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Interdependence between green compact property and powder agglomeration and their relation to the sintering behaviour of zirconia powder

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Abstract

Interdependence of green density and corresponding powder agglomeration and their influence on the sintering behaviour of commercial fine zirconia powders under a constant rate of heating (non-isothermal sintering) were investigated. Agglomeration of the powder was controlled by different time periods of ball-milled processing and was defined as the size ratio of sedimentationally-measured particle size to the size of primary particles which were microscopically-determined (hereinafter termed agglomeration parameter or AP). Green compact density shows to be approximately linearly related to powder agglomeration under identical consolidation technique, which is decreased with increasing degree of agglomeration. Both the green density and powder agglomeration affect sintering behaviour over entire sintering schedule. For a given AP the shrinkage rate reduces with increasing green compact density and vice versa, which is consistent with the literatured reports. The experimental results also showed that compacts with identical starting density showed a lower shrinkage rate when the compacts contained less agglomeration (i.e. low AP) than does for high-AP compacts. However, a higher end-point density can be obtained for low-AP compacts, suggesting a better packing structure of the powders. The use of agglomeration parameter defined currently, which is taken as an indication of the level of powder agglomeration in commercial fine ceramic powders, is likely to provide some useful understanding in characterising the sintering behaviour and possibly potential evolution of sintered microstructure on sintering.

1. Introduction

Dense, uniform particle packing geometry in a green ceramic powder compact is of prime criterion in achieving high end-point density body with desired microstructure and this is always the goal to be achieved by the relevant researchers and manufacturers. It is well-recognised that initial homogeneity of green microstructure strongly affects the final homogeneity and integrity of the sintered microstructure. Many attempts have been used to obtain and to control green compact with physically/chemically homogeneous microstructure through a number of processing techniques and have received satisfactory accomplishment in some of them.

In powder processing, one important consideration is to eliminate agglomerates which are formed as clusters of primary particles bonded strongly, i.e. "hard" agglomerates, (e.g. due to sintering) or weakly, i.e. "soft" agglomerates, (e.g. short-range surface forces) with interconnective pore network, prior to shaping. The presence of agglomerates in powders frequently reduce particle packing efficiency, suppress sintering activity, and finally deteriorate sintered properties due to the loss of microstructural homogeneity/integrity and crack-like voids formation [1–3]. Therefore, effect of agglomerate on powder processing has been the subject of considerable interest [4–9]. In the early 1980s, Rhodes [6] observed that agglomerates, having a mean size ranging from 1.7 to 6.3 μm, retard almost entire stages of sintering and limit the potential achievement of fine powder towards dense and fine-grained microstructure. However, Rhodes's study is somewhat qualitative, particularly provides little understanding on whether the agglomerates undergo morphological change under relatively high compaction pressure (276–483 MPa). Similar effort was conducted by Sacks et al. [4] Although their work provides some understanding on

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the effect of agglomeration on sintering kinetics, further analysis of how "extent" of the agglomeration on sintering kinetics has not been reported. A later evaluation by Dynys et al. [5] presented a better understanding on the effect of agglomerate on sintering of alumina by controlled amount of agglomerate blended with agglomerate-free powder. They indicated a significant decrease in shrinkage rate by as much as a factor of 10 under the presence of agglomerate at early stage of sintering. Green compact density has long been recognized to affect sintering behaviour, an earlier observation for Al_2O_3 by Brush [10] indicated that sintering rate increases as green density is reduced for the "normal" sintering regime. This has also been observed by Vasilos et al. [11] in the sintering of ZrO_2. Therefore, on this basis, one may conclude that sintering behaviour is essentially microstructure-dependent. This investigation is attempting to realise the interrelationship between green density and agglomerate, and how sintering behaviour interplays between these two factors on a commercial fine zirconia powder.

Agglomerates are commonly observed in commercial fine ceramic powders. The "agglomeration" in the starting powders may frequently be determined with difficulty in a quantitative manner. (This may be one of the primarily unsolved problems that appeared in many related studies; instead, controlled agglomerates, i.e. for both content and size, were intentionally added to further characterise the resulting behaviour/property of interest.) Moreover, it becomes even more ambiguous and uncertain, for either commercial or intentionally-prepared powders when these agglomerate-contained powders were consolidated by high-pressure compaction (a pressure of few hundreds of MPa is frequently used to consolidate the powders), e.g. die pressing, cold-isostatically pressing, and pressure filtration, primarily because the agglomerates may undergo deformation and collapse into smaller fragments and primary particles under high compressive forces. This causes a less reliable prediction or assessment on agglomerate-related sintering behaviour and sintered property. Unfortunately, high-pressure consolidation techniques have been widely-used in many agglomerate-related studies such as those publications mentioned above. This is one reason for the current study to adopt a colloidal casting without or with a slightly external force (when the cast is still wet) to consolidate ceramic powders. This technique ensures to a large extent the retention of initial powder agglomeration and is believed to be practically and physically meaningful in the interpretation of experimental results. Since it is impossible to accurately determine the "degree of agglomeration" (particularly in terms of the quantity, size, and geometry) in commercial powders, one simple and probably physically meaningful method is to compare the relative size of the actual particle (or agglomerate) size of a given powder (usually determined by sedimentation method) and primary particle size (determined microscopically) as previously being used by Roosen et al. [12] This relative size is defined as agglomeration parameter (abbreviated as AP) and will be tentatively used as an indication for the "degree of agglomeration" for the ceramic powder in current investigation. Accordingly, the greater value of the AP, the more extensive agglomeration of the powder is.

The use of nonisothermal technique (i.e. sintering under constant rate of heating) for the study of sintering kinetics has been well-documented and has been confirmed to provide sufficiently accurate kinetic information in comparison to the conventionally time-consuming isothermal method [13,14]. In this technique, the specimen is fired under a constant heating rate to the preset temperature. The shrinkage or shrinkage rate can therefore be accurately determined using a computer-equipped dilalometrical instrument as a function of temperature. One important consideration in kinetics study with nonisothermal technique is the influence of surface diffusion particularly at initial-stage sintering [13]. However, since surface diffusion is usually expected to occur at temperature at or below initial shrinkage temperature, it is thus possible to avoid such interference by carefully selecting and analyzing the obtained sintering data as had been treated previously [13,15].

Briefly, the basic assumption for nonisothermal technique is identical to that for isothermal method at any given shrinkage and corresponding temperature, isothermal sintering theory is then applicable to the former technique. Thus for nonisothermal sintering, the densification behaviour can be generally expressed under a constant heating rate by,

$$\mathrm{d}(\Delta L/L_o)/\mathrm{d}t = K/(\Delta L/L_o)^n \tag{1}$$

where $K = K_o \exp(-Q/RT)$ and $\Delta L/L_o$ stands for specimen shrinkage at any temperature. Young and Cutter [13] estimated the sintering activation energy of oxides with success through an Arrhenious-type plot, i.e. $T\mathrm{d}(\Delta L/L_o)/\mathrm{d}T$ vs $1/T$, used a derivation by Johnson [16] for intermediate-stage sintering. In principle, the plot of $T\mathrm{d}(\Delta L/L_o)/\mathrm{d}T$ vs $1/T$ yields a straight line with a slope of $-nQ/R$, where n is the characteristic of sintering mechanism, e.g. $n = 1/2$ for volume diffusion and $n = 1/3$ for grain-boundary diffusion, and Q is the activation energy for corresponding diffusion mechanism. The term nQ is representative of the *effective activation energy* of sintering.

2. Experimental procedures

Ceramic suspensions containing 75 wt% zirconia powder (Daiichi-HSY3.0, 3 mole% yttria-stabilized powder) in distilled water, 1 wt% (based on the powders) plastisizer and 0.5 wt% dispersing agent. The suspension was ball-milled in a polyethylene jar with a fixed ratio of zirconia milled ball weight to powder weight. In order to obtain the powders of different levels of agglomeration, the suspension was milled over a time period from 0 to 48 h. Owing to the intimate interdependence between agglomeration and packing density of the slip-cast compacts, i.e. a higher-agglomerated powder usually results in lower-density compacts, a pressure (up to 50 MPa) was used to further consolidate the casts when they were still wet to form powder compacts with higher densities with the same level of agglomeration. A follow-up analysis of particle size in these pressure-cast compacts ensures the retention of starting agglomeration under such pressure range. Green density as well as the pore size distribution of the compacts were determined using mercury porosimetry (Autopore, II-9220). Three to four specimens were used to determine the average green density of the compacts, which has an average error of measurement less than 0.45%. A small portion of the suspension was used to measure the resulting particle size distribution (Horiba, LA-910) and the rest of which was cast to form powder compacts. Specimens with $5\times5\times5\,\mathrm{mm}^3$ were cut from the cast and subjected to a dilatometer (Netzsch, Model 415) for shrinkage measurement at a constant heating rate of $300°\mathrm{C\,h}^{-1}$ up to 1500°C. The primary particle size (d_{primary}) was determined using SEM (Cambridge Instruments, Model 360) by averaging over 500 particles from a dilute, dispersed suspension. Powder morphology and green microstructure of the powder compacts were examined microscopically.

3. Results and discussion

3.1. Characterization of powder and powder compacts

Fig. 1 shows the morphology of the starting powders. The powders show somewhat irregular geometry and some clusters of particles can clearly be seen, indicating the presence of agglomeration. The particle size distribution of the powders after varying periods of ball milling is representatively shown in Fig. 2, which is characteristic of uni-model distribution. A shift in the distribution towards a smaller-sized region is evident as ball-milled time is increased; however, the slow reduction in the mean particle size (d_{50}) of the powders with milling time (Table 1) suggests a strong interparticle bonding in the agglomerates, i.e. "hard" agglomerates. Table 1 listed the mean (d_{50}) particle/agglomerate size for varying time periods of milling and corresponding agglomeration parameter in terms of the measured d_{primary}. The greater value of the parameter indicates a greater level of agglomeration.

The influence of agglomerates on powder packing efficiency is significant and has been an important subject of considerable interest [1,9,17]. The packing efficiency in a powder compact can be explicitly and directly demonstrated in terms of pore size distribution of the green compacts. Fig. 3 showed the selected pore distributions

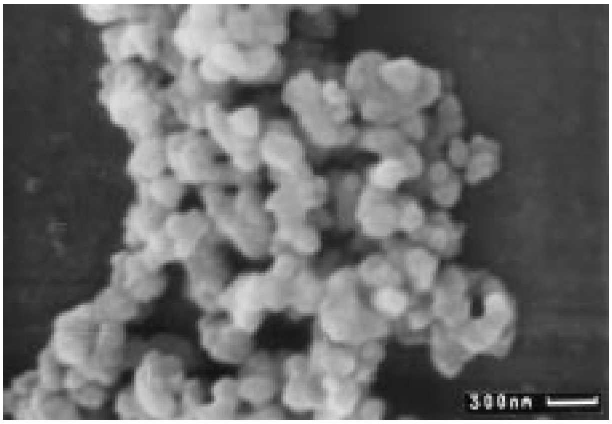

Fig. 1. Morphology of the zirconia powder used in this investigation.

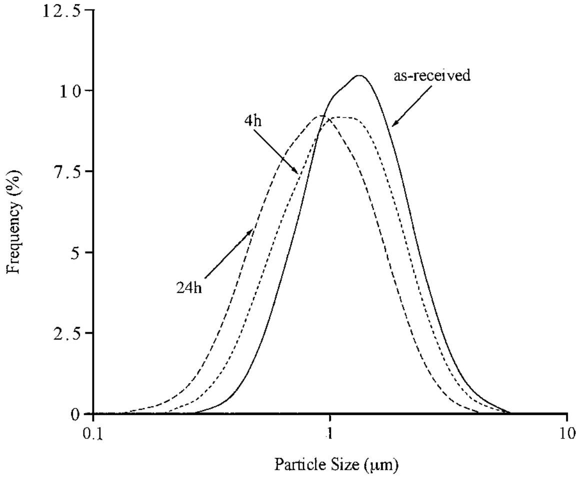

Fig. 2. Particle (or agglomerate) size distribution of the powders after varying time periods of ball milling.

Table 1
The measured mean particle/agglomerate size (d_{50}) and corresponding agglomeration parameter (AP) of the zirconia powder after different time periods of ball milling in this investigation

Milling time (h)	d_{50} (μm)	AP ($=d_{50}/d_{\mathrm{primary}}$[a])
As-received	1.208	5.49
0.5	1.091	4.96
2	1.071	4.87
4	1.028	4.67
8	0.995	4.52
10	0.992	4.51
16	0.933	4.24
24	0.823	3.72
48	0.681	3.1

[a] $d_{\mathrm{primary}}=0.22\,\mu\mathrm{m}$.

of the powder compacts after varying milling times. The pore distributions are uni-model and show somewhat sharper/narrower characteristic, particularly pronounced when the milling time is increased. This clearly indicates an improved particle packing efficiency can be reached by extensive milling. The green densities of the compacts increased from 41.6 to 54.2% of theoretical density with increased milling time from 0.5 to 48 h. An extensive agglomeration (e.g. for short milling-time powder) causes green microstructure inhomogeneity by developing large interagglomerate pores (Fig. 4).

It has been well-recognised that agglomerates frequently reduce green compact density of a given powder by inhibiting particle packing. How such inhibition is related to the degree of powder agglomeration in a given powder would be critically important in powder processing control. An attempt to relate the powder agglomeration with respect to the green compact density is made and the resulting relation is given in Fig. 5. The compacts used to construct Fig. 5 were made under identical green-shape processing, i.e. casting without pressing, those with pressuring were excluded. The green density exhibits a roughly linear relation against the agglomeration parameter over the range of approximately 3–5.5. This is consistent with that observed by compaction of agglomerate-containing alumina powder reported by Dynys et al. [5]. Although the AP range is narrow (it represents essentially a status of current limitation on powder processing and mostly ascribed to the given nature of the powder used), as a first approximation, the green compact density follows a linear dependence on the as-defined agglomeration parameter of the powders. In other words, the powder in the suspension is likely to deposit in a linear fashion (at least within the AP range of current study) related to the starting level of agglomeration in the powders. This finding implies that a potential correlation can be deduced between the defined AP value and particle packing efficiency for the commercial powders and similar concept may be applicable to other ceramic powders. By extrapolating to AP = 1, i.e. finely-divided particles, the obtained density is about 71.3%, which is relatively closed to the theoretical value (~74%) for close-packing spheres of identical diameter obtained by McGeary [18]. A small difference between these values may result from the fact that the powders currently-used are not exactly spherical in shape and identical in size. Applying pressure causes an increase in green density of the compacts by a density increment of 4.5–8% in comparison to those without pressing (will be seen in a later discussion). However, such an improvement in packing density is observable only for high-agglomerated compacts, i.e. for AP≥4.51, as illustrated in terms of the variation in pore/pore volume distribution in Fig. 6 for AP = 4.96 compacts, and the density has little or no improvement for low-agglomerated compacts

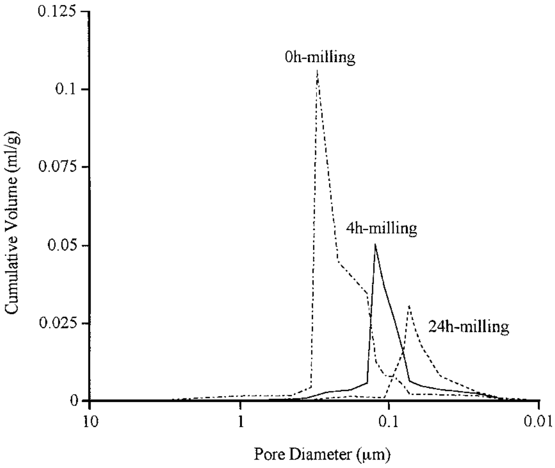

Fig. 3. Pore size distribution of the powder compacts consolidated with the powders under varying ball-milled times.

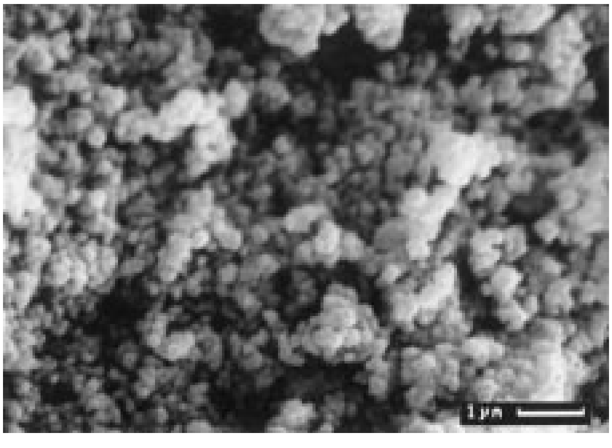

Fig. 4. Some larger voids formed due to agglomerates.

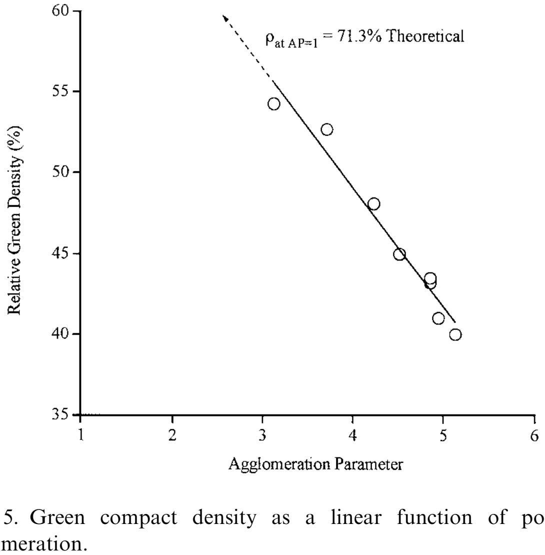

Fig. 5. Green compact density as a linear function of powder agglomeration.

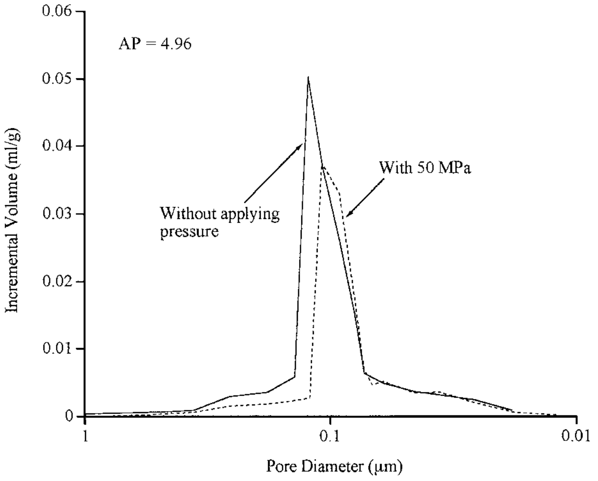

Fig. 6. The variation of pore size distribution of the compacts with AP = 4.96 after pressing at 50 MPa, where the larger voids were removed.

(higher starting density). As illustrated in Fig. 6, a higher compaction pressure tends to eliminate larger voids which were formed due to agglomerates, and shifts the pore distribution toward a small-sized region, which substantiates a further removal of larger voids. Similar observation was also reported by Zheng et al. [19] on the dry compaction of alumina powder. The pore size at maximum frequency is reduced by about 12% from 121.8 to 107 nm when 50 MPa pressure was applied. A calculation based on this shift indicated a reduction of approximately 9 vol% of voids greater than the pore at maximum frequency is eliminated. The fractional change in pore volume for those pore size smaller than 0.155 *r* (where *r* represents the radius of primary particle and the value of 0.155 *r* indicates the largest radius of a void developed by closed packing of three identical spheres) which is assumed to be constructed by the agglomerated particles (i.e. intraagglomerate pores) is relatively unchanged. This observation further supports the retention of original agglomerate structure as previously discussed. The plastically "compressible" characteristic for high-AP compacts indicates that the powders consolidate in a "loose" random packing structure within which the voids constructed by either interagglomerate or agglomerate-particle contact can be further removed by deformation or fracturing the "weak" structure (not agglomerates themselves as confirmed by almost identical particle distribution and invariant intraagglomerated pore volume before and after pressing) or alternatively forcing the agglomerates/particles to slide over one another to a certain extent upon pressing. On the contrary, the seemingly plastically "incompressible" low-AP compacts suggest a "strong" interagglomerate or agglomerate-particle contact structure; in other words, the agglomerates and particles were lock somewhat firmly (because the pressures used to further consolidate the cast are not relatively high and a higher pressure may again cause the cast to become "compressible") in position during initial filtration.

As the primary concern of sintering, a complete elimination of pores within a compact is one of important requirements in modern technical ceramics. A recent investigation by Zheng et al. [20] indicated that a ratio of pore size to particle size as one relatively important parameter in determining whether the pores can be completely removed after sintering, leaving a full-dense (also for small-grained) ceramic body. The smaller the ratio, the easier the compact's pore can be eliminated. Therefore, the pore size/particle size ratio is essentially crucial to the green compact (here we do not intend to determine what the critical ratio is in obtaining full-dense ZrO_2 body). Attempt is thus made to see how the ratio can be related to green density for compacts with a variety of "agglomeration". Fig. 7 showed the resulting trend. The pore size used here is the average pore diameter calculated by intrusion volume-pore diameter data from mercury porosimetry. In general, compacts with higher green density exhibits lower pore size/particle size ratio, suggesting the pores are more likely to be eliminated than those in lower-density compacts. Without pressing (circle symbols), compacts with higher AP value have lower density and higher pore size/particle size ratio. A further compaction improves packing density and reduces the ratio even when the AP value is high, e.g. for AP = 5.13 compacts. Under pressing, larger voids removed and the agglomerates appeared to have no significant effect on resulting packing structure. This limited inhibition of agglomerates on particle packing under pressing might be due to somewhat small-sized agglomerates in the powders, generally distributed over the range of 0.5–3 μm.

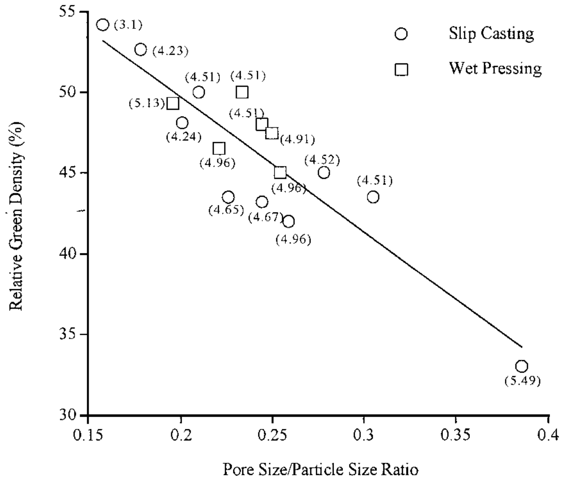

Fig. 7. Green density of the compacts as a function of pore size/particle size ratio.

3.2. Shrinkage behaviour

Fig. 8 showed the shrinkage rate of the powder compacts of varying milling times (expressed in terms of green densities ρ_g) with respect to the relative sintered density. Compacts with a lower starting density exhibit a higher shrinkage rate and this is consistent with those reported in the literature [10,21]. As commonly observed in sintering experiments, Lange [2] recently suggested that the maximum shrinkage rate corresponds to an inflection in relative density ($\rho_{\max}$) to be a transition from densification kinetics to coarsening (i.e. grain-growth) kinetics. Below $\rho_{\max}$, the sintering is dominated by densification kinetics and above which coarsening kinetics dominates over further sintering schedule. This suggestion implies that the sintering profile enables to reflect the potential microstructure evolution as well as the corresponding starting packing structure within a given powder compacts. The higher the sintered density achieved at corresponding maximum shrinkage rate appears to ensure the potential evolution of desired sintered microstructure, i.e. fine-grained, dense ceramic body. This further indicates the potential benefit for ceramics with desired microstructure for the powder compacts with lower AP and higher ρ_g. Although the shrinkage rate is higher for low-ρ_g compacts, a lower end-point density usually results under current sintering schedule. This observation on which the low-ρ_g compacts densifies faster than high-ρ_g compacts is in accordance with an earlier observation by Bruch [10] in the sintering of Al_2O_3 for the as-defined "normal" sintering regime and also consistent with that experimentally observed by Vasilos et al. [11] in ZrO_2. However, a close examination of the compacts used to characterise Fig. 8, one can find that two green compact parameters are essentially involved, i.e. green density and agglomeration, which may cause different effects on the sintering. Therefore, a separate understanding of each parameter on sintering behaviour, particularly for a commercial fine ceramic powder as model material, is essentially important as can be seen in a number of publications.

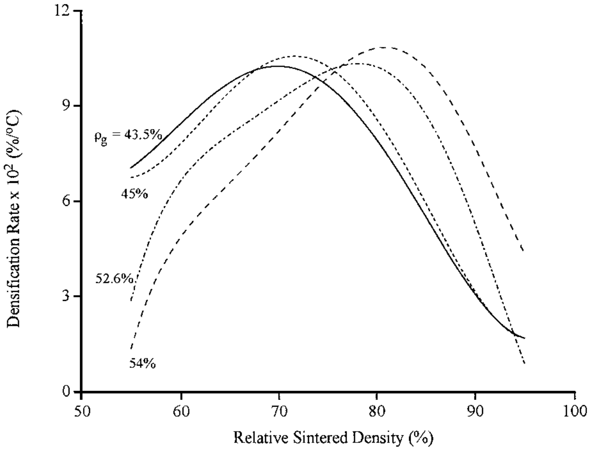

Fig. 8. Shrinkage rate-sintered density curves for compacts with different ball-milled times (differing in both green density and degree of powder agglomeration).

The influence of green density on sintering behaviour can be easily obtained by consolidating the given powder suspension (having a fixed value of agglomeration parameter) with varying pressures. Figs. 9(a) and (b) showed the density–shrinkage rate curves for the powder compacts of different green densities at a constant agglomeration parameter (AP) = 4.96 and 4.51, respectively. Clearly, compacts with lower starting density exhibit higher shrinkage rate at a given sintered density below approximately the region at which maximum shrinkage rate occurred. Furthermore, the sintered density at which maximum shrinkage rate ($\rho_{\max}$) occurred is increased with increasing starting density and with decreasing agglomeration (Fig. 10); however, no simple analytical correlation is likely to be deducible under investigation. If according to the suggestion of Lange

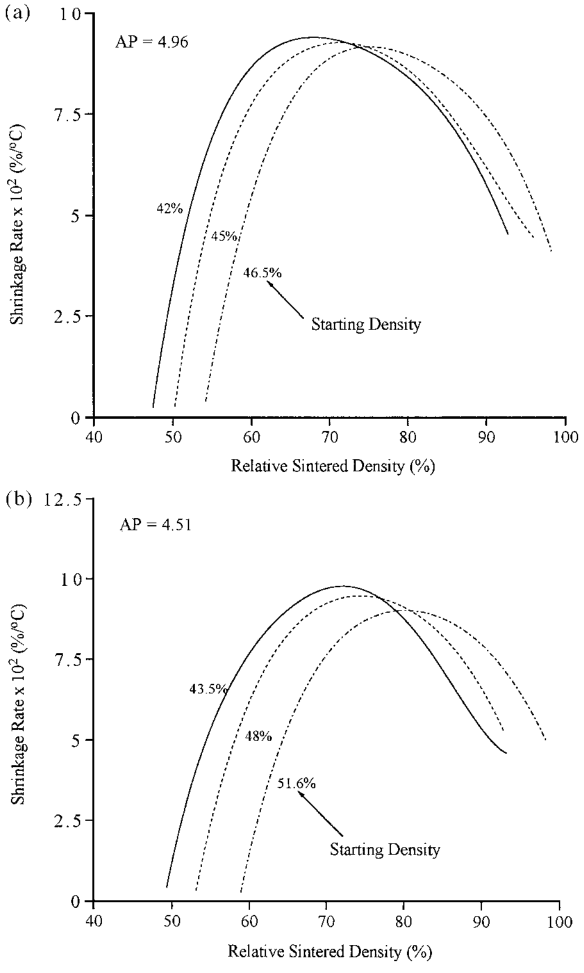

Fig. 9. Shrinkage rate-sintered density curves for the compacts of different green densities, each has a constant AP value of (a) 4.96 and (b) 4.51.

[2], the present observation indicates that a dominant densification kinetics should be operative for high-ρ_g and low-AP compacts up to sintered density of ~74% theoretical (in fact, a higher $\rho_{\max}$ is achievable for higher-ρ_g and lower-AP compacts as shown latter in Fig. 11). As generally realised that a desired sintered microstructure would usually be expected.

The influence of agglomeration on the sintering behaviour is shown in Figs. 11(a) and (b) for the compacts with $\rho_g = 45$ and 54%, respectively. Compacts with lower AP have generally a lower shrinkage rate, but have a higher value of $\rho_{\max}$. The highest $\rho_{\max}$ currently attainable is about 88% for the compacts with $\rho_g = 54\%$ and AP = 3.1. This observation clearly indicates the inhibition of densification due to the presence of agglomerates. An investigation by measuring the sintered density (via Archemede's principle) at various sintering temperatures for compacts ($\rho_g = 45\%$) of various AP values, as illustrated in Fig. 12, further justified that high-AP compacts are generally more difficult to densify than do for low-AP compacts. Similar result was also observed for $\rho_g = 54\%$ compacts. A differential densification between agglomerate and matrix particle causing a further re-opening of crack-like pores at agglomerate–particle interfaces may be explainable as one of the prime factors for such poor densification [3]. Such agglomerate-induced inhibition not only reduces the sinterability of the powder compacts but also promotes the onset of the transition of sintering mechanism from densification kinetics to coarsening kinetics at lower sintered density. As generally realised that under such circumstance, the voids within the sintered compacts may frequently be retained and larger grains developed, which would accordingly largely reduce a desired performance of the final products.

Plotting the $\rho_{\max}$ data with respect to the corresponding pore size/particle size ratio, Fig. 13 showed

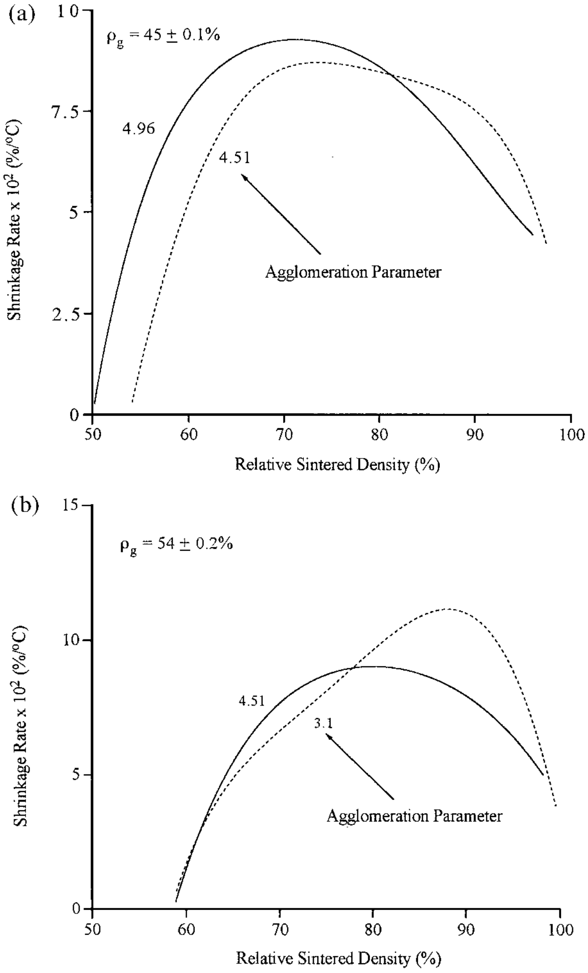

Fig. 11. Shrinkage rate-sintered density curves for the compacts of different AP values, each has a constant relative green density of (a) 45% and (b) 54%.

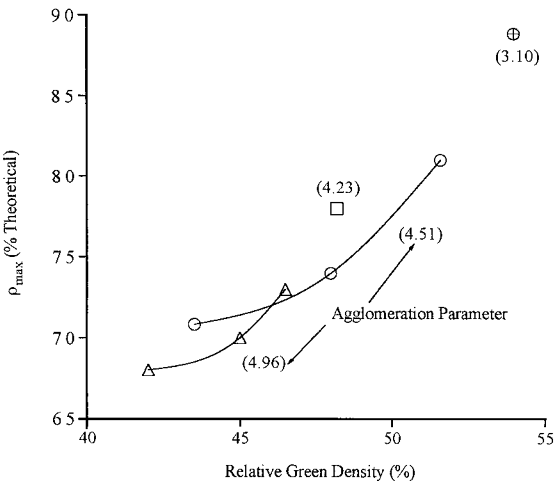

Fig. 10. The sintered density at maximum shrinkage rate, i.e. $\rho_{\max}$, changes with green density and AP of a given powder compact.

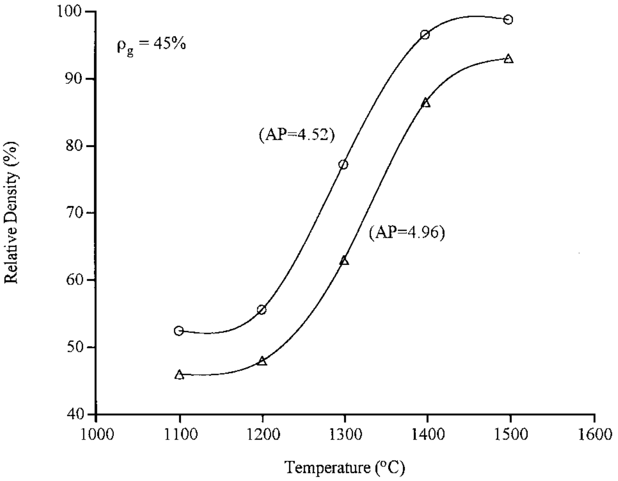

Fig. 12. Sintered density as a function of sintering temperature for compacts of identical green density but with varying degrees of agglomeration.

the resulting relation with each data point designated with a parenthesis of (AP/starting density). Generally, the smaller the ratio in a given compacts, the larger the $\rho_{\max}$ can be obtained. The high-ρ_g and low-AP ensure a small-pore, uniform green powder compact (i.e. narrow pore distribution) and which is able to reach a highest $\rho_{\max}$ at $T_{\max}$, suggesting a greater potential of developing dense, pore-free sintered ceramic body. However, it also revealed that the pore size/particle size ratio under a higher AP, the compacts with even a higher ρ_g exhibit a somewhat larger value of the ratio, suggesting a potential difficulty in completely eliminating the compact's voids [19]. The higher pore size/particle size ratio for the higher-AP compacts designated in Fig. 12, having lower sintered densities, seems to provide further supports.

Therefore, based on a combined knowledge from these literatured reports and current observations, one can conclude that improved starting density may not be of prime consideration ensuring desired sintered microstructure/property, instead, a complete (or relatively extensive) elimination of the agglomerates associated with a reasonably efficient particle packing structure (reducing pore size/particle size ratio) would ascertain a satisfactory green property and consequent sintered property. However, due to some difficulty in obtaining compacts of identical starting density over a wide variety of AP, the ranges for both green density and AP under investigation are restricted. Although current investigations provide only a limiting data basis, the influence of green density and agglomeration can be comparatively differentiated.

3.3. Activation energy

As mentioned previously, the nonisothermal (constant-heating-rate) technique provides a simple and reliable way to assess the sintering kinetics of powder compacts. Fig. 14 showed an Arrhenious-type plot, i.e. $Td(\Delta L/L_o)/dT$ vs $1/T$, for powder compacts with varying time periods of milling. Some low-temperature data scattered and the initial slopes of the lines were relatively high for both compacts (corresponding to a linear shrinkage below ~0.5%). This has readily been observed in a number of related studies and is believed to be a result of several interferences by, e.g., surface diffusion, thermal equilibrium, and/or instrumental limitation [13,15]. After which fractional shrinkage, the data points follow nearly a straight line up to a shrinkage of approximately 8.6% for both compacts (some up to 12%), indicating a single diffusion mechanism dominates. A change in slope in this Arrhenious-type plot, e.g. above 8.6% shrinkage, indicates the change in mass transfer mechanism.

On checking, the straight lines in Fig. 14 for compacts of varying milling times (representing different values of green density and AP) showed slightly different slopes, indicating different nQ values. Such difference might be caused by a number of factors such as measurement error and/or probably green microstructure inhomogeneity. However, despite the possible influence of above factors on sintering behaviour, the *effective activation energy* for all these compacts is averaged to a value of $30.02 \pm 2.78\,\text{Kcal}\,\text{mol}^{-1}$ (± represents the standard deviation of the measurements), corresponding to a sintering activation energy of $90 \pm 9\,\text{Kcal}\,\text{mol}^{-1}$ which is closely in agreement with the value obtained by Young et al. [13], $90\,\text{Kcal}\,\text{mole}^{-1}$, and Jorgensen [22], $92.5\,\text{Kcal}\,\text{mole}^{-1}$, in the sintering of yttria-stabilized zirconia powders under a grain-boundary diffusion mechanism ($n = 1/3$). This agreement together with reasonable scale of standard deviation implies that both green density and agglomerate may exert relatively small or negligible effect on the sintering law or acti-

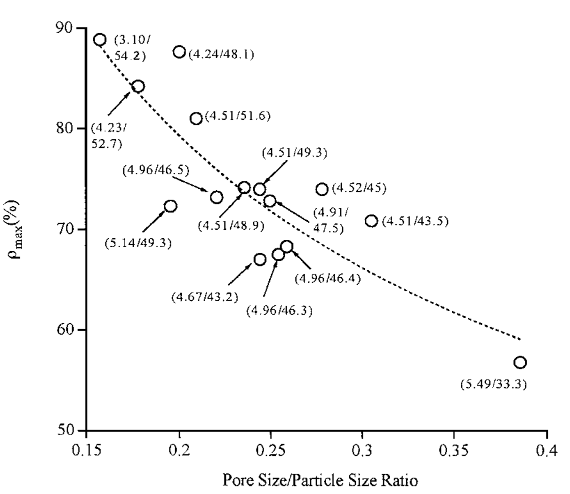

Fig. 13. Sintered density versus pore size/particle size ratio, indicating $\rho_{\max}$ increased with decreasing ratio.

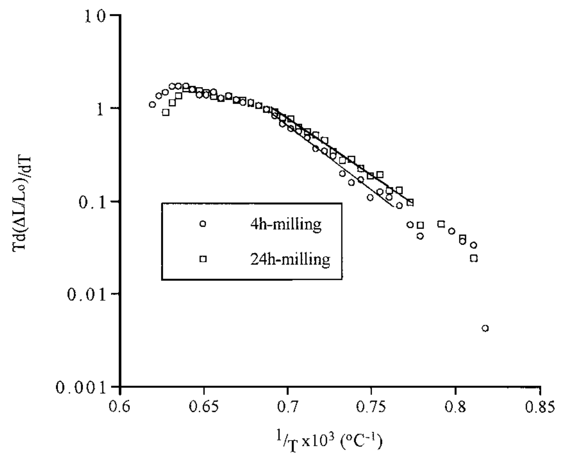

Fig. 14. A $Td(\Delta L/L_o)/dT - 1/T$ plot for the powder compacts consolidated by a 4-h and a 24-h milled powder.

vation energy for sintering of the zirconia powder; the former factor observed presently is in agreement with a previous report by Woolfrey [23] while the latter may be considered as a new understanding.

4. Conclusion

Influence of green density and powder agglomeration on the sintering behaviour of zirconia powder was investigated. Both factors are interdependent and a linear density–agglomeration relation is experimentally deduced over a small range of agglomeration. They have shown to affect in different extents the sintering behaviour over the entire sintering schedule. Low-density powder compacts (usually are high-agglomerated compacts) exhibited higher initial shrinkage rate in comparison to high-density compacts (low-agglomerated compacts), which is consistent with the observation by other researchers. Less agglomeration in the starting powder and associated with a smaller pore size/particle size ratio after consolidation ensure a better sinterability and potential evolution of desirable sintered microstructure of the ceramic. The variation in green density and agglomeration in the powder compacts showed a relatively small or negligible effect on activation energy or sintering law for sintering of the ceramic powders. The use of the defined agglomeration parameter to characterize powder agglomeration in commercial fine ceramic powders appeared to provide as a useful indication in characterizing the sintering behaviour and possible evolution of sintered microstructure by referring to the corresponding density-shrinkage rate curve upon sintering.

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