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Influence of Solid Loading and Particle Size Distribution on the Porosity Development of Green Alumina Ceramic Mouldings

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Abstract: Alumina ceramic mouldings with different solid contents ranging from 55 to 70 vol% and different ratios of coarse/fine powders, i.e. 0.4 μm (fine) and 3 μm (coarse), respectively, were prepared by compression moulding at 75°C under a compressive stress of 10 MPa. The porous parameters, such as porosity, pore size and pore size distribution, of the green compacts were evaluated after removal of organic vehicles. Experimental evidence showed that the green density, as well as the sintered density, of the moulded alumina increased linearly with increased solid loading to an optimum of 65 vol% and decreased roughly linearly with increased coarse/fine ratio. Further increase in solid loading reduced particle packing efficiency, resulting in lower green and fired densities. No considerable improvement in green and sintered density of the moulded alumina was achieved by adjusting the coarse/fine ratio, which is due to the fact that coarse particles suppress the driving force of densification. The green compacts generally showed a bimodal pore size distribution character which may be the most important factor in dominating the densification of the powder compacts. The peak frequency at larger pore region is approximately 20–35 μm in diameter and at the smaller pore region is ~50–95 nm in diameter. The larger pores are believed to be due to the presence of internal voids originating from entrapped gas and are probably caused by the removal of organic vehicles. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Powder injection moulding is well-known as a means to obtain products with complex shape and for mass-production purposes. This technology usually employed for the plastic industry, however, provides an alternative methodology for ceramic powder processing. To achieve this goal, a ceramic blend containing both inorganic ceramic powders and organic vehicles is prepared followed by injection moulding. During the injection moulding the blend was subjected to a series of temperatures causing the vehicle to melt and the blend behaves like a fluid. The fluid-like blend was then injected into a cavity with pre-determined geometry. After moulding, the as-moulded green compacts were heat-treated at various stages of temperature for both debinding and densification purposes.

A number of parameters, such as blend characteristics, injection moulding conditions and subsequent thermal treatments, determine the properties of the final products.[1] A careful selection of ceramic powder/binder systems and control of moulding and thermal debinding treatments to avoid defects formation in the green compact are critically important in obtaining a ceramic product with dense, fine and uniform microstructure and have been summarized by German *et al.* [2] recently.

In principle, injection moulding should be capable of dealing with ceramic powders with relatively wide ranges of particle size, type, shape and particle size distribution. These particle-related properties directly affect injection moulding behaviour to a significant extent and in some critical aspect dominate the microstructure of the final products after binder burnout and densification stages.[3,4] Numerous investigations have concerned the microstructure of the green compact during thermal debinding,[5,6] usually in a relatively slow pyrolysis rate, and have observed that the binder removal from moulded ceramic bodies was facilitated without causing visualized green compact defects while using coarse ceramic powders.[4,7] In some reports the formation of internal voids of sufficient scale in size due to organic vehicle removal or other improper treatments affects final densification and deteriorates the microstructure and sintered properties of ceramic products eventually. Therefore, control and understanding of the porosity formation on pyrolysis is a critical necessity not only in quality control but also for stepwise processing evaluation and becomes an increasingly important subject in many investigations.

Porous properties, such as pore size, porosity and pore size distribution, of a green compact have long been known to play an important role in dominating the sintering activity; however, the relevant reports on the moulded ceramic compacts are not extensive[7–11] and this is the main concern of this investigation — attempting to gain better understanding of those pore-related properties of the green compacts and subsequent densification behaviour.

2 EXPERIMENTAL PROCEDURES

Mixtures containing alumina (A16SG, Alcoa; having an average size of 0.4 μm), microcrystalline wax, paraffin oil and stearic acid were first prepared using ball milling in a polyethylene jar with methyl ether ketone as liquid medium. The alumina powder content was in the range of 55–70 vol% and the content of the wax, paraffin oil and stearic acid was fixed in the weight ratio of 6:4:1 in all the prepared blends. After oven drying at 40°C, the resultant blends were further mixed and compounded in a kneading machine (Model 70-20vex-6, KCK Industrial Co. Ltd) using barrel temperatures (feed to exit) 60–70–85–80 and were then granulated.

In order to understand the influence of particle size distribution on the porous properties of the moulded green compact, alumina powders with an average particle size of ~3–4 μm (Showa Denko, Al-45-2) were arbitrarily selected and were mixed with the fine alumina powders (0.4 μm) in a weight ratio of coarse/fine of 0/100, 50/50, 70/30 and 100/0, followed by the same compounding and moulding procedures described earlier.

Specimens of cylindrical shape (12 mm in diameter and 15 mm in height) were prepared using compression moulding at 75°C under 10 MPa. The cylinders were heated in air at a heating rate of 6°C/h to 600°C, held for 1 h to drive off the organic vehicles, followed by furnace cooling. The resulting green compacts were characterized in terms of pore size, porosity and pore size distribution using mercury penetration method (AutoPore 9220) and microstructure observation using scanning electron microscopy (Cambridge Instruments). During pyrolysis, six specimens of identical dimensions were heat-treated at the same time. Part of the specimens were companion-fired at 1550°C for 2 h, followed by microstructure examination and measurement of the sintered density of the specimens using the Archimedes' principle.

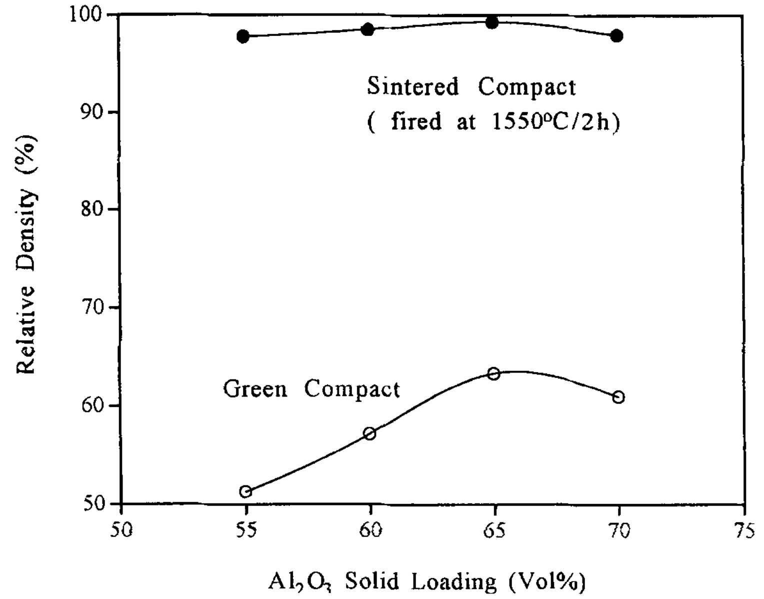

Fig. 1. Relative density of the green density and sintered compacts vs the solid loading of the alumina ceramic mouldings.

3 RESULTS AND DISCUSION

To ensure the solid content of the moulded specimens, the weight change of the specimens was recorded before and after binder burnout and the resulting values indicated that an accuracy of within 0.2 vol% relative to the starting solid loading can be obtained. This indicates a uniform distribution of the organic vehicles in the moulded compact. Three to four green specimens of each formulation were used to determine the porosity, pore size and pore size distribution using the mercury porosimeter technique and an accuracy of within 0.67% was achieved.

3.1 Influence of solid loading

Figure 1 shows the relationship of the relative densities of both the green and the fired compacts versus solid loading. A similar trend in relation to the solids loading for both compacts is clearly illustrated. A linear increase in both densities with solid content is observed and reaches a density maximum, i.e. 63% theoretical density in the green compact and 98.5% in the fired one, at 65 vol% solid loading. A further increase to 70 vol% decreases both the densities. Such a decline in density at 70 vol% loading may result from poorer particle packing efficiency originating from deficient preparation procedure. Furthermore, a higher solid content significantly reduces the flowability of the molten blend by increasing blend viscosity[12,13] while under the moulding condition and this may also give rise to insufficient packing of the particles, resulting in lower green density.

Two theoretical mechanisms explain the porosity formation during the removal of organic vehicles.[9,14] One indicates the porosity formation from the surface inwards as a continuous phase when the vehicles recede into the inner region of the moulded ceramic body. The other involves the outward diffusion of the organic vehicles from the ceramic surface to the ambient environment and this results in redistribution of the organic vehicles. On the basis of the binder redistribution and shrinkage due to the removal of organic vehicles, Shaw and Edirisinghe[8] indicated that a lower value of measured porosity than expected porosity was observed at the early stage of pyrolysis; however, they did not show a comparative result after complete removal of the vehicles. In this study, a solid loading–measured volume fraction porosity relationship (Fig. 2) reveals a distinct expectation that the measured porosity is greater than the expected value for all batches of formulation, suggesting other factors should be involved. One possible explanation is due to the presence of entrapped gas incorporated during the preparation procedure and the micrograph shown in Fig. 3 of a fracture surface (55 vol% as-moulded specimen) containing numerous large pores appears to confirm this. Increasing the solid content to 65 vol% gave a porosity value closest to the expected value. Since the redistribution of the organic vehicles accompanied by particle rearrangement could inevitably be operative during pyrolysis (such an effect should be more pronounced for blends with lower solid content), a lower measured total porosity can be expected. The higher measured porosity suggests a considerable amount of gas phase

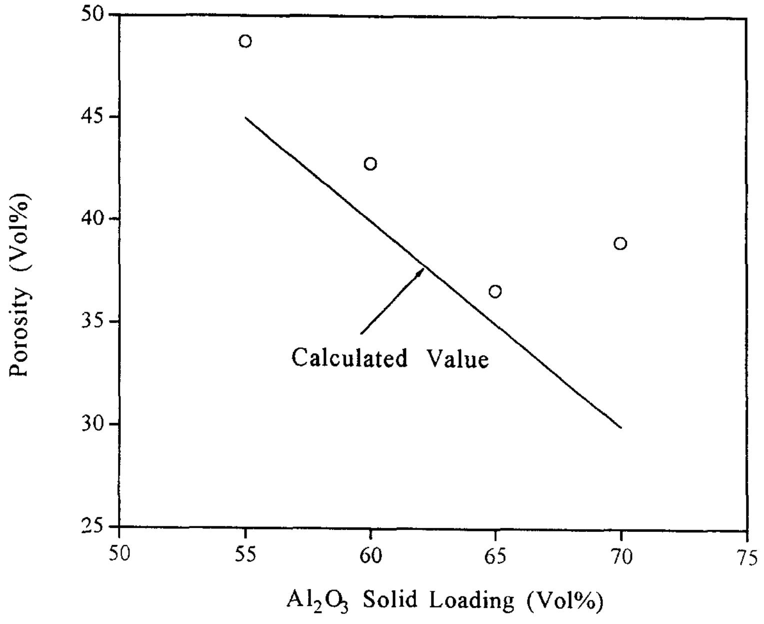

Fig. 2. Change in the porosity fraction of the green alumina compacts with solid content (the solid line indicates the calculated or expected porosity corresponding to the total organic phase).

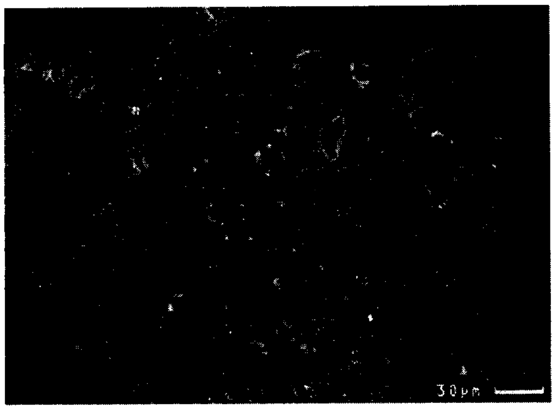

Fig. 3. Fractured surface of the as-moulded specimen revealing the presence of entrapped gas.

being trapped into the as-moulded specimens. The formation of internal voids due to binder burnout may not be a major cause because no direct evidence of bloating and serious surface cracking can be visually observed on the green compacts after slow pyrolysis.

A detailed examination of the pore size distribution (PSD, Fig. 4) illustrates a bimodal PSD. The minor peak frequency at large pore size region of approximately 20–35 µm is observed, which is similar in dimension with the previous SEM observation (Fig. 3). The major peak frequency at small pore size region is in the range of 50–95 nm. The difference in the peak frequency at the small pore region directly reflects a particle packing configuration, i.e. the smaller the pore diameter of the peak frequency, the closer the particle packing that can be achieved. It is interesting to note that the smallest pore size at peak frequency of 52 nm is observed for 65% solid content, which is much smaller than those values for 55%, 60% and 70% content, having 91.4 nm, 79.6 nm and 60.5 nm, respectively. This finding suggests a closer packing of particles for the green compact of 65 vol% formulation, which, in turn, promotes densification (Fig. 1). The total volume fraction of the large pores (here defined as pore size larger than 1 µm) is calculated to be 17.3%, 12%, 3.2% and 8.5% for solid content of 55%, 60%, 65% and 70%, respectively. The presence of these large pores may be a result of either air entrappment, binder burnout, or a combination of both, in the green compact and can be effective in suppressing high-temperature densification. Figure 5 shows the presence of pores of various forms and of sufficiently large dimension after sintering the green compact of 70% loading at 1550°C for 2 h. The crevice-like defect in Fig. 5 (indicated by an arrow) may have originated from the interfacial boundary between the granulated starting powders.

According to the preceding discussion on pore size distribution, the greater content in smaller pores and less in larger pores, the denser the final sintered ceramic compacts that can be expected. An attempt is made to utilize the average pore diameter (APD) of the green compacts accompanied with the sintered density in terms of solid loading. Figure 6 shows the resulting relationships which clearly demonstrate that the sintered density exhibits as an inverse function of APD. This finding suggests that the APD of the green compact may be used qualitatively as an index for the resultant density of the sintered ceramics, i.e. the lower the value of the APD, the higher the value of the sintered density results.

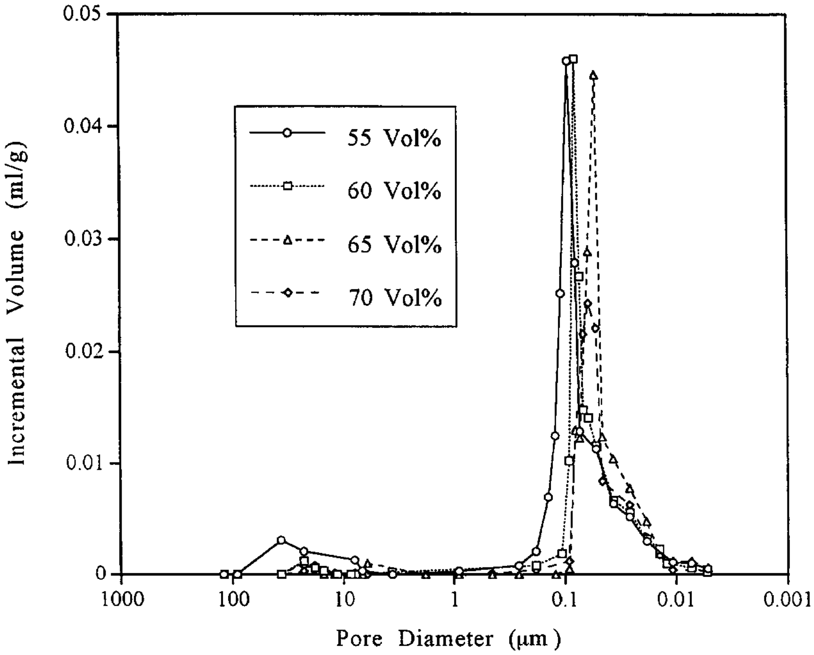

Fig. 4. Pore size distribution of the green compacts with various starting solid contents.

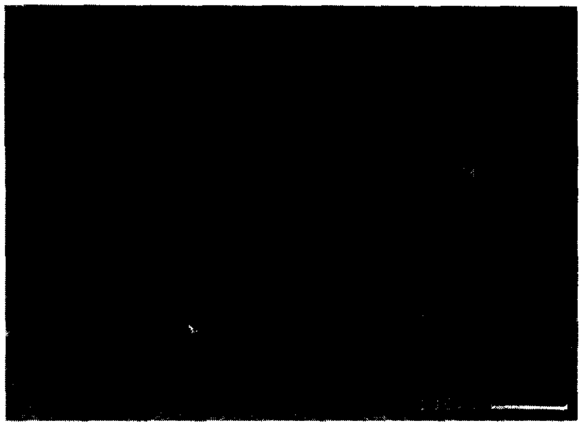

Fig. 5. Numerous large voids of different geometries present in the sintered compact.

3.2 Influence of particle size distribution

Change of particle size distribution can generally alter the particle packing configuration within the green powder compacts and, in some instances, a green compact with a high density can be obtained.[15,16] In this study two kinds of alumina powders — one with an average particle size of 0.4 μm in diameter (fine powders) and the other with a particle size of ~3–4 μm (coarse powders) — were employed. The weight ratio of the coarse to fine powders was controlled at 0/100, 50/50, 70/30 and 100/0 and the solid loading was fixed at 60 vol%. Figure 7 shows the resultant green and sintered densities of the powder compacts. The incorporation of coarse powders appeared not to improve particle packing efficiency and the sintered density was reduced as the coarse/fine ratio was increased further. This appears to contradict a previous study by Mangels and Williams[16] who found a considerable reduction in relative viscosity of a powder suspension while incorporating powders of a mixed-modal particle distribution and suggested that the mixed-modal powders should increase packing efficiency to high green density of ceramic mouldings by increasing the volume fraction of the powders.

The previous discussion of this study on the influence of solid loading on green and sintered densities is generally in agreement with Mangel and Williams' finding. However, their argument may not be suitable for the present case, since the prepared blends contained a fixed solid fraction and a varying coarse/fine powder fraction ratio. Reduction in viscosity of a blend or suspension by varying powders of different sizes can be obtained.[16,17] However, such a decrease in blend or suspension viscosity may not be fully responsible for the achievement of high green density compact at a given solid volume fraction. For example, in the case of ceramic casting, a reduction in ceramic suspension viscosity by either adding powders of different size or adjusting surfactant content is not the only critically necessary condition in the improvement of green compact density.[18,19] Such an argument may give rise to an implication that for a given solid loading, a decrease in particle size (assumed to be spherical in shape) leads to an increase in the green density of the powder compact. Accordingly, the highest green density of the prepared blends in this study should be the 0/100 formulation and this is in good agreement with the experimental result illustrated in Fig. 7. Theoretically, the size of the smallest voids constructed by

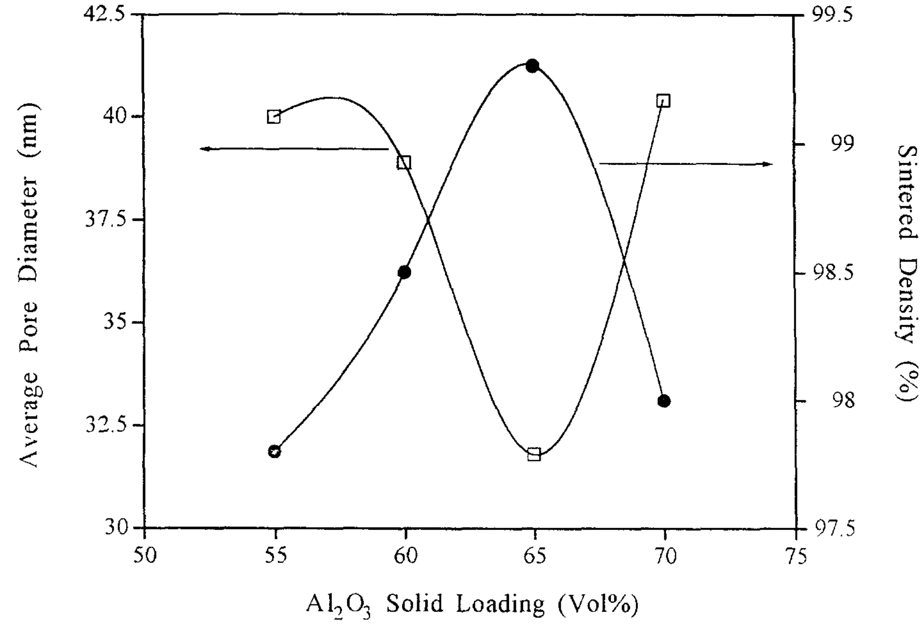

Fig. 6. Relationship between sintered density and average pore diameter with respect to various solid loadings.

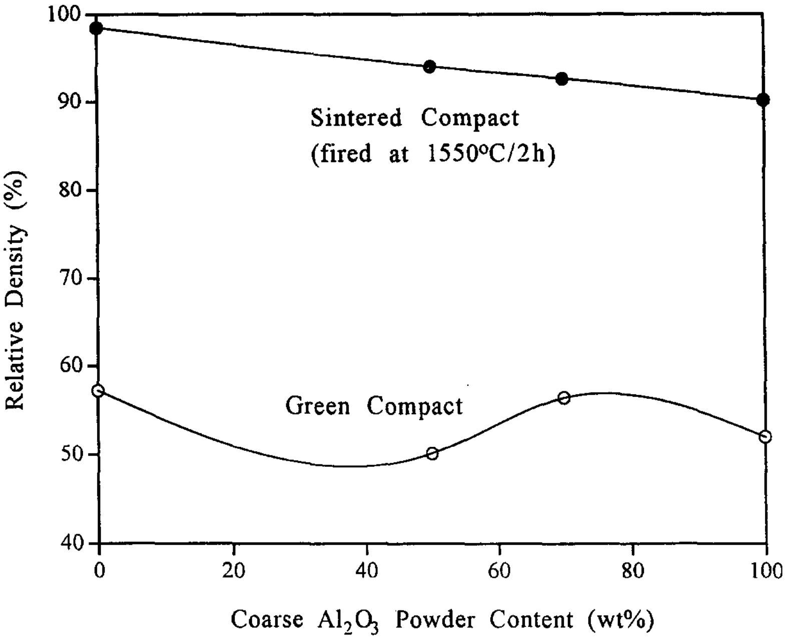

Fig. 7. Change in the relative density of the green and sintered compacts with different coarse/fine powder ratios.

closely-packed uniform-sized spherical particles of radius r is $0.155r$,[20] and the smallest void having a pore size between the 3–4 μm particles is 0.233–0.31 μm, which is smaller than the size of the fine particle (0.4 μm) employed. This further reinforces the aforementioned argument that no improvement in green density can be achieved; the fine particles which can be fitted into the interstices of the coarse particles may be relatively limited (the exact fine particle size and shape are unknown).

Some improvement in green density was observed for the green compacts from 50/50 to 70/30 ratio, but the latter formulation resulted in a lower sintered density. Before a more satisfactory explanation can be addressed for such a controversial phenomenon, the pore size distribution of these green compacts is examined (Fig. 8). Both 50/50 (open square) and 100/0 (close circle) formulations show a bimodal PSD with a pronounced peak frequency at large pore region of ~35 μm in diameter. The other two formulations, i.e. 0/100 (open circle) and 70/30 (open triangle), illustrate a less pronounced bimodal PSD with large pores peak at ~20 μm. In comparison with the PSD of the 50/50 and 70/30 formulations, the 70/30 formulation has a particle assembly more closely-packed than the

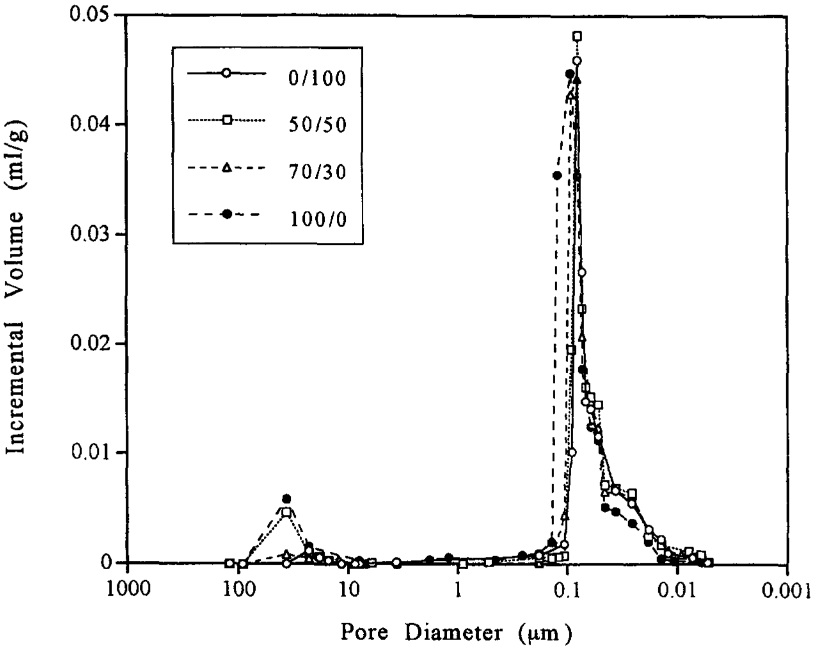

Fig. 8. Pore size distribution of the green compacts with varying coarse/fine power ratios.

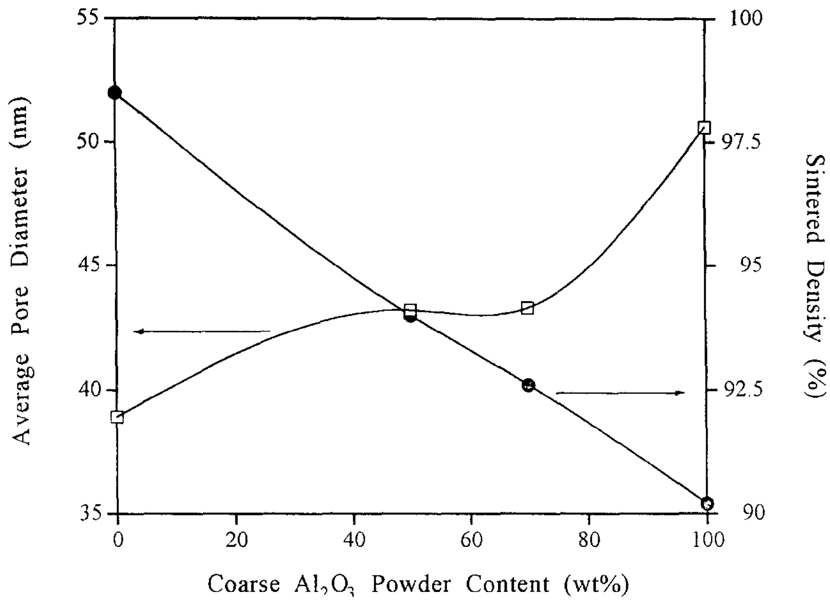

Fig. 9. Relationship between sintered density and average pore diameter in terms of varying coarse/fine powder ratios.

50/50 one, it therefore should have a higher sintered density. This contradicts the measured values. Thus, it seems to be reasonably assumed that this difference in measured and expected sintered density between 50/50 and 70/30 formulations is primarily due to the presence of coarse powders that strongly retard the driving force of sintering. This can be further verified by the 100/0 formulation, which showed an even lower sintered density after the same firing conditions.

In the preceding discussion (Fig. 6) the concept of APD of a green compact was employed as an index to relate the final densification property and received an encouraging result for the green uniform-sized powder compacts. A similar correlation was used for green compacts of different particle size distribution as illustrated in Fig. 9. Although the trend of the APD in relation to the sintered density is roughly similar for a given coarse/fine fraction ratio (Fig. 9), a detailed comparison between the 50/50 and 70/30 formulations strictly implies that the attempt to correlate only the APD with sintered density of the powder compacts may be unsatisfied. Such correlation may only be valid for an assembly of uniform-sized particles.

One important advantage of using the coarse powders is to facilitate the removal of organic vehicles without causing defects in moulded compacts on pyrolysis.[7] In most cases, the pore architecture plays a crucial role in the gaseous diffusion of organic vehicle on pyrolysis from as-moulded powder compact to ambient.[7,9] In this case as-moulded compacts having an identical dimension of 15 mm in diameter and 23 mm in length were prepared. The moulded particles assembly with various coarse/fine fraction ratios was subjected to pyrolysis at a constant rate of 6°C/h to 500°C.

Fig. 10. The appearance of 15 mm×23 mm specimens with various coarse/fine powder ratios.

Figure 10 shows that serious damage, i.e. cracking and bloating, is observed for the 0/100 formulation and slight surface cracking was found for the 70/30 formulation. However, no visual surface damage can be seen for the 50/50 and 100/0 formulations. These findings suggest that the latter two formulations possess an interconnected and sufficient-sized pore architecture which facilitates the removal of organic vehicles. The pore size distribution shown in Fig. 8 for these formulations reveals that a more closely-packed particle assembly with smaller-sized interconnected pore structures increases the difficulty for binder removal, which eventually enhances the possibility of damage to the thicker ceramic mouldings during pyrolysis. A detailed examination of the porosity and pore size development within the compacts, consisting of varying particle distributions during pyrolysis, is necessarily important for practical purpose and will be reported shortly.

4 CONCLUSIONS

The influence of solid loading, as well as particle distribution, on the green and sintered densities in alumina–wax blends was investigated in terms of the development of porosity, pore size and pore size distribution of the green compacts. An increase in volume fraction of solid up to 65 vol% increases the green density and sintered density as well. Further increase in solid content provides no improvement in the green and sintered densities and this may result from poorer particle packing efficiency. An attempt to correlate the sintered density with the initial average pore diameter of the green compacts was tried and the results were not satisfied, especially for powder compacts consisting of larger ceramic particles which considerably suppress the driving force to densification. Factors such as pore size, and particularly the pore size distribution of the green compacts, strongly dominate the final density of the sintered compacts and are important in preventing damage to the green microstructure during pyrolysis, this is especially pronounced for ceramic mouldings with thick cross-section, e.g. 15 mm in this case.

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