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Journal of the European Ceramic Society 30 (2010) 3291–3296

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Correlation between slurry properties and structures and properties of granules

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Received 21 December 2009; received in revised form 9 June 2010; accepted 1 July 2010
Available online 14 August 2010

Abstract

Two types of granules were fabricated from a flocculated slurry (dispersant: 0.3 wt%) and a dispersed slurry (dispersant: 1.0 wt%), respectively. The slurry properties affected the packing density and morphology of the granules markedly; the granules obtained from the flocculated and dispersed slurries have spherical and dimpled shapes with densities 50.2 and 54.0%, respectively. A new crossed polarized microscopy showed a direct influence of slurry property on the packing structure of particles in the granules. The packing structure of particles affected the deformation behavior of granules; the loosely packed particles in the spherical granules make them easily deformable and the highly packed particles in the dimpled granules make them resistant against deformation.

Keyword: Alumina; Pressing; Microstructure-prefiring; Strength; Optical microscopy

1. Introduction

Slurry is involved and plays a key role in virtually any kind of ceramics fabrication processes.[1] It affects the structures and properties for all intermediate and final products involved in the fabrication of ceramics.[2–5] However, we still have a little fundamental understanding on these effects explicitly. In the ceramic fabrication through the die-pressing route, the slurry is spray-dried to form granules and then dry-pressed to make green compacts, which is then sintered to ceramics. A close correlation is known between the characteristics of slurry and properties of ceramics[6–8] and between the properties of granules and of the ceramics.[9–11] The origin of the correlation has been explained as follows. The slurry characteristics affect the morphology and mechanical properties of granules.[12,13] This in turns affect the compression response of the granules[14,15] and thus the pore size distribution of green body.[16] Therefore, indirectly, slurry characteristics may control the structure and the properties on sintered bodies. Works have been reported on the effect of slurry characteristics of the particle packing.[17–20] However, there is a very little direct understanding for the relationship between the slurry characteristics and the internal structure, i.e., particle arrangement and mechanical properties of granules. Clearly, full understanding of this relationship is the starting point to understand the influence of slurry characteristics and so the properties of granules on the properties of ceramics.

In this study the relationship between the characteristics of the slurry and of the granules will be examined on two typical slurries; flocculated and well-dispersed slurries. These two types of slurries can yield solid and hollow granules, respectively, with the control of level of flocculation via dispersant amount.[21] A significant difference is expected in the packing structures of the granules formed with respective slurries. Particles in the former slurry should be agglomerated forming a network, and only small rearrangement of them should be allowed in the drying process of spray-dry. Particles in the latter slurry will be freely mobile, and they should undergo drastic rearrangement in the drying process. The new cross-polarized microscopy[22,23] can be applied to characterize the resultant

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doi:10.1016/j.jeurceramsoc.2010.07.004

structures of the respective granules. A micro-compression machine can be applied to examine the deformation behavior of the granules directly.

2. Experiments

A commercial alumina powder (AL-SG3, average particle size 0.6 μm, purity 99.8%, Showadenko, Co., Japan) was used as a raw material. Particles of this powder have platelet-shape, which is characteristic for this type of industrial grade powder. Aqueous slurries of 30 vol% with 0.3 (for flocculated slurry) and 1.0 wt% (for dispersed slurry) of ammonium polyacrylate-base dispersant (SERUNA D-305, Chukyoyushi Co., Japan) were added, respectively. 0.5 wt% of polyvinyl alcohol (PVA) polymer was also added as binder in both slurries. PVA was chosen because it is widely used in the ceramic production due to its comparatively high green strength enhancement of the "as-formed" compact. Findings in this study will be useful to the ceramic industry. The slurries were prepared by ball milling for 2 h, and were further mixed using zirconia beadsmill (SC Mill, Mitsui Mining, Japan) with beads of 300 μm in diameter as milling media. The former slurry is designated as Slurry A and the latter as Slurry B, respectively, hereafter. The rheology of the slurries was measured by a concentric cylinder viscometer (HAAKE VT550, Ekoseiki, Japan). The shear rate was increased from 0 to 1000 s^{-1} in 600 s and then returned to 0 s^{-1} in 600 s at a constant temperature of 25 °C. A spray dryer of inner diameter 1.3 m (SD13, Mitsui Mining, Japan) was used to form granules at the inlet air temperature 200 °C. Porosities of the granules were measured by a mercury intrusion porosimeter (Porosimeter Pascal, Thermo Electron Corp., Italy). The deformation behavior of the granule was examined by a micro-compression-testing machine (MCTM/MCTE-500, Shimadzu, Japan) with a flat indenter at the loading rate 0.089 mN/s. The temperature and the relative humidity were fixed at 25 °C and 50%, respectively, to avoid the effect of ambient conditions on the deformation property of the granules. Packing structure of granules was examined by the liquid immersion technique using an optical microscope (OPTIPHOT2-POL X2TP, Nikon, Japan) with cross-polarized light. The immersion liquid was a solution of methylene iodide saturated with sulfur powder (99.5% of purity) and diluted with the same liquid at a concentration of 1:1.

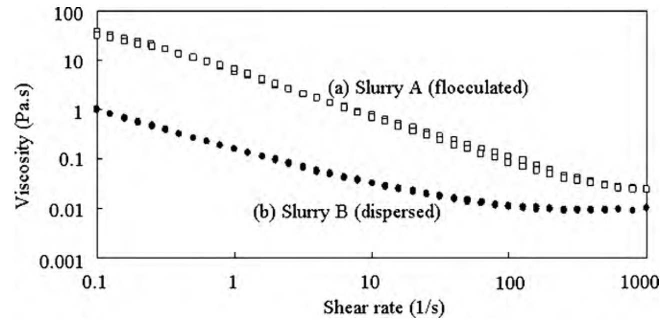

Fig. 1. Variation of viscosity with shear rate of slurries prepared.

3. Results

Fig. 1 shows the viscosity flow curves for Slurry A and Slurry B. They were reversible and no significant hysteresis was noted in the increasing and decreasing stages of shear rates. Both slurries shows shear thinning behavior with yield stress, τ_y of 32.0 Pa s for Slurry A and 0.94 Pa s for Slurry B. High yield stress and the overall viscosity of Slurry A are due to insufficient amount of dispersant to induce repulsive force among particles for optimum dispersion, thus flocculation of the particles increases the viscosity of the slurry.

Fig. 2 shows the scanning electron micrographs of the alumina granules prepared from (a) Slurry A and (b) Slurry B.

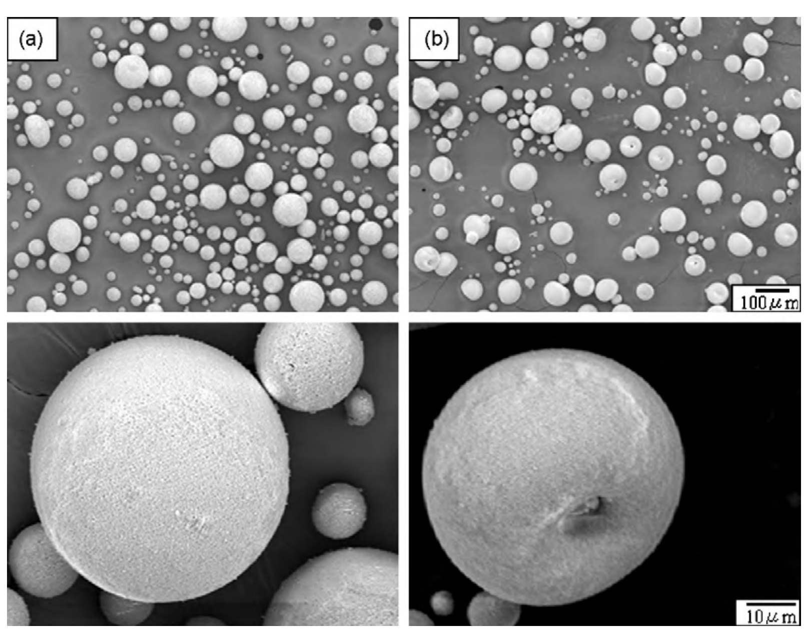

Fig. 2. SEM micrograph of morphology of granules made from (a) Slurry A (Granules A) and (b) Slurry B (Granules B). Bottom diagrams are of higher magnification.

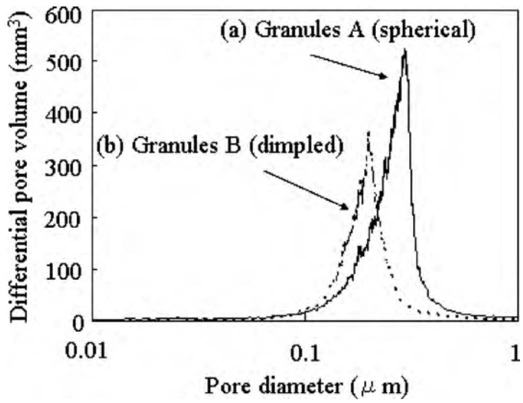

Fig. 3. Mercury porosity curves of granules prepared from respective slurries. Granules A show higher intragranular pore volume compared to Granules B.

The above and bottom micrographs were taken at low and high magnification, respectively. The slurry characteristics affect the morphology of the granules significantly. Highly spherical granules were formed from flocculated Slurry A, whereas spherical granules with dimple were formed from well-dispersed Slurry B. Hereafter, the spherical granules prepared from flocculated Slurry A will be named as Granules A and the dimpled granules prepared from Slurry B as Granules B. Similar range of granule size was taken for both type of granules which is 10–100 μm, however Granules A show higher mean granules size of 61 μm compared to 54 μm for Granules B. This is expected due to the higher viscosity of Slurry A. From the bottom diagrams, the granules surface appears less smooth for Granules A compared to Granules B. This observation suggests that the particles are more loosely packed in the spherical Granules A than in the dimpled Granules B.

Table 1
Granules properties.

	Granules A	Granules B
Porosity (vol%)	72.0	69.8
Density (g/cm^3)	2.01	2.16
Relative density (%)	50.2	54.0

Fig. 3 shows the pore size distribution of the granules prepared from respective slurries. Both size and the volume of pores are larger in the Granules A than the Granules B. The pore size ranges in a narrower region for Granules B (0.08–0.4 μm) with a mean pore size of 0.19 μm compared to Granules A (0.06–0.5 μm) with a mean pore size of 0.29 μm. Table 1 shows the some of the properties of granules measured with mercury intrusion porosimeter. The porosity of Granules A is higher than Granules B and, as expected, the relative density was lower in Granules A compared to Granules B.

Fig. 4 shows the cross-polarized light micrographs showing particle packing structures of the granules. The spherical Granules A show dark matrix with scattered bright features which much of them being less than 10 μm in size. These features changed their brightness when rotated under the microscope. They should be coarse particles or agglomerates, which were present in the raw material and survived the milling process during slurry preparation. In the dimpled Granules B, a specific structure is observed in the micrograph. A dark cross pattern centered at the dimple is noted in a majority of granules; bright zones appear like quadrants in the granules and these are stationary even though the granules are rotated on the sample stage of the microscope. This particular image shows that particles are oriented in the dimpled granule. This observation is further proven by a platelet-shape extremely coarse particle observed within

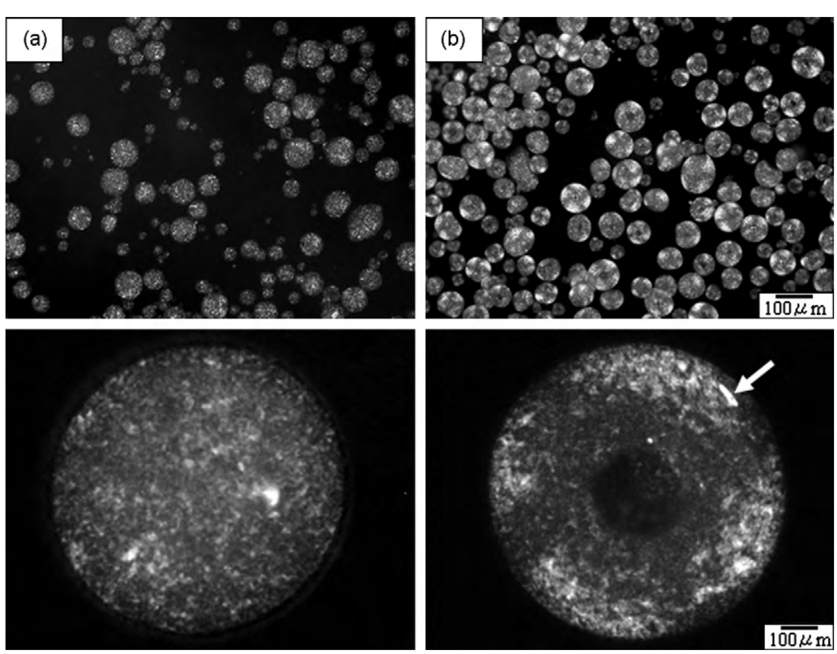

Fig. 4. Cross-polarized micrograph showing particle packing structure within granules of (a) Granules A and (b) Granules B. Bottom diagrams are of higher magnification.

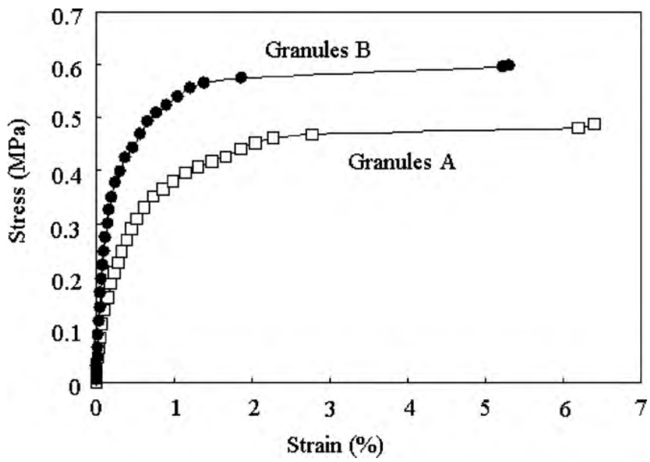

Fig. 5. Stress–strain curve of single granule compression test.

the dimpled Granules B (marked by arrow). The coarse particle oriented normally to the diameter direction of the granule as proposed in the past report.[22]

Fig. 5 shows the representative deformation behavior for individual granules under compression. The granules deformed nearly linearly with increasing stress and started to deform drastically at a critical stress. The inflection point in the stress–strain curve indicates the break point of the granule. The Granules A and B show different deformation behaviors. The dimpled Granules B are shown stronger than the spherical Granules A. The breakage of dimpled Granules B occurs at higher stresses and accompanied by a lower deformation than the spherical Granules A. The breakage stresses were about 0.56 and 0.47 MPa and deformations for breakage were 1.4 and 2.3%, for the Granules B and A, respectively.

4. Discussion

The correlation was established systematically between the slurry characteristics, and the morphologies, structures and properties of resultant granules. These results are consistent to past reports,[12,13] although the structure was much well understood in this study. The structures and properties of granules can be understood in terms of the dispersing structure of particles in the slurries. The present results successfully fill the gaps of knowledge, which were left in the past studies.

Two granules types were obtained from two extreme types of slurries, Slurry A (flocculated) and Slurry B (dispersed). The effect of slurry characteristics on the morphology of granules has been explained,[12] and is consistent with the present study as follows. In flocculated slurry, a major rearrangement of particles is difficult during drying, due to the network formed among them. Reduction of distance and/or change of relative angles among neighboring particles are the only allowed changes of structure in the drying of droplet of this slurry type, resulting in the spherical granules. In the dispersed slurry, particles are separated and mobile, and their relative positions are readily changed in the drying of droplets. Dense layer of particles are developed on the drying surface, forming a shell, which cannot shrink further. The collapse of shell, i.e., granule's surface cave in occurs in the subsequent drying process resulting in the dimple granules.[7] The collapse of shell is an important occurrence in further increase of granules density as well as orienting the particles within the granules.

The packing structure was expected to be a direct consequence of the flocculation or dispersion of the slurry. This should depend also on the structure adopted by particles during the formation of granules, i.e., drying from the slurry. In the flocculated slurry with low amount of dispersant, weak repulsive force exists between powder particles. Therefore, particles are flocculated by the strong Van der Walls attraction force. These flocculated particles create porous structure after drying, leading to granules of loosely packed particles. In the dispersed slurry, the particles were dispersed by a dispersant where repulsive force is generated between the particles. This simultaneously separate and provide mobility to the particles for major arrangement. Thus, granules of tightly packed particles are formed from this slurry.

These packing structures directly affect the porosity of the granules. It is obvious that the porosity is higher in granules made from the Slurry A than the Slurry B, as it is shown in Fig. 3. Loose and dense granules are formed from flocculated and dispersed slurry, respectively.

The cross-polarized micrographs showed the clear evidence for particles rearrangement in the drying process of the Slurry B. Free movement and rearrangement of particle allows the development of the specific structure shown in Fig. 6. This figure shows the scheme of the formation of the packing structures of particles for the Granules A and B deduced from cross-polarized microscopy observation (Fig. 4). The particles orientation is random and ordered for Granules A and B, respectively. The deduction is explained as follows. During observation, the linear polarized light produced is passed through the specimen. Here, the polarized light will experience birefringence depending on the direction of the light propagation. Birefringence occurs if the polarized light propagates along an off-axis of direction of the crystallites. Whereas, if the light propagates parallel to any principal axes of the crystallites, the linear polarized light will pass without any birefringence, i.e., without any changes in the wave vibrational direction.[24] In this case, the linear polarized light which passed through the crystallites will have the original wave vibration direction as produced by the polarizer. Therefore, it will be totally blocked by analyzer resulting in dark image of the particular region. In order to produce this effect, the crystallites axes must either be oriented parallel or perpendicular to the polarizer's aperture, or in other words, parallel or perpendicular to the radial axis of the granule. Based on the coarse alumina particle shown in Fig. 4b (of higher magnification), it is concluded that the particles is oriented perpendicularly to the radial axis of the granule.

In addition, for other crystallites which neither parallel nor perpendicular to the polarizer's aperture, linear polarized light will experience birefringence resulting in production of ordinary ray (o-ray) and extraordinary ray (e-ray). These rays are able to propagate through the analyzer, due to their difference in wave vibrational direction, thus the crystallites whose produces these rays appeared bright in the micrograph. The cross pattern observed in granules is the resultant of the repetition of dark and

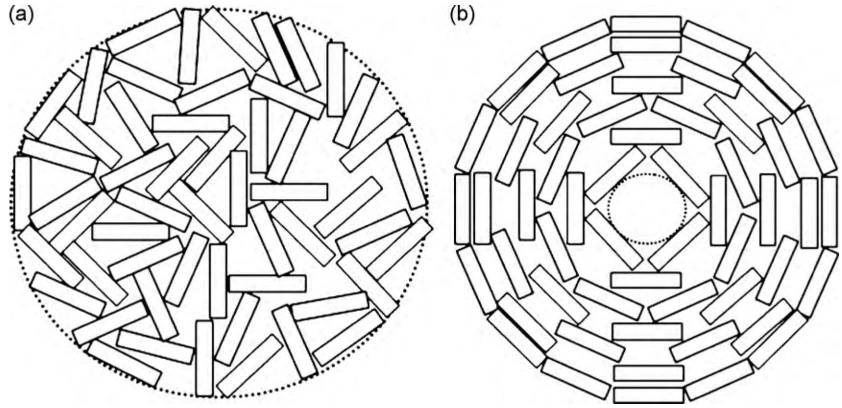

Fig. 6. Schematic diagrams of particle packing structures within granules of (a) Granules A and (b) Granules B.

bright regions which occurs for every 45° rotation. Furthermore, the rotation of granules does not have any effect on the cross pattern which suggest similar orientation of crystallites within the entire granule. A similar observation was reported on particle packing in an injected molded green body.[25]

Packing structure of particles in the granules affects the mechanical property of granule remarkably. The strength and deformation behavior are clearly different for the Granules A and B. The spherical Granules A have lower strength and deforms easily, since the particles are loosely packed and able to move easily under compression. In contrast, particles are densely packed in the dimpled Granules B, thus lack of spaces to move under compression. Therefore, the dense Granules B can resist deformation, i.e., particle rearrangement more than the Granules A. Similar changes in mechanical behavior with respect to slurries properties is also reported elsewhere.[26]

Despite of granules plastic or brittle properties as a single granule, they are more likely to experience plastic deformation more than brittle fracture during compaction. This can be related to the stress distribution within the compact where only a small fraction of compaction stress is actually reached to a particular granule. This also depends on the packing fraction within the compact where higher packing fraction may have higher stress distribution among granules thus less compaction stress on a single granule. In contrast, lower packing fraction will increase compaction stress on a single granule thus resulting in granule fracture. Furthermore, isostatic pressure is considerable for a particular granule within the compact where their deformation is more likely different compared to compaction of a single granule. They are unlikely to fracture such as in single compaction test due to less space for deformation to achieve fracture. Granule appeared deformed rather than fracture within the internal structure of green compacts observed using liquid immersion technique under microscope in transmission mode in our past publication.[27] However, plastic or brittle properties of granules may be further investigated by observing the fracture surface of green compact. For granules which still remain its structure, plastic properties can be known by the clean surface deformation, whereas brittle properties can be seen from cracks on the granules surface. Packing density may also show significant effects on granules deformation behavior. Low packing density in flocculated granules makes them more plastic compared to dispersed granules of higher packing density. Plastic/brittle properties of granules can be further investigated by plotting the relative density against pressure curve, i.e., compaction response diagram during uniaxial pressing.

Differences in granules deformation behavior should affect the internal structure of green compacts. Loose granules deform easily at lower pressure in the die-pressing process, and the formation of granules traces often acting as defects in the ceramics, should be minimized. However, there should be a problem. A considerable change in dimension should occur in the compaction as a consequence of high deformability of granules. The sintering deformation of the compact should be high since the particles orientation should be accompanied in the compaction. This sintering deformation is expected to be less for dense granules; however, the problem of granules traces should rise. In the real process of compaction, it is very important to adjust the slurry property to the requirement of granules types for each specific use. These will be the subjects of the future studies.

5. Conclusions

The correlation between the slurries property and granules characteristics was clearly determined. The morphology and the packing structure of particles in granules are strongly dependent of the slurry dispersion state. Granules of loosely packed particles are formed from flocculated slurry, while granules of densely packed particles are formed from dispersed slurry. Characteristic packing structure of granules was successfully observed by the cross-polarized microscopy. Particles in the loose granules are randomly packed, while particles in dense granules are densely packed and oriented along the surface of granules. Packing structure of particles in granules has significant influence on the granules characteristics. Loose granules are more deformable and weaker than dense granules.

Acknowledgement

This study is supported by The Program for Developing the Supporting System for Global Multidisciplinary Engineering Establishment under The Japanese Ministry of Education, Culture, Sports, Science and Technology.

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