PII: S0272-8842(97)00039-4

Ceramics International **24** (1998) 471–481
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0272-8842/98 $19.00+.00

Influence of Debinding Rate, Solid Loading and Binder Formulation on the Green Microstructure and Sintering Behaviour of Ceramic Injection Mouldings

Dean-Mo Liu* & Wenjea J. Tseng

Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu, 31015, Taiwan

(Received 1 November 1996; accepted 14 February 1997)

Abstract: Zirconia powders with submicrometer particle size are consolidated using injection moulding technique. The green microstructure evolution and sintering behaviour of the moulded compacts after binder removal is characterized. Factors involving solid content, binder formulation, and debinding rate are considered to have a significant effect on the green microstructure of the mouldings and subsequent sintering behaviour, which have been verified under current investigation. Powder–binder suspensions with high solid content favours to develop homogeneous green compact microstructure with dense particle packing. This enables the sintering of the green compacts to be achieved at lower temperatures.

INTRODUCTION

In ceramic powder processing, injection moulding route has been receiving great attention for many years[1–3] due to its attractive advantages in massive production of ceramic parts with complex shape and with relatively high dimensional precision. In ceramic injection moulding, the green compact was formed in a conventional plastic forming route. The moulded article is essentially a two-phase composite composed of an inorganic powder and an organic binder. The presence of organic binder is to facilitate flowability of the powder–binder suspension into mould cavity during injection moulding and to keep the particles attached firmly. The organic binder is temporary and will eventually be removed in subsequent thermal cycle. The removal of organic binder is a procedure (usually termed debinding) that is known to be critical in obtaining a green compact with desired microstructure. The most widely-used method to remove organic binder to date is by thermolysis and is the method mainly employed in current investigation. Improper binder removal usually makes the green microstructure to an unacceptable level by creating macro-defects such as bloating, blistering, surface cracking, and large internal voids.

Porosity evolution is one of the main phenomena occurring in the moulded article while on debinding. Although it has received great interest both experimentally and theoretically,[4–9] only very few of them have characterized the pore-size distribution in the debound article. Reports on the influence of factors such as solid content, material formulation (for both inorganic and organic phases), and debinding rate on the development of PSD are not extensive. This is thus the main concern of this paper. An efficient particle packing may frequently result in a uniform and narrow PSD, which facilitates densification[10,11] and leads to the formation of ceramics with desired sintered microstructure. Therefore, the achievement of green powder compacts with a PSD of unique characteristic becomes an increasingly important subject for the fabrication of technological ceramics for high-performance applications.

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*To whom correspondence should be addressed.

The characterization of pore size, porosity, and particularly PSD of the green compact is significant as a direct indication for particle packing in the powder compacts. The importance of PSD to the sintering behaviour has been addressed by many researchers[10,12–14] who have particularly stressed that a homogeneous PSD facilitates the densification of the green compact to high density.

As one realizes, the green compact microstructure influences the sintering behaviour and results in a specific sintered microstructure under a specific sintering schedule. For engineered ceramics, high sintered density, fine grain size, and homogeneous sintered microstructure are essential requirements to be achieved. Such a microstructure can generally be attained if the starting ceramic powders are relatively small in size (easy to densify at low temperatures) and the green microstructure of the powder compacts is chemically and physically homogenous. However, reports on the sintering behaviour of the injection-moulded articles of varying green microstructural features derived from different processing variables are barely found and is one of the objectives to be discussed in current study.

Among numerous powder techniques, colloidal filtration route has been well-recognized as one of the most simple and reliable methods to fabricate high-technology ceramics.[15,16] One of its unique features is that the powders allow to pack efficiently in a configuration exhibiting a uniform and narrow PSD and ease of subsequent high-temperature sintering. Based on its unique characteristic of the colloidal filtration methodology, we take the PSD of the colloidal filtrate article as a reference green compact and a comparative assessment of the developed PSD between the injection-moulded and cast articles is conducted following debinding in order to provide a comparative basis for process control and property optimization.

EXPERIMENTAL PROCEDURES

Low-molecular-weight organic binder composed of paraffin wax (having an average molecule weight 380 and melting point ~60°C), vinyl acetate polymer (an average molecule weight of 4500 and melting point ~140°C), and stearic acid in varying weight ratios of 5:5:1, 6:4:1 and 7:3:1 was used as major ingredient, minor ingredient, and lubricant, respectively. The wax-based zirconia ceramic suspension with zirconia (HSY3.0, 0.25 μm in average particle size and specific surface area 15 m^2 g^{-1}) content of 45–60 vol% was prepared using ball mill to homogenize the suspension with chloroform as medium. The powder has a fixed volume fraction of 22% relative to the total volume of the powder and the medium for all batches. The organic components can be dissolved entirely into the medium and the resulting powder–binder slurry was dried in air under a vigorously stirring condition to ensure suspension homogeneity. The suspension was then granulated through an extruder (Model 70-20vex-6, KCK Industrial Co.), following injection into a cavity of 5×5×40 mm^3 dimension with a barrel temperature series of 70-120-140-160-180°C. The hold pressure is fixed at 90 MPa for 5 s and mould temperature is 45°C.

The as-moulded compacts are placed into a muffle furnace followed by increasing the temperature to 600°C for 1 h at a constant heating rate in the range of 5°C h^{-1} to 30°C h^{-1} to completely remove the organic binder. The actual content of the organic binder in the moulded compacts was then determined and compared with the calculated values (based on the content of starting powder and organic binder) to be within an error of ±0.3–0.5 wt% for all the mouldings. A flowing nitrogen (300 ml min^{-1}) is used for atmosphere control throughout the binder removal operation.

The resulting green compacts after binder removal is characterized using mercury porosimetry (Autopore II 9220). For the mercury porosimetry measurement, a mercury surface tension of 485 dyn cm^{-2} and a contact angle of 130° were assumed to calculate the pore size distribution. All measurements are performed under identical procedures for pore size analysis. The standard deviation for porosity (or green density) measurement is ±0.76% and for the maximum pore size distribution, ±3.06%. Since several assumptions and parameters have been made on PSD determination using the mercury porosimetry,[17] absolute values can hardly be obtained and it is still a useful tool for relative comparisons. In contrast to injection moulding, a conventional colloidal filtration (slip casting) method is used to fabricate zirconia powder compact for comparison purposes; a ceramic slurry containing 35 vol% of zirconia powder (the same powder as that for injection moulding), 2 wt% plasticizer, and 0.5 wt% commercially available organic dispersant was prepared using a ball milling route. The slurry after degassing is caste onto a plaster mould to form ceramic powder compacts. The compacts are subject to mild thermal treatment to remove the organics slowly. The porosity parameters of the cast compact were determined also by using the mercury porosimetry and were compared directly with the compacts derived from injection moulding.

The sintering behaviour of the powder compacts after debinding was measured using dilatometry (Netzsch, Model 402 E) from room temperature to 1450°C with a constant heating rate of 5°C min^{-1}. Microstructure examination of the green compact was performed using a scanning electron microscopy (Cambridge Instruments, S360).

RESULTS AND DISCUSSION

Influence of heating rate

In a previous study, the present authors have demonstrated that the organic binder can be removed completely from the injection-moulded articles without creating macro- and micro-defects by slow thermolysis.[18] Interconnective porosity develops throughout the article during the initial stage of binder removal (~25% loss of binder phase).[4] This should accordingly allow binder removal using a faster heating rate without generating defects because the developing interconnected pore channels are expected to act as conduits for the diffusion or migration of organic species.[6,9]

Therefore, an attempt was made to investigate the influence of heating rate on green microstructure evolution on thermolysis and Fig. 1 shows the resulting pore size distribution (PSD) of the green compact for 55 vol% solid content. No apparent macro-defects such as surface cracking, blistering, are visually observable on these specimens even when the heating rate is relatively high as 30°C h^{-1}. The PSD for the 55% compacts is similar, exhibiting a unimodal but with a long-tailed characteristic. The distribution is essentially asymmetrical and is suggestive of the presence of non-ideal particle packing. The peak for the slowest rate of heating is sharper than those for other heating rates. Further, difference in the pore channel size (especially the most frequent pore size) can be clearly differentiated. A slower heating rate results in greater amount of smaller pore size. The most frequent pore size is increased by about 15% as the heating rate increases from 5°C h^{-1} (corresponding to 79 nm) to 30°C h^{-1} (91 nm). Such a change in the PSD is believed to be a result of heating rate which is the only variable that has been considered presently. However, it is interesting to note that increase in solid content to 60 vol% (the same binder formulation, 6:4:1, as that for 55% loading), little change in PSD has been observed (Fig. 2) for both extremes. This result is virtually different from that of 55 vol% case. Since the pore structure is a direct indication of particle packing, the invariant PSD with respect to different heating rate (corresponding to different rate of binder removal) observed in Fig. 2 strongly suggests that the particle mobility (defined here as an overall behaviour of particle movement and rotation) is restricted. Accordingly, particle mobility becomes essentially important in resulting particle packing configuration, and hence PSD.

For a low-molecular-weight binder as employed currently, Wright *et al.*[19] have pointed out that the binder removal is primarily dominated by evaporation mechanism and this has been verified recently using a dynamic thermogrmetric analysis on the removal of the binder system.[20] The liquid binder migrates along pore channels from interior of the article to surface region by capillary action for further evaporation. During binder migration the particles are expected to draw towards each other by movement and rotation until particles are closely in contact. (In fact, some of the particles

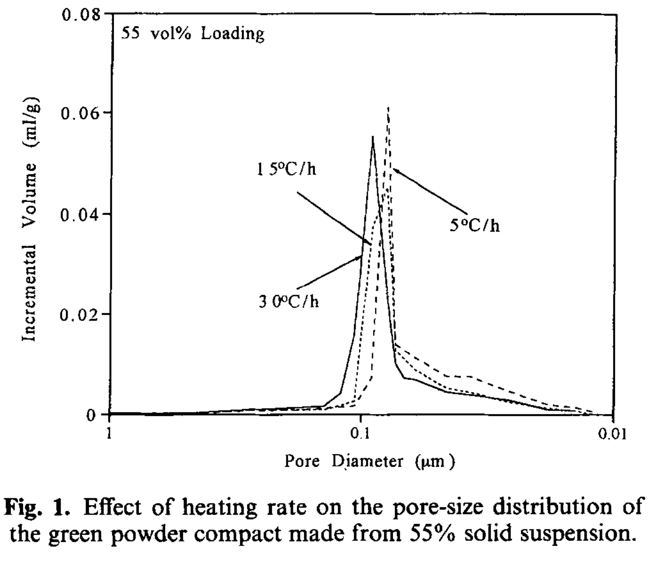

Fig. 1. Effect of heating rate on the pore-size distribution of the green powder compact made from 55% solid suspension.

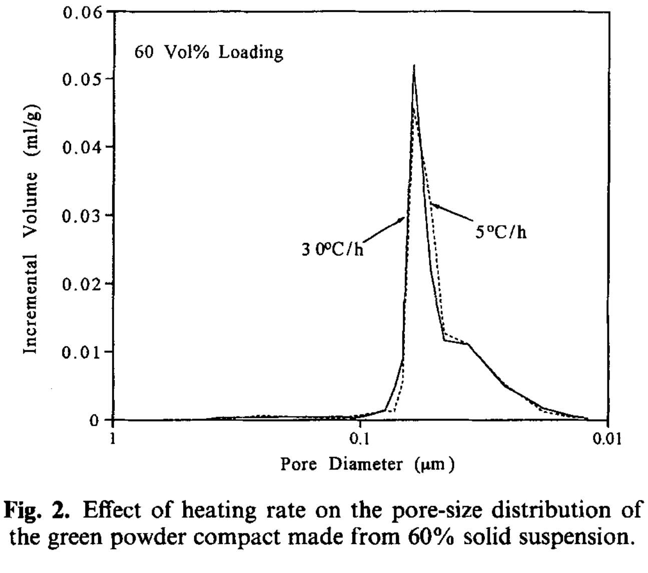

Fig. 2. Effect of heating rate on the pore-size distribution of the green powder compact made from 60% solid suspension.

may have readily in close contact according to percolation principle.) The ability of particle rotation depends on the shape of the particles and becomes difficult for particles having irregular shape. In this case, the zirconia powder illustrates a uniform and narrow-sized particle characteristic (Fig. 3). Some of the particles are roughly equiaxed but not identical in shape at all, although they look like sphere in appearance. Strictly speaking, the particles are somewhat irregular in dimension. Therefore, restriction of particle rotation under investigation, although it cannot be quantitatively assessed, should be taken as one important factor on particle packing efficiency. The restriction should become more pronounced as the difference in shape/dimension of the particles becomes large.[21]

The change in the PSD due to heating rate can thus be reasonably considered as the fact that at lower heating rate, the removal of binder is slow and the time for particle mobility within the liquid binder matrix is supposedly longer than that at higher heating rate. The particles have sufficient time for movement and rotation until the particles are in contact and lock in position until the binder is completely eliminated. The particles are thus expected to pack more densely at lower heating rate. This finding on the PSD is similar to that observed for powder consolidation by both filter-cast and centrifugal-cast methods by Roosen *et al.*,[22] who indicated that the rate for the centrifugal casting at which the packing structure is built up is too fast to achieve the most dense particle packing in comparison with that for the filter casting.

Since particle mobility is important in resulting packing configuration, it would be interesting to estimate the space available for particle to move freely. Therefore, particle spacing, i.e. defined as particle center-to-center distance, turns to be a dominant factor. The particle spacing (λ) within the mouldings can be approximated by considering the moulded article as a two-phase particulate composite within which the discrete ceramic particulate is assumed to disperse uniformly within a continuous organic phase (the particulates are essentially surrounded with a layer of organic binder) and is given:[23]

$$\lambda = 1.085\,{}^{D}/_{x^{1/2}} \qquad (1)$$

where D is the particle size and x is the volume fraction of particulate phase. Equation (1) is originally derived by statistical analysis to estimate the separation of void within a two-phase particulate composite and is considered to be allowable for particle spacing calculation under investigation without causing considerable error. The calculated particle spacing for 55% loading is 366 nm which is greater only by 4.3% than for 60% loading, 350 nm. The nearest distance between two particle–binder interfaces is then determined to be 116 nm and 100 nm for 55% and 60% solids loading, respectively. In comparison, the former distance has a value greater by ~13.8% than the latter distance. Such a large difference in interfacial distance is assumed to be important for particle to move and rotate and may be critical in accounting for the difference in porous network development described in Figs 1 and 2.

Fig. 3. Zirconia powders used in current investigation.

Since the interface distance between the well-dispersed particles is relatively short, the thickness of an adsorbed binder layer onto particle surface turns to be important because particle mobility may be interrupted by steric hindrance or intermolecular force exerted by the adsorbed layer. However, such effect cannot be experimentally verified at present. In principle, binder adsorption involves short sequences which are attached to the surface separately by loops which extend into the matrix. Priel *et al.*[24] pointed out that the adsorption layer has a thickness comparable to the dimensions of a random coil for the organic adsorbate. Taking such an adsorption factor into consideration, the effective space available for particle movement and rotation should be reduced, and probably in a significant extent for 60% solid content where the overall surface area available for organic adsorption is larger but the organic binder is less than those for 55% case.

However, it may be too optimistic in interpretation of the particle mobility to considering only the effect of adsorbed layer (since the layer thickness according to the analysis by Evans *et al.*[25] may be reasonably estimated to be in the range of the order of 10–15 nm which is substantially smaller than the interface separation determined above). In realistic system, the particles are not well-dispersed (will be discussed in detail latter) and agglomerates are practically present, particularly when the powders used are relatively small in size (having a greater tendency to form agglomerates)[26] as employed currently. Some large voids due to powder inhomogeneity are inevitably formed and these voids are initially filled with the binder. Such that the binder distributed in between particles decreased and the interface separation should certainly be reduced in a significant extent. The particle mobility is thus suppressed, and accordingly increase in solid loading enhances the difficulty of particle mobility as that observed in the case of 60% loading. A further examination on green microstructure will be conducted, which provides a better understanding of particle packing and powder dispersion. The factors affecting particle mobility as well as the development of PSD will then be proposed in forthcoming analysis.

Influence of solid content

The influence of solid content on the green microstructure evolution of the moulded articles is investigated using a constant heating rate of 5°C h^{-1}, which is the slowest rate for thermolysis presently. Figure 4 shows the resulting PSD, together with the PSD of a powder compact made from slip casting technique for comparison purpose. The PSD shifts toward smaller pore diameter as the solid content is increased from 45 to 60%. The PSD for the cast compact is located between that of 55 and 60%, suggesting that the moulded article exhibits an attractive green microstructure which is comparable to or even better than that of the cast compact. However, the optimization of the green microstructure of the cast compact may not be achieved currently and thus the present result may only provide as a rough and relative comparison.

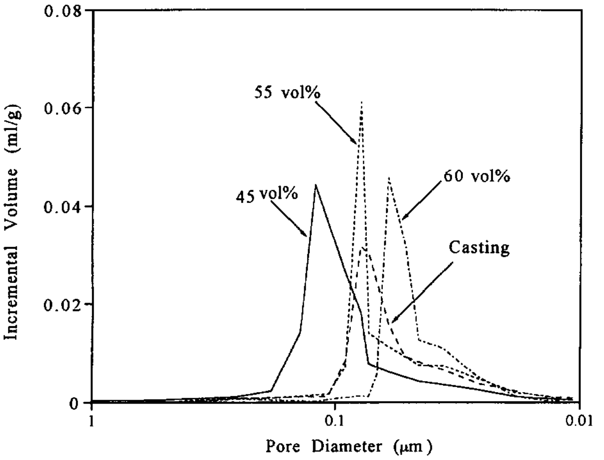

Fig. 4. Effect of solid content (45–60%) on the pore-size distribution of green compacts after removing the organic binder at a rate of 5°C h^{-1}.

Since the slowest heating rate tends to allow the structure to build up over a sufficient time period, the particles are thus supposed to be reasonably densely packing during thermolysis. The particle spacing is expected to reduce when the liquid binder is extracted by capillary action irrespective of the initial distance of the spacing, e.g. a large spacing is expected for suspension with low solid content, and in many instances, shrinkage occurs, leading to an increase in effective solid content.[27] However, the present results can hardly agree with such argument. One of the main reasons is due to the fact that the moulded article expands mostly rather than shrinks during thermolysis (as shown representatively in Fig. 5 for 50 and 60% mouldings), leading to a decrease in effective solid loading. A slight shrinkage is observed for 50% loading at initial temperature range, suggesting to be a result of particle rearrangement because a larger space is expected to be available for some, if not all, of the particles to move freely at 50% loading than that at 60%. A direct microstructure examination by SEM reveals that a porous green microstructure results (Fig. 6(b)) after completely removing the binder from moulded article (Fig. 6(a)) for 50% moulding. Powder agglomerates appear to be visually observed and some of which show bridging effect. The interparticle voids are comparable to the particle size, some of them are relatively large in size, primarily in the order of approximately 1 μm. Otherwise, a somewhat dense particle packing is observed for 60% moulding (Fig. 7). These findings may provide clearer picture to account for the experimental results by recognizing that insufficient dispersion of the fine powder is responsible for the agglomeration of the resulting green microstructure.

In fact, returning to the procedure of powder–binder slurry preparation, a fixed powder fraction relative to the solvent medium could cause a considerable increase in slurry viscosity for the slurry containing a higher fraction of organic binder (i.e. for the case of lower solid fraction) and a measurement of slurry viscosity (Brookfield, Model VII) with a resulting viscosity of 1560 centipoise (cps) and 3190 cps for solid content of 60% (or 40% binder) and 50% (or 50% binder) at a shear rate of 10 s^{-1}, respectively, confirmed this. The particle packing configuration observed under investigation is also consistent with the principle of colloidal filtration, where the green microstructure or PSD would frequently be coarsened by the presence of agglomerates.[16,22]

Based on above discussion, it may reasonably to assume that the particulate network should readily be developed on the mixing step by the inter-

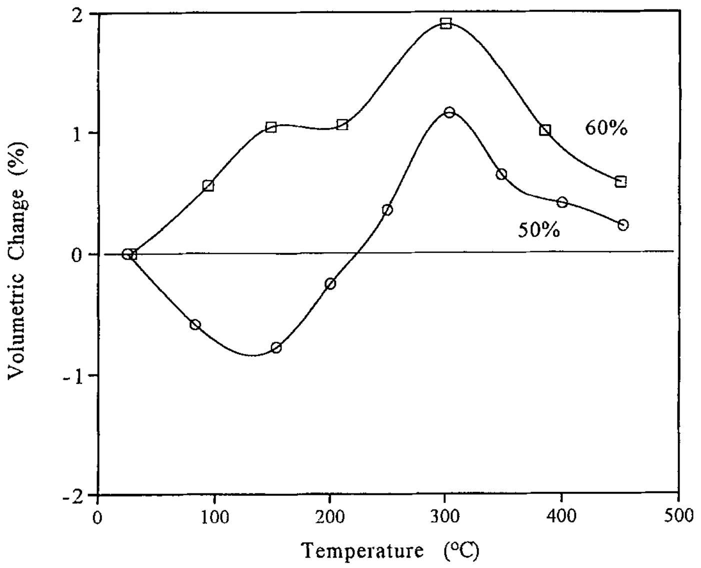

Fig. 5. Volumetric change of the moulded compacts with 50% and 60% solids loading subjected to different levels of thermal treatment.

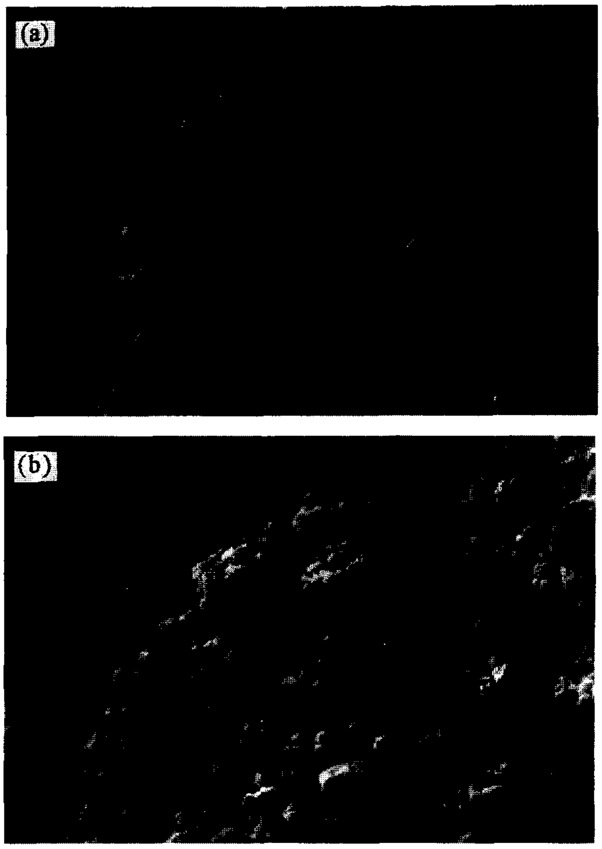

Fig. 6. Microstructure of the moulded compact made from 50% solid suspension: (a) before and (b) after thermolysis.

Fig. 7. Microstructure of the moulded compact made from 60% solid suspension after thermolysis.

connection of particles and agglomerates. The particle interconnectivity would be minimized or eliminated once the particles are perfectly dispersed in the binder matrix. Any imperfection of dispersion could cause particle interconnection. For the given particulate network, most parts of the binder would likely to fill into the interparticle and inter-agglomerate voids, only a minor part between the interfaces of the particles and/or the agglomerates. This means that the binder is distributed inhomogeneously in micrometer scale. The removal of the binder, although in large part, within these large voids has little or no effect on particle movement, hence on article shrinkage. The small part of interfacial binder contribute a minor effect on particle mobility, and such effect is negligible as the solid content is relatively high (such that the available binder for particle slide over each other is largely reduced). The original particulate network may somehow retain as a rigid network until the binder is largely or completely removed. This phenomenon would become more pronounced for suspension of higher solid content. This provides a more reasonable explanation to describe the variation in PSD previously discussed. The interparticle spacing and interface distance should therefore be much smaller than that deduced according to eqn (1). Under which condition, particle mobility is restricted and has little contribution to overall shrinkage of the moulded article as evidenced previously.

Since the PSD is strongly affected by the starting solid content and acts as a direct indication of particle packing, an attempt to correlate the starting solid content with the resulting particle packing configuration is made. This relationship appears to be linear (with a correlation coefficient of 0.965) as indicated by a plot of the most frequent pore size vs solid content shown in Fig. 8. Deviation from the linearity tends to increase at lower solid content suggesting a result of powder agglomeration.

Influence of binder formulation

Different wax to polymer weight ratios were used for investigation of green microstructure evolution for 60% mouldings. The resulting PSD is illustrated in Fig. 9 where the binder is removed under a heating rate of 5°C h^{-1}. The PSD shifts to smaller pore diameter as the wax content is reduced. According to preceding discussion, this shift in PSD to a sharper and smaller-sized characteristic should be inferred from improved powder dispersion. A viscosity measurement as conducted in the preceding section verified this, which shows an increased viscosity from 680 cps to 1560 cps under a constant shear rate of 10 s^{-1} when the weight ratio of wax to polymer varies from 5:5 to 7:3. (Capillary rheometry, being a powerful tool in measuring the degree of mixing,[28] can hardly provide an equal basis of comparison because of the inherent difference in binder formulation.) This result indicates that the powder is more likely to efficiently disperse in the slurry containing a 5:5 formulation in comparison with that for other formulations and accordingly improves particle packing efficiency towards a dense packing feature. The powders are then considered to be well-dispersed and distribute homogeneously within the moulded compact. The shortest distance between particle–binder interfaces can thus be reasonably approximated using eqn (1) as determined previously to be of the order of magnitude of 100 nm for 60% moulding. This separation may allow particle mobility to a certain extent, promoting the tendency to achieve dense particle packing. Figure 10 shows the volume change of the moulding with varying temperatures for various binder compositions and a greater tendency toward original network dimension occurring for 5:5 formulation at slightly higher temperatures substantiates this hypothesis. In general, the variation in volume change upon thermolysis is less significant for 60% moulding in comparison with that for lower solids loading. It may thus be concluded that the degree of particle mobility under high solids loading is limited and the most plausible way to reach high-efficient packing is to obtain a well-dispersed powder–binder slurry under current technique. The principle deduced from preceding analysis is also

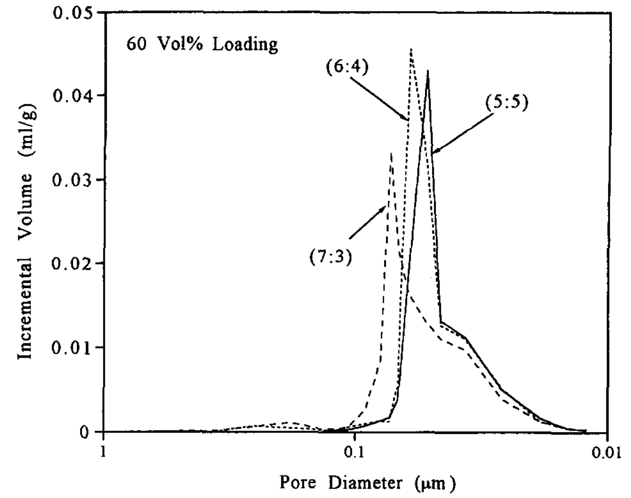

Fig. 9. Effect of binder formulation on the pore-size distribution of the green powder compacts made from 60% solid suspension.

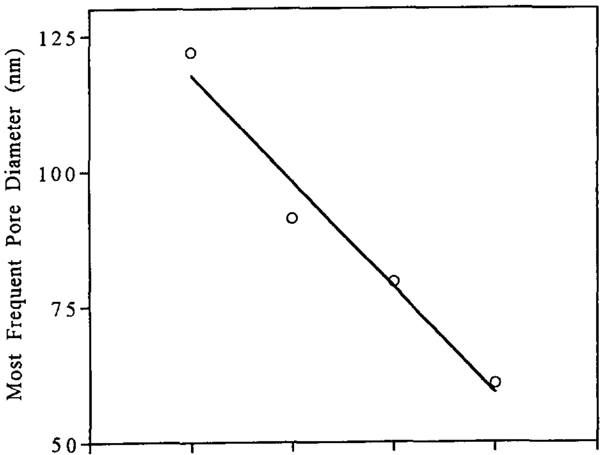

Fig. 8. Linear correlation between the solids content and the most frequent pore diameter.

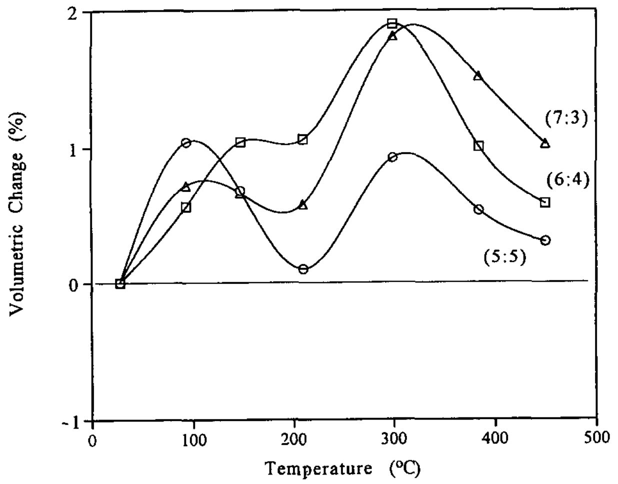

Fig. 10. Volumetric change of the moulded compacts containing various ratios of wax to polymer subjected to different levels of thermal treatment.

consistent with that recently proposed on the subject of mixing by German.[29]

Green density vs PSD

Plotting the green density of all mouldings (in terms of the per cent of theoretical density of the powder, 6.078 g cm^{-3}) vs the most frequent pore diameter results in a linear relationship as illustrated in Fig. 11. This relationship appears to be independent of the variables stressed in this investigation and is in good agreement with the results obtained from various researchers using various consolidation techniques such as Roosen and Bowen,[22] consolidating alumina powder with casting and die-pressed methods, and Frey and Halloran,[30] with die-pressed technique. The maximum green density of the injection-moulded compact is about 57.2% of theoretical density, corresponding to the most frequent pore diameter of near 50 nm. In comparison, this green density is smaller by ~6–7 vol% than that obtained by Roosen and Bowen, who consolidated the classified powders (0.3–0.5 μm in particle size) using colloidal pressing and centrifugal casting techniques, at a given most-frequent pore diameter of ~50 nm. This finding suggests that more efforts should be made to further improve particle dispersion under investigation to increase the homogeneity of green microstructure.

Sintering behaviour

The importance of PSD on sintering behaviour of ceramic powder compact has long been an interesting subject for many researchers.[15,22,31–33] The densification process of a green compact at high-temperature sintering is essentially a process of porosity elimination. Pore structure and its homogeneity in distribution within a powder compact strongly affect sintering behaviour.

It is generally recognized that the sharper and smaller PSD of a given powder compact, the easier to densify to high density. Therefore, it is reasonable to assume that compacts with smaller pores and higher green density are easy to densify at lower temperature. A plot of the most frequent pore diameter vs the temperature at which the compacts start to shrink, from dilatometric shrinkage data, is made (Fig. 12). The overall correlation of the data involving the cast sample is relatively poor, i.e. 0.542. One most plausible explanation could be induced from their distinct difference in microstructure inhomogeneity, e.g. the presence of agglomerates. Although a quantitative estimate of how agglomerates affect diffusion on sintering is not the focus of present investigation, it is ascertained that such microstructural inhomogeneity causes a decrease in driving force for densification[34] and a higher temperature is required to initiate shrinkage. In fact, Fig. 12 shows that increase in the most frequent pore diameter (as for suspensions with lower solids content) causes an increase in shrinkage onset temperature. A homogeneous green microstructure such as that at 60% loading with a 5:5 binder formulation, a minimum shrinkage onset temperature of 920°C is thus expected.

Similar concept is used to correlate the temperature at maximum shrinkage (T_{max}) with the most frequent pore diameter, as illustrated in Fig. 13. The overall correlation is rather poor, i.e. 0.538, however, if considered separately as depicted by the solid lines in Fig. 13, the correlation coefficient is relatively good for solid content above 50% including the slip-cast compact, i.e. 0.976 and also for those below 50%, i.e. 0.988. The temperature to

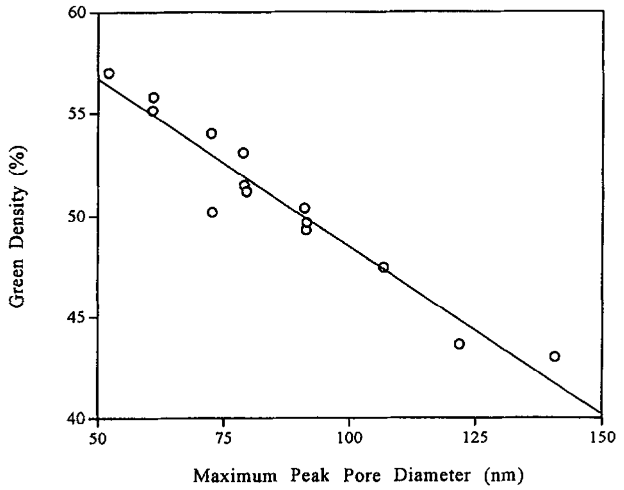

Fig. 11. A linear correlation results in between the most frequent pore diameter and green compact density.

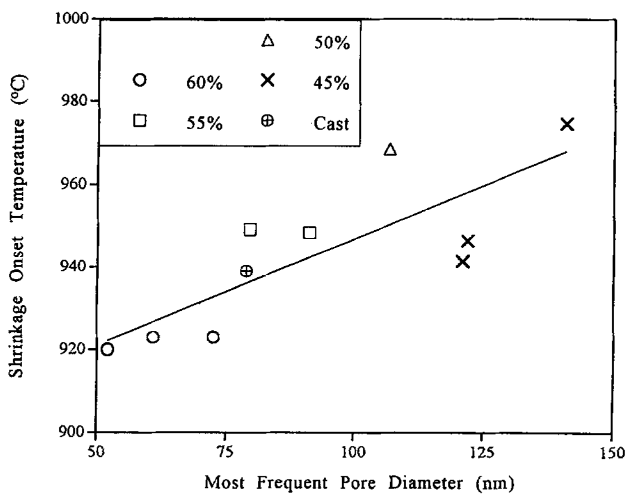

Fig. 12. Correlation between the most frequent pore diameter and shrinkage onset temperature for powder compacts made from varying solid contents and consolidation methods.

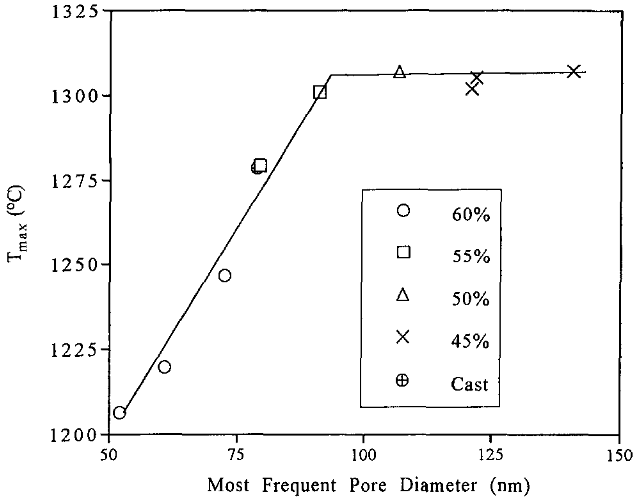

Fig. 13. The change of the maximum temperature at maximum shrinkage with respect to the most frequent pore diameter.

reach the maximum shrinkage increases linearly with increased maximum pore diameter to a value of approximately 90 nm. Above which value, the T_{max} remains roughly constant at about 1305°C and which is assumed to be the highest temperature attained in current case. We do not understand if the most frequent pore diameter at about 90 nm represents any physical significance to the sintering behaviour at present. Since the 90-nm pore diameter appears only when the solid content is below 55% at which the powders are essentially poorly dispersed, the corresponding green microstructure consists of large pores and pore clusters (for example, see Fig. 6(b)) and it may represent a status of microstructure inhomogeneity.

Since the densification behaviour is essentially a process for pore elimination and the pore elimination depends strongly on pore size and/or pore coordination number,[33] then, it might be assumed that some critical value of the maximum pore diameter may be present (representing a specific particle packing configuration). The powder compacts with the most frequent pore greater than the critical size, for instance, about 90 nm, a temperature of as high as 1305°C under examination is required to reach the maximum shrinkage.

The 60% green compact having a green density of 57.2% TD (theoretical density) can be densified to 95% at 1400°C and to 99.3% at 1500°C, whereas the 50% green compacts reach only 84% and 97.8% at 1400 and 1500°C, respectively. The coarser green microstructure of 50% compact in comparison with that of 60% is mainly responsible for the increasing difficulty of densification. The sintered microstructure of the 50% compact fired at 1500°C reveals the presence of large pores having a pore size ranging from approximately 1–2.7 µm (Fig. 14). The grain size is relatively small, 0.5–0.6 µm, and appears to be uniform, indicating dominance of the normal grain growth mechanism.

Fig. 14. The sintered microstructure of the compacts made from 50%-solid suspension after densification at 1500°C, showing numerous large pores.

In general, analogous to the relationship between the maximum pore diameter and shrinkage onset temperature, a decreasing maximum pore diameter of the PSD facilitates pore elimination at lower temperatures. As a result, a more rapid densification with a fine sintered microstructure can be achieved for the green powder compacts with smaller and sharper PSD as that observed in the injection-moulded articles containing 60% solid loading.

SUMMARY

The green microstructure evolution and sintering behaviour of injection-moulded fine zirconia powder compacts were investigated. The green microstructure of the moulded article depends strongly on the solid loading and initial binder formulation. The restriction of particle mobility, i.e. particle movement and rotation, within the moulded compacts during thermolysis due to the presence of agglomerates causes poor particle packing efficiency, which coarsens and broadens the pore size distribution. However, particle packing tends to improve at higher solid loading, e.g. above 50%, even though particle mobility is highly restricted, resulting a smaller and sharper pore size distribution. The preparation of powder–binder slurry on the mixing step under investigation plays a crucial role in determining the status of powder dispersion and for slurry with higher solids loading (relative to binder content) allows an efficient dispersion to be achieved. Green compacts derived from these high-solid suspensions, having a more homogeneous green microstructure, as expected, are more susceptible to densify at lower temperatures than do the compacts made from lower-solid suspensions. Shrinkage behaviour of the injection-moulded articles depends strongly on the pore microarchitecture and the most frequent pore diameter. The shrinkage of the articles is likely to be predictable at loadings greater than 50 vol% based on the understanding of the pore structure and this allows the optimization of sintering profile to achieve sintered compacts with a dense and fine microstructure suitable for high-performance engineered applications.

ACKNOWLEDGEMENT

The authors are gratefully indebted to the Ministry of Economic Affairs, Taiwan, for funding and supporting this research under contract No. 853KG2230.

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