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Ceramics International 37 (2011) 3445–3450
CERAMICS INTERNATIONAL
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The effect of polyvinyl alcohol as a binder and stearic acid as an internal lubricant in the formation, and subsequent sintering of spray-dried alumina

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Received 29 November 2010; received in revised form 18 April 2011; accepted 3 May 2011
Available online 12 June 2011

Abstract

The production of ceramic components using fewer processing steps on a shorter timescale is very important when considering the industrial and economic aspects of the manufacture of these materials in bulk. Spray-dried granules are expected to give compacts with fewer defects due to their low shear strength compared to conventional powders. Several extent studies show results for product of high relative densities (∼50% at 10 MPa), however, this study arrives at a process for making ceramic components with comparable density (48–49%) at 10 MPa), using less processing time and fewer processing steps which becomes extremely important when one considers the industrial aspects such as bulk production and manufacturing cost. In the present investigation, 35 vol% alumina slurries with 0.5% weight dispersant (ammonium polyacrylate) have been synthesized with different contents of binder (PVA) and lubricant (stearic acid). It is found that variations in the amounts of these additives plays a significant role in the formation of spray-dried granules, as well as the subsequent consolidation and densification of the compacts made using the granule particles. There is support for adopting the concept of a 'compact process'.

Keywords: A. Sintering; A. Grain growth; B. Microstructure; D. Al_2O_3; Densification

1. Introduction

Fabricating ceramic components to demanding tolerances is critical to the quality of a final product, but there are difficulties in producing such components with accurate size, shape and flatness, since sintering results in inhomogeneous shrinkage and microstructure. As a consequence, machining processes are necessary to produce a final product with optimum geometrical properties. However, it is generally accepted that the processes of grinding and polishing result in sub-surface damage which, in turn, causes deleterious effects on the strength and performance of a component. In addition to the need to retain high performance by avoiding defects such as cracks, flaws and pores, there is also a strong incentive to reduce the number of processing steps, as well as time, in order to reduce manufacturing costs. Overall, the production of ceramic parts, without the need for final machining, is an important goal to achieve.

Spray drying is one of several versatile processing methods for the manufacture of ceramic powders [1,2]. The low shear strength of the granules formed by spray drying suggests that the process may contribute to a novel and industrially viable approach to the manufacture of ceramics in which the number of processing steps and overall processing time is reduced. This would be economically beneficial without compromising the need for high quality components for advanced applications. Since the uniformity of a green body, as well as a sintered body, is determined by the characteristics of the slurry to be spray

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.05.149

dried, then optimizing the slurry properties will be a key factor in the overall process of ceramic fabrication. Previous studies have focussed not only on the effect of the spray drying conditions, such as atomizer design, the drying temperature, etc., but also on the characteristics of the feed. Investigations have considered the influence of the initial solid content, as well as the effect of the viscosity of the slurry, on the morphology of the granules produced [3–6]. Generally, it is reported that the solid content of most slurries is limited to 30–40% mass in the presence of deflocculating agents and organic binders, before the viscosity increases excessively [4].

Dispersants have been used to achieve stabilized slurries, and, in particular, ammonium polyacrylate has been established as a novel material for this purpose [7]. Addition of binder is necessary to confer cohesive strength to spray-dried granules so that they have free flowing properties [8–10] and various authors have discussed potentially useful agents [4,11,12]. The most commonly used binder when spray-drying ceramics is probably polyvinyl alcohol (PVA). Dispersant-binder compatibility is necessary in order to ensure optimal slurry rheological properties. In this context, several researchers have investigated the interactions between dispersants and different types of binder [13–18]. In turn, the rheological characteristics of a slurry affect the quality of the granules produced and attempts have been made to correlate these properties [19–21]. Finally, the addition of a lubricant is essential to reduce the friction between particles; it reduces the shear between two surfaces which is necessary during the forming process. The role of internal lubricants on the characteristics of compacts prepared from spray-dried powders has been investigated by Walker et al. [22]. The effects of external lubricants have also been reported [23].

The optimized binder-lubricant composition, which is one of the most important parameters for obtaining uniformly shaped, spray-dried granules and thereafter green bodies and sintered compacts with appropriate density, has not been studied in detail for the alumina system. Furthermore, from the perspective of the fabrication of uniform ceramic bodies, it is important to gain a deeper understanding of how to obtain spray-dried granules with reduced shear strength. In the present work, spray-dried alumina granules have been prepared with different concentrations of binder (PVA) and lubricant (stearic acid) and the densification behaviour has been characterised. An ideal composition for ceramic fabrication is suggested which has the potential to reduce the number of processing steps and time, and hence cost, in a manufacturing process without reducing the quality of the final product.

2. Experimental procedure

35 vol% alumina slurry was prepared by mixing 300 g alumina powder (Al160SG4, Mean particle size-0.5 μm, Showa Denko Co., Ltd, Tokyo, Japan) in 139.9 ml distilled water, adding 0.5 wt% dispersant, ammonium polyacrylate (Seruna D305, Chukyoyushi Co., Japan), and ball milling for a period of 24 h. Just before spray drying, the ball-milled slurry was sieved into a beaker and stirred for 5–10 min, incorporating polyvinyl alcohol binder (WF-804, Chukyoyushi Co., Japan), and stearic acid (Selosol 920, Chukyoyushi Co., Japan) as the lubricant. The binder and the lubricant contents were varied from 0.5–4 wt% and 1–4 wt%, respectively. The slurry was spray dried using a spray drier (Eyela Spray Dryer, SD-1000, Tokyo Rikakikai Co., Ltd. Japan) with an atomizing pressure of 8×10 kPa. The inlet and outlet temperatures were 100 and 65 °C, respectively, and the slurry flow rate was 1.5. The spray-dried powder was collected and used for further characterization.

The viscosities of the slurries were measured using a Brookfield Viscometer (Model HBT, EA, PV-4880) and the granulated powder particle sizes were measured using a Particle size analyser, (Horiba, Japan). The stress–strain curves for various samples were obtained by using an Autograph stress–strain testing instrument (Model AGS-500D, Japan). The SEM of granules, as well as calcined and sintered samples, were observed using a Scanning Electron Microscope (SEM: JEOL, JSM 5600 LV, Japan). Cylindrical pellets were made by uniaxially pressing powders using a 10 mm die and applying a pressure of 400 MPa. The pellets were calcined at 1000 °C and they were then sintered over a period of 2 h at a heating rate of 300 °C h^{-1} to reach a final temperature of 1600 °C.

3. Results and discussion

The variation in apparent viscosity with dispersant content is presented in Fig. 1. It is observed that the slurry containing 0.4 wt% dispersant has the lowest viscosity. However, a dispersant concentration of 0.5 wt% has been selected as the ideal dispersant content. This is to ensure the complete saturation of particles with the dispersant and so achieve stable slurry for the reasons discussed in [7]. The variation in relative density *versus* binder content is presented in Fig. 2. The relative density increases as the percentage of binder increases.

Fig. 3 shows the surface SEM of pellet samples, calcined at 1000 °C, with 1.5 wt% PVA and 4 wt% PVA, respectively. A uniform homogeneous distribution is observed for the sample containing 1.5 wt% PVA while the granule shape is retained in the sample containing 4 wt% PVA. For the latter sample there

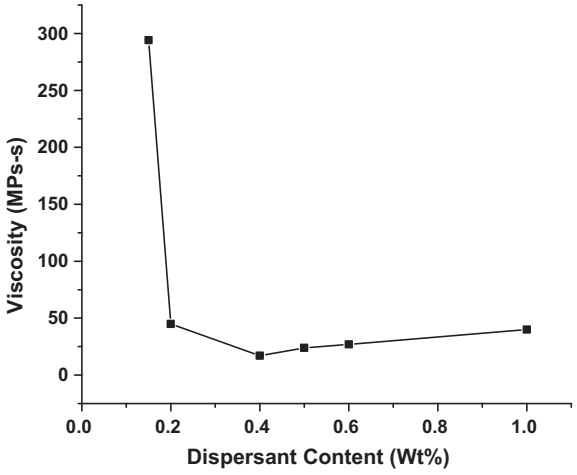

Fig. 1. Variation in apparent viscosity with dispersant content.

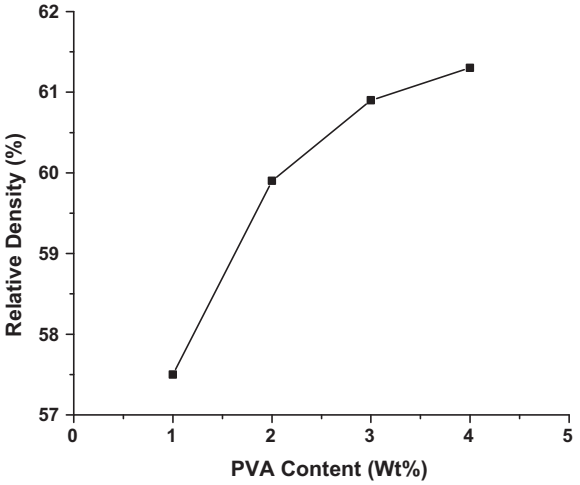

Fig. 2. Variation in relative density (%) with different % binder (PVA).

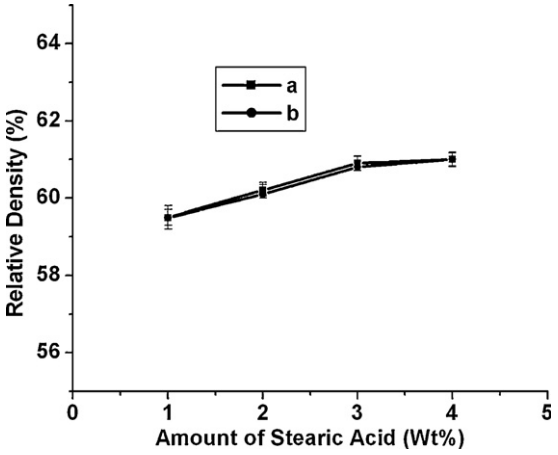

Fig. 4. Relative density (%) vs. lubricant content for samples with different binder content (a) 1.5 wt% PVA (b) 2.5 wt% PVA.

are more irregularities and this is due to comparatively greater shear strength of the granules. A good compact should have no granule relics or remnants of the initial granule structure. In addition, it should knit across granule boundaries so that the green strength is not reduced by intergranular fracture and, in this way, separation at granule boundaries is prevented during sintering [22]. Also, it is not advisable that granules retain their shape after compaction since the non-uniform particle distribution will result in the formation of cracks in the sintered sample. Even if the relative density is high when the binder concentration is high, an increased PVA content will result in less lubrication and, as a consequence, particles will stick together. High binder content also creates burn-out problems which result in crack formation.

A plot of relative density (%) *versus* lubricant (stearic acid) content for samples with different binder content (1.5 wt% PVA

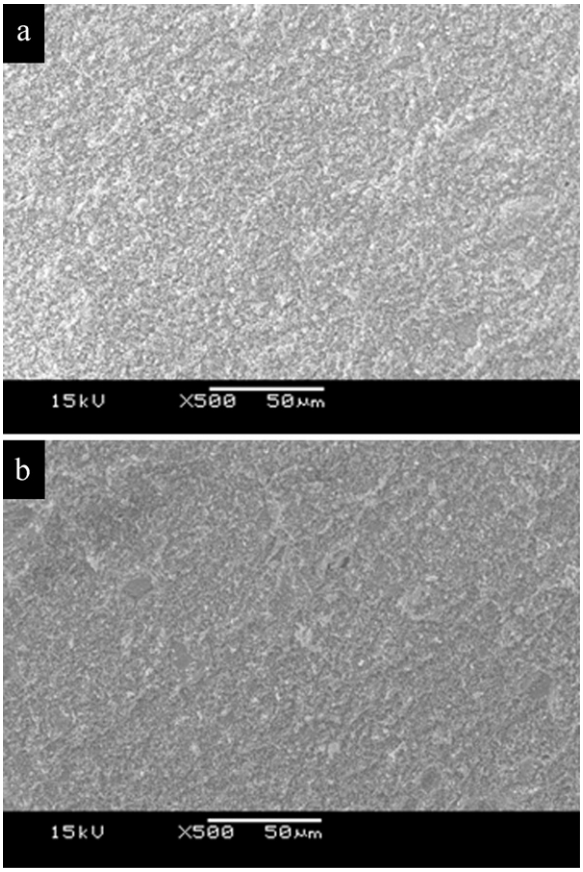

Fig. 3. Surface SEM of samples with different % PVA content, calcined at 1000 °C (a) 1.5 wt% PVA (b) 4 wt% PVA.

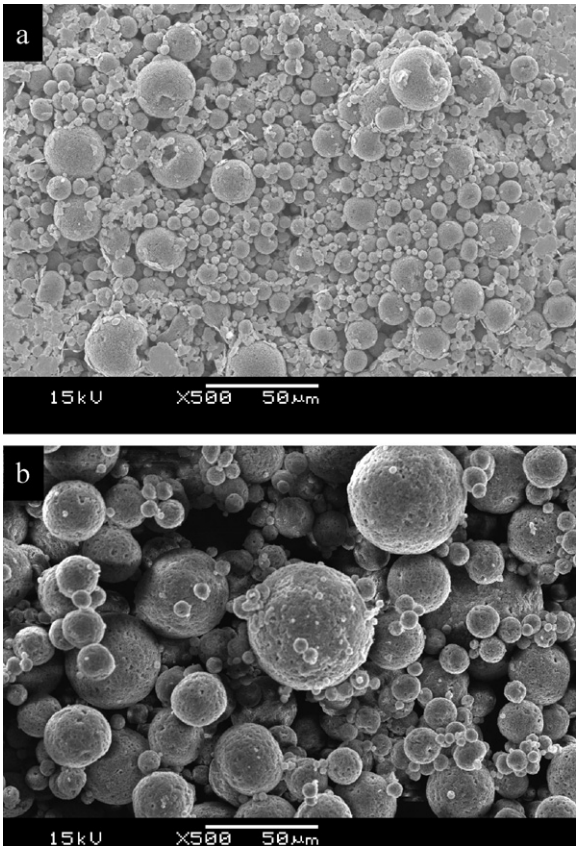

Fig. 5. SEM of spray dried granules with 1.5 wt% PVA (a) 1 wt% stearic acid (b) 4 wt% stearic acid.

and 2.5 wt% PVA) is presented in Fig. 4. The difference in the percentage relative density for these samples is relatively small when the stearic acid content is varied from 1 to 4 wt%. Overall, it is reasonable to select a 1.5 wt% PVA content to be optimal for the production of a uniform compact.

The SEM of spray-dried granules, prepared using slurry with 1.5 wt% PVA, and containing 1 wt% and 4 wt% stearic acid are presented in Fig. 5. A uniform granule size distribution is observed for the sample with 4 wt% lubricant. By contrast, a less homogenous distribution, with dough-nut shaped and irregular granules, is observed for the sample containing 1 wt% stearic acid.

Fig. 6 shows the surface SEM of samples containing 1.5 wt% PVA, with 1 and 4 wt% stearic acid, calcined at 1000 °C. A homogenous distribution, as well as less porosity, is observed for the sample containing 4 wt% stearic acid. This might be due to the reduction in friction caused by the presence of stearic acid which influences the shear strength of the granules. A lower shear strength enables the granules to form with uniform microstructures and, in turn, less defects. The extent of the distribution deviations in the sintered compacts is found to be directly proportional to the extent of the density variations generated within the corresponding green compacts. SEM fractographs of samples containing 1.5 wt% PVA, with 1 and 4 wt% stearic acid, calcined at 1000 °C are presented in Fig. 7. A more uniform size distribution is observed for the sample containing 4 wt% stearic acid.

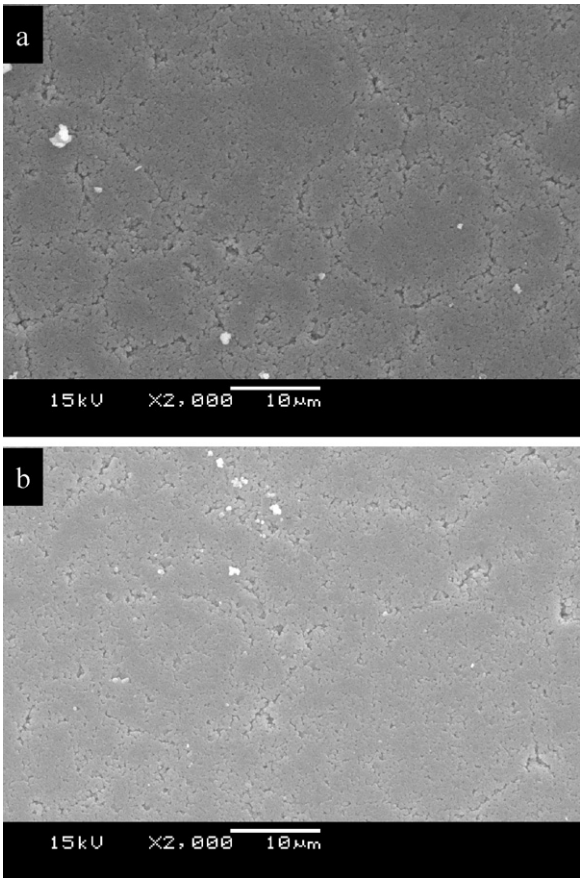

Fig. 6. Surface SEM of samples with 1.5 wt% PVA, calcined at 1000 °C (a) 1 wt% stearic acid (b) 4 wt% stearic acid.

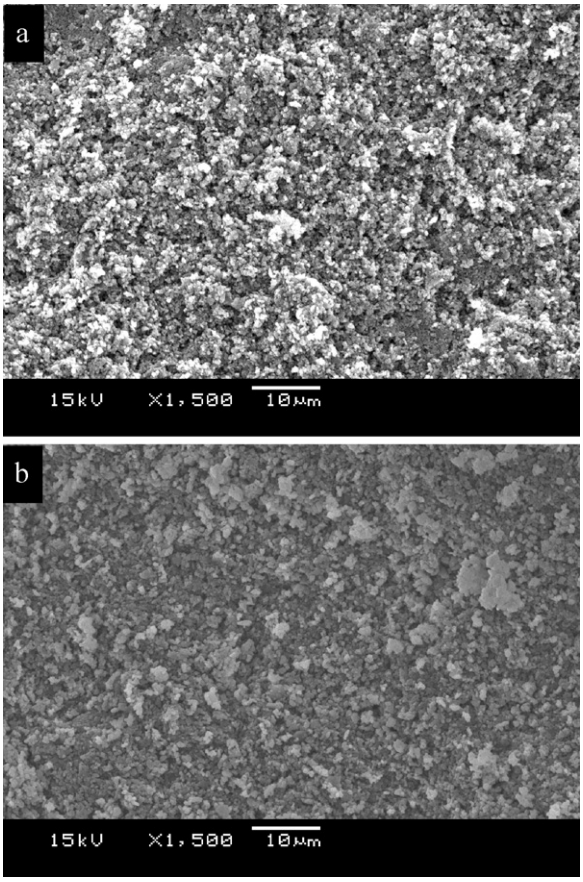

Fig. 7. SEM fractograph of samples with 1.5 wt% PVA calcined at 1000 °C (a) 1 wt% stearic acid (b) 4 wt% stearic acid.

SEM of samples sintered at 1600 °C with 1.5 wt% PVA, and 1 wt% and 4 wt% stearic acid, respectively, are presented in Fig. 8. A more irregular grain growth is observed for the composition containing 1 wt% stearic acid, while a homogeneous grain distribution is observed for the sample containing 4 wt% stearic acid. This result shows that alumina compacts prepared from slurries containing 1.5 wt% PVA and 4 wt% stearic acid are ideal for uniform grain distribution in green, as well as sintered bodies.

The variations in relative density with apparent pressure for samples with 1.5 wt% PVA and different lubricant contents (1 wt%, 3 wt% and 4 wt%) are presented in Fig. 9. The relative density (%) is observed to be greater for the compositions containing the higher lubricant content for an apparent pressure of 1 MPa, and higher (28–30%). At 10 MPa pressure, the relative density (%) is in the range 48–49%, and at 100 MPa pressure a value of 60% is observed for the sample containing 4 wt% stearic acid. The general behaviour observed for the present results is consistent with general ideas about compaction. Compaction curves (*S*–*S* curves) are widely believed to occur in three stages: granule rearrangement (stage I), deformation and fracture of granules (stage II), and rearrangement of primary particles that constitute the granules (stage III) [24,25]. The transition from stage I to stage II, namely the

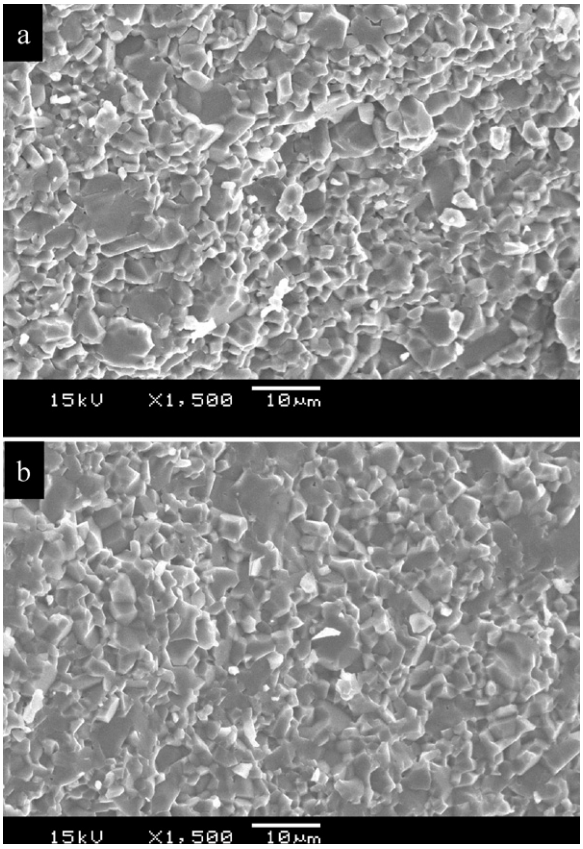

Fig. 8. SEM of sintered samples (sintered at 1600 °C) with 1.5 wt% PVA (a) 1 wt% stearic acid (b) 4 wt% stearic acid.

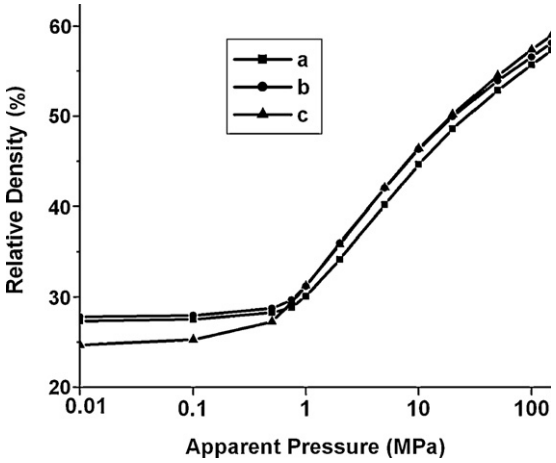

Fig. 9. Relative density (%) vs. apparent pressure for samples with 1.5 wt% PVA and different lubricant content (a) 1 wt% stearic acid (b) 3 wt% stearic acid (c) 4 wt% stearic acid.

apparent yield pressure (P_y), is believed to be a measure of the granule strength. In the present work, P_y is found to be less for the sample with a high lubricant content. At the stage I–II transition, the horizontal intergranule interfaces unite to form a planar layer of uniform density. The force chains then follow the direction of applied pressure. Also, the net downward transmission of pressure becomes more effective. The deformed layer then behaves as a continuum solid, and this change in character is responsible for the change in slope between stages I and II. The formation of a continuum solid provides justification for the observed dependence of the stage I–II transition point on granule strength: the weaker the agglomerates, the lower is the pressure needed to fully deform the uppermost layers. Rigid granules may optimize flow during die-filling and rearrangement during the initial stage of compaction. However, beyond a specific point in the compaction process, deformable granules are then required to produce the most homogeneous, high-density compact [25].

The granule characteristics must be such as to allow a generalized subsequent force transmission in the downward direction over a large fraction of the granule population [26]. In the present system, at low pressures, because of the presence of the lubricant on the surface of the particles, friction between the granules is reduced and, hence, allows easier rearrangement of the granules. At low compaction pressures, the amount of deformation of the granules is determined by the stiffness of the granules which, in turn, is dependent on the granule density. Initially, the granules are stiff and do not deform/fracture sufficiently, and only particles that are located near the contacting areas of the granules are free to rearrange. At higher pressures, corresponding to stage II of the compaction curve, the granules deform/fracture sufficiently and rearrangement of most of the primary particles that comprise the granules becomes possible. When the granules have deformed/fractured sufficiently to induce movement of a significant percentage of the primary particles in the compaction process, the internal lubricant should reduce interparticle friction, thereby allowing easier particle rearrangement and better particle packing. This improved particle rearrangement in the presence of the internal lubricant should enable the particles to fill and eliminate intergranular pores at lower pressures. The granule rearrangement starts easily, even at relatively low apparent pressure, when the lubricant content is high. Furthermore, the primary particle rearrangement starts, and proceeds, at much lower pressures for the sample containing high lubricant content, which is more effective in the densification of the compact. Addition of stearic acid prevented the particles from making a direct surface-to-surface contact which lessens the friction offered by the particle. The overall microstructural features are in concurrence with densification properties.

4. Conclusion

The effects of variations in the content of dispersant (ammonium polyacrylate), binder (PVA) and lubricant (stearic acid) in the production of homogeneous, reduced shear strength granules which give compacts with uniform-grained microstructures have been investigated. The overall aim is to identify and refine methods of reducing the number of processing steps and processing time in ceramic manufacturing. As the PVA content increases, it has been found that the density increases, but there is also less lubrication which, in turn, causes sticking of the particles. Stearic acid, which is used as a lubricant in the present work, is very effective in increasing the densification behaviour of the compact. If the lubricant content is increased,

it is observed that the effect of the binder is reduced. The granule rearrangement starts easily, even at relatively low apparent pressure, when the lubricant content is high. The primary particle rearrangement starts and proceeds at a much lower pressure for the sample containing a high stearic acid content. Furthermore, the densification of the compact is more effective in this case and this may reflect the fact that the particle with more lubricant content offers less friction. It is concluded that a 35 vol% alumina slurry, spray-dried using 0.5 wt% dispersant, 1.5 wt% binder and 4 wt% lubricant, is an ideal composition in order to manufacture uniform alumina compacts with homogeneous grain distribution and dense microstructure. We suggest that this provides an example of using the concept of a 'compact process'.

Acknowledgement

One of the authors Padmaja Parameswaran Nampi acknowledges National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan for a Postdoctoral Research Fellowship. Useful technical discussion with Dr. Michael Mortimer of The Open University, UK is gratefully acknowledged.

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