 g/cm^3, the in-house granules 1, 2, and 3 required compaction pressures of 85, 75, and 80 MPa respectively, while the commercial granule 4 needed only 30 MPa. It can be explained that granules 1, 2, and 3 tend to have a significant quantity of hollow granules with a densely packed shell, such that higher forces are needed to fully fracture and fragment them.[7] The non-spherical and agglomerated granules result in a low tap and packing density. In addition, the presence of excess binder between the particles in the granules increases the mean separation distance between the particles, and hence also decreases the green density of the compacts.[8]

The compression behavior of the in-house granule 1 and the commercial granule 4, with varying press pressures from 25 to 300 MPa, is shown in Figure 3. The figure shows that at the same compaction pressure, the commercial granule achieves a higher green density than the in-house granule. This indicates that the commercial granules are more easily deformed. Conversely, the in-house granules, with an agglomerated, hollow morphology and with a higher concentration of polymeric additives, such as binder, have increased yield pressure.

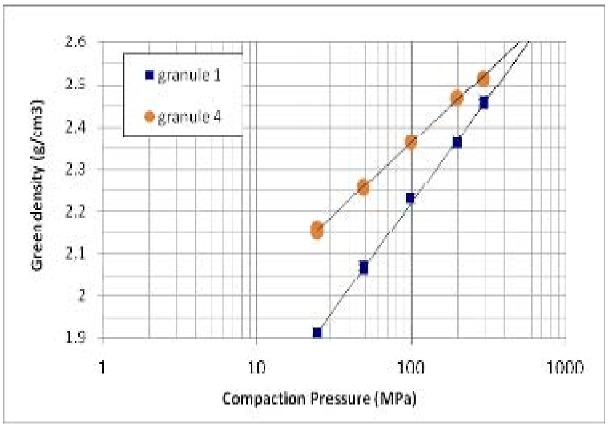

Figure 3. Compression behaviour of in-house granule 1 and commercial granule 4. Granule 1 is predominantly agglomerated and non-spherical with a hard shell and hollow shape. Granule 4 represents a spherical, unagglomerated granule.

Flexural Strength

The flexural strengths of compacted bars produced from granules 1, 2, 3, and 4 with controlled green density of 2.2 g/cm^3 are shown in Table 3. It is shown that bars produced from granules 1, 2, and 3 have higher flexural strength (~4 MPa) than bars produced from granule 4 (~1.2 MPa). This rather large difference in strengths can be explained in two ways. First, granules 1, 2, and 3 are predominately hollow and agglomerated which requires higher forces to fracture during compaction, than granule 4. The use of a higher compaction force tends to generate a higher flexural strength in samples. Second, the presence of a larger amount of polymeric additives, especially binder, in granules 1, 2, and 3 can promote increased strength during bend tests of the bar samples. The flexural results are the same when varying the compaction pressure in bar samples produced from granules 1 and 4, as shown in Figure 4. The bar sample produced from granule 1 has a higher flexural strength than the sample produced from granule 4, for all the compaction pressures. There is an observable trend for granule 1 samples to have increasing flexural strength in the compaction pressure range of 25 to 300 MPa, while granule 4 samples tend to have a constant flexural strength after ~200 MPa. The fracture surface of compacted alumina bars using granules 1, 2, 3, and 4 (Figure 5) can confirm this observation. The figure shows that samples from granules 1, 2, and 3 have present some unbroken granules on the surface, while the granules in the granule 4 sample are completely fractured. The fracture surface characteristics are nearly identical for granules 1, 2, and 3, and thus only the fracture surfaces of granule 1 and granule 4 were compared when varying the compaction pressure at 25, 100, and 300 MPa, as shown in Figure 6. Granule 1 shows unbroken granules at all compaction pressures. This means that many of the granules have not yet reached a yield pressure for compaction. The application of excessively high compaction pressure results in an increase of flexural strength, seen in Figure 4. The samples produced from granule 4 show no unbroken granules when the compaction pressure was above 100 MPa. This means all of granules were completely fractured at this compaction pressure. Increasing the compaction pressure beyond this point did not provide any increase of flexural strength, seen in Figure 4.

Table 3. Compaction pressure and fracture strength of compacted alumina bars at a green density 2.20 g/cm^3

Granule No.	Compaction pressure (MPa)	Flexure strength (MPa)
1	85	4.00 ± 0.37
2	75	3.39 ± 0.26
3	80	4.20 ± 0.68
4	30	1.19 ± 0.10

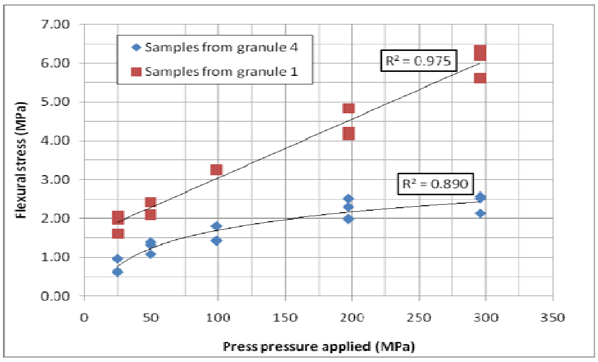

Figure 4. The flexural strength of compacted alumina bars using in-house granule 1 and commercial granule 4, produced with varying compaction pressure between 25 and 300 MPa.

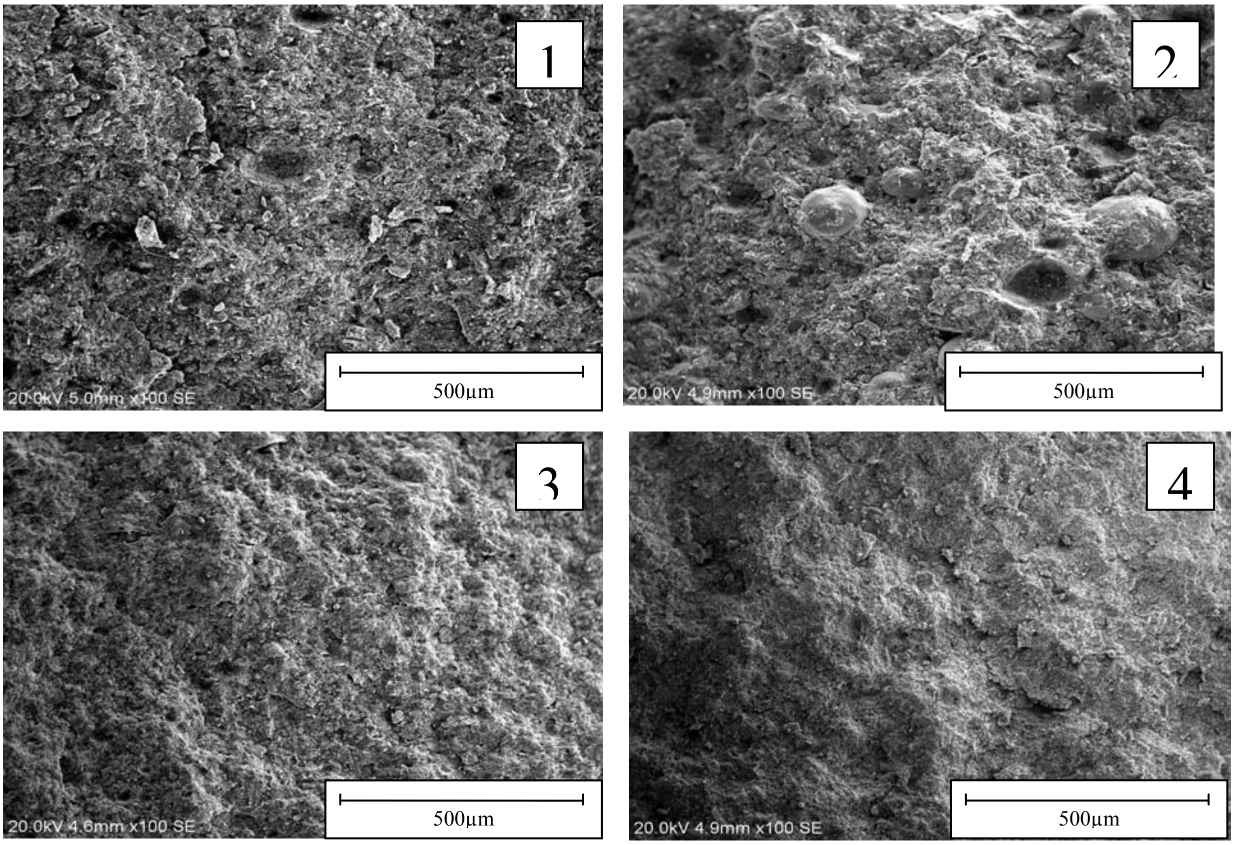

Figure 5. Fracture surfaces of compacted alumina bars produced from granules 1, 2, 3, and 4 with a constant green density of 2.20 g/cm^3.

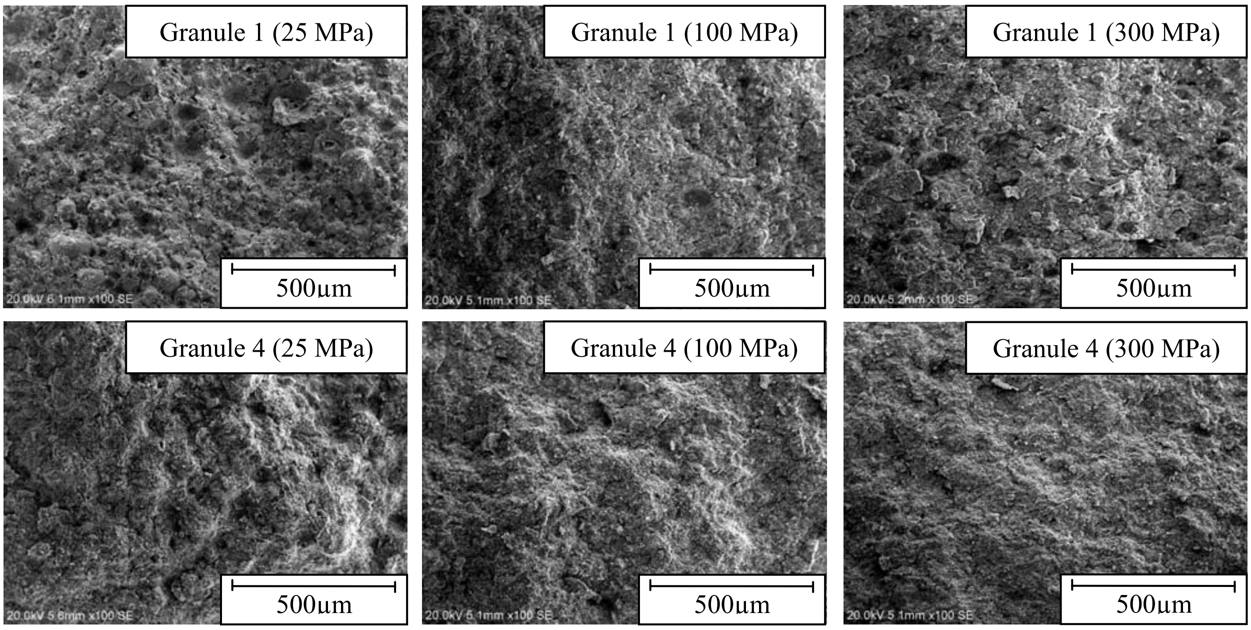

Figure 6. Fracture surfaces of bars produced from in-house granule 1 and commercial granule 4 at 25, 100, and 300 MPa.

Conclusions

It is shown that the granule morphology can affect the compaction behavior and flexural strength of die pressed alumina bars. Agglomerated, hollow and/or dimpled granules reduce the flow-ability, and create empty spaces between granules resulting in low measured tap density. The internal structure of the in-house granules, which are hollow and have a densely packed outer shell, required a high force to achieve acceptable compaction. The use of high compaction pressures generated a high flexural strength. The use of increased binder can increase the yield pressure which will necessitate a higher compaction pressure. The higher flexural strength of the in-house green samples will not necessarily lead to good strength after sintering likely due to the excessive amount of residual porosity, and the poor internal structure.

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