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Effects of powder processing on the characterization of magnesia derived from alkoxide precursors

Part II *Compaction and sintering behaviour*

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Compaction and sintering behaviour of three magnesia powders derived from three different processes were compared. Powder preparation and properties have been reported in Part I. It was found in this study that the starting powder morphologies, especially the state of hard agglomeration, strongly affect the uniformity and microstructural evolution during forming and densification. However, a uniform, high-strength, dense (98–99%) and translucent magnesia can be achieved by sintering the modified powder compacts at temperatures much lower than those required for conventional magnesia powders.

1. Introduction

It is widely recognized that in the production of reliable and reproducible ceramic materials with the required properties it is important to use powders with improved and controlled properties [1–3]. In general, densification and microstructural development during sintering are significantly affected by the characteristics of the starting powders and the uniformity of the green compacts. Many reports pointed out that hard agglomerates within powders could impede the compaction and retard the sintering [4–7]. Several pioneering works have shown that small, unagglomerated ceramic powders can yield dense and uniform microstructures at relatively low sintering temperatures [6, 8, 9]. The chemical approaches for preparing unagglomerated powders, such as by suspension and sedimentation, have been investigated and recently reviewed [2, 10].

It has already been shown in Part I [11] that particle morphologies of the prepared powders are strongly affected by the powder processing for a given composition condition in the initial processing. In the present study, the compaction and sintering behaviour of these powders were investigated and qualitatively described.

2. Experimental procedure

Powder preparation has been described in Part I [11]. Three batches of powders were classified: (1) precipitated powders, designated PPT, obtained via the hydrolysis of magnesium methoxide, (2) sol–gel-derived ground gel powders dried at relatively high temperature, labelled HT, and (3) modified powders obtained via freeze-drying clear sol at low temperature, labelled LT. The molar ratio of water to methoxide was 100 : 1 for all processes, and the sol solution was peptized with 0.1 mol ammonia per mol methoxide for sol–gel routes. The as-prepared powders were uniaxially pressed at 28–278 MPa, and the same quantities of powders were used in all the experiments. Their compaction behaviour is illustrated by the plot of relative density versus pressure, which is also shown as a plot of the logarithmic pressure versus the green density. The pressure–density compaction data are also replotted by showing the compaction rate, $d\rho/dP$, as a function of the relative density, where ρ is the relative density and P is pressure, using the method proposed by Dynys and Halloran [5]. These as-dried powders were calcined at a selected temperature between 400 and 800 °C for 2 h in air. The calcination temperature dependence of the green density was also investigated. The average green density obtained from duplicated specimens for each data was calculated from the dimensions measured in micrometres ($\pm$ 0.01 mm) and from the weight of compacts. The porosities of selected compacts were also characterized by mercury-penetration porosimetry (Micromeritics Pore Sizer 9300).

For the sintering study, these as-prepared powders were die-formed by uniaxially pressing at 166.5 MPa and subsequently sintered at 1300 °C for 6 h in air using a heating rate of 10 $^\circ\mathrm{C\,min^{-1}}$. After being fired, polished samples were thermally etched, followed by coating with a thin gold layer prior to observation by scanning electron microscopy (SEM; JSM-T330, Jeol). The sintered densities were estimated by the Archimedes method using distilled water as a displacement

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liquid. The relative bulk density of the compacts and the sintered body were calculated based on the theoretical density of 3.581 g cm^{-3}. Vickers microhardness of the sintered body was measured on a polished surface under the load of 100 or 300 g for 15 s (Matsuzawa Seiki MHT-1). Optical transmittance of the sintered body was observed within the wavelength range 250–850 nm (Hitachi, U-3410), and specimens were polished down to 1 μm surface finish prior to characterization.

3. Results and discussion

3.1. Compaction behaviour

Fig. 1 shows the pressure–density compaction curves for the three processed powders. It can be clearly seen that LT specimens have a higher green density than the other two at all the given consolidation pressures. As shown in Part I [11], the as-dried LT powders had a narrower size distribution and fewer hard agglomerates; apparently, these attributes are implemental to achieve a more uniform and higher green density for LT specimens. Compaction behaviour of fine ceramic powders is known to be largely influenced by their particle morphologies and hardness [4, 5, 12]. The most important effect to be considered is the state of agglomeration, because that strongly influenced the rearrangement of particles and the uniformity of the packed particles. As shown in Fig. 1, in the low consolidation-pressure range, both HT and PPT specimens are of low green density which is believed to be associated with the presence of porous aggregates. As compaction progressed, the soft agglomerates and some of the porous aggregates should be broken up or crushed, resulting in an increase in density as initially observed. However, in contrast to PPT specimens, increasing the compact pressure was not accompanied by a pronounced increase in green density for HT powders. This implies that the crushing effect is limited for HT powders, because of a greater amount of stronger hard agglomerates within HT powders which should resist the mechanical pressure, and thus the compaction pressure dependence is less sensitive at higher pressures.

The compaction data can also be illustrated by a plot of relative density versus the natural logarithm of pressure, as shown in Fig. 2. It is revealed that the three processed powders all present the "yield pressure", which has been cited as a characteristic of agglomerated powders [4], implying that all the as-dried powders are agglomerated. However, the agglomerate state of these powders is known to differ, especially in the degree of hard agglomeration, suggesting a reason for the great difference in the compaction behaviour for these powders. The effect of consolidation pressure on increasing green density is dependent on the resistance of each agglomerated particle group to rearrangement or deformation. Generally, soft agglomerates can be readily crushed during forming, whereas hard agglomerates often resist crushing and impede particle rearrangement. In comparison with the compaction data for HT and LT powders as shown in Fig. 2, it is apparent that compacts pressed from LT powders are of higher green density with more joined agglomerates of higher green strength.

Dynys and Halloran [5] have shown that the presence of hard agglomerates tends to retard the compaction rate of alum-derived alumina powders. As reported [5], the compaction rate dρ/dP was replotted by showing it as a function of the compact density. By this method, some additional information on the compaction rate is plotted as a function of the percentage of theoretical density, as illustrated in Fig. 3, in which the compaction rate of these processed powders decreases sharply as the volume fraction of the available porosity decreases. In any void volume, the compaction rate of LT powders is higher than the other two, suggesting that this powder facilitates the joining of agglomerated particles in contrast to HT and PPT powders, in which the necessity to crush the hard agglomerates continuously acts to retard the compaction. Powders with hard agglomerates usually have poor compaction behaviour, because the aggregates are difficult to crush [4]. As shown in Fig. 2, the very hard agglomerated HT powders pack so poorly that the green densities cannot exceed 41% of the theoretical density under the pressure range used.

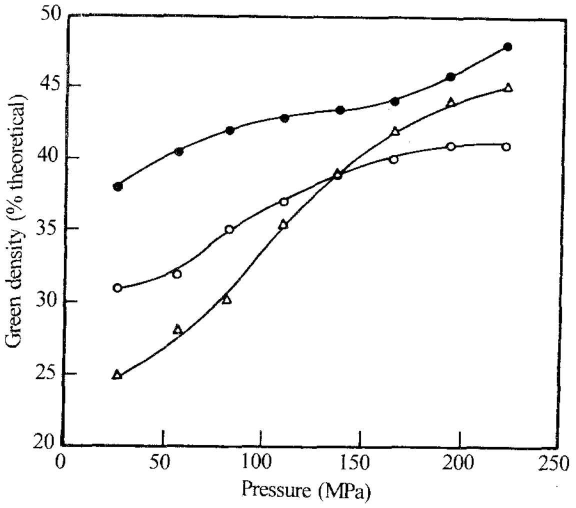

Figure 1 Green density versus compaction pressure for the processed powders. (○) HT, (●) LT, (△) PPT.

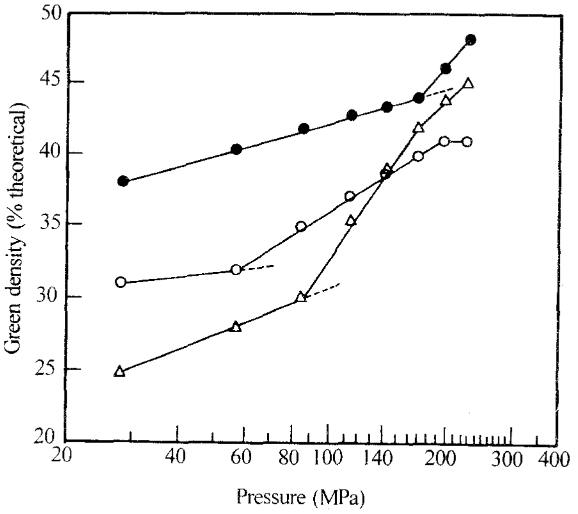

Figure 2 Compaction behaviour of the processed powders. (○) HT, (●) LT, (△) PPT.

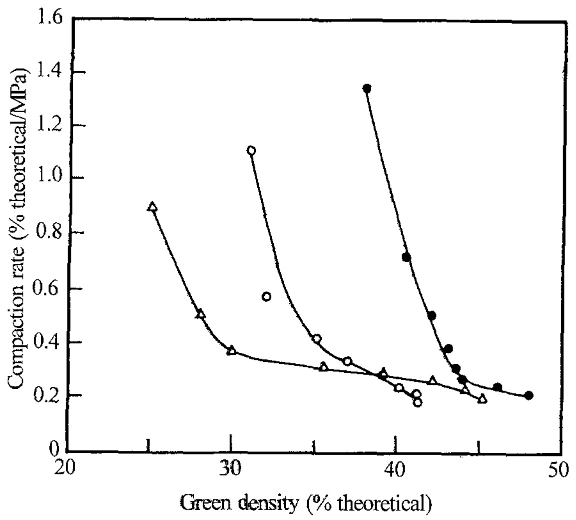

Figure 3 Compaction rate, dρ/dP, as a function of the green density of the processed powder compacts. (○) HT, (●) LT, (△) PPT.

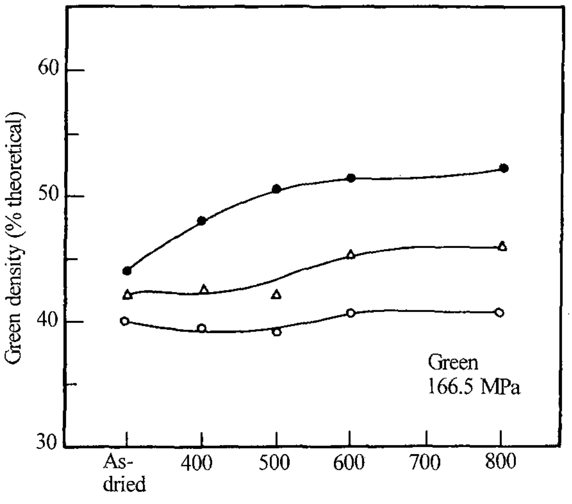

Figure 4 Relative green density versus calcining temperature for the processed powders after 2 h calcining cycle in air. (○) HT, (●) LT, (△) PPT.

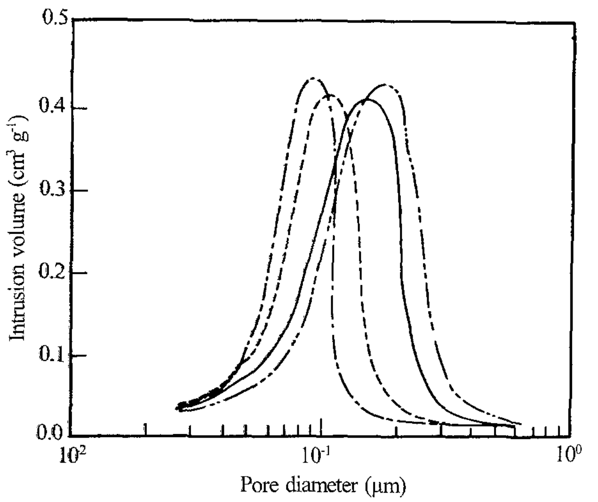

Figure 5 Pore-size distribution in compacts of as-dried and calcined powders for HT and LT pressed at 166.5 MPa; calcined powders were obtained by heating at 500 °C in air. (——) HT, (- - -) LT, (— — —) LT-500, (— - - - —) HT-500.

The results presented in Fig. 3 also suggest that the crushing of PPT powder is more effective than HT powders, even when the compaction rate is low.

Fig. 4 shows the calcination temperature dependence of the green density for HT, LT and PPT powders. It is seen that the elevation of calcining temperature leads to an increase in green density for LT powder compacts, whereas the calcined HT and PPT powders have relatively poor packing at a constant pressure. This tendency correlates with the lower green density which is associated with the porous nature and higher strength of hard agglomerates within HT and PPT calcined powders. As has been shown in Part I [11], after calcining at 500 °C for 2 h, both HT and PPT powders possessed a broader size distribution and a larger agglomerated particle size than either the as-dried states or the relative LT powders, which seems to result in a lower packing density. However, it was recognized that the gel route was distinguished from a precipitation mechanism in which separately aggregated particles are formed in contrast to the continuous particle network. Namely, the degree of hard agglomeration of HT powders is greater than that of PPT powders and the agglomerates become stronger after the calcination. This is probably the reason for the lower density of the HT specimen in Fig. 4. However, the change of green density with calcination temperature could be related to the degree of agglomeration of the powders. In contrast, the higher green density for LT powder compacts implies a lower degree of hard agglomeration of powders that can result in a more closed arrangement of the green state.

Fig. 5 compares the size distribution of the accessible porosity, as determined by mercury porosimetry, for the compacts of as-dried and calcined powders all pressed at about 166.5 MPa. The calcined powders were prepared from calcining the as-dried powders at 500 °C for 2 h in air. It is clearly shown that the pore-size distribution is more uniform and narrower for LT powder compacts in either the as-dried or calcined state, suggesting that the uniformity of LT compacts appears to be greater than in the HT specimens. The results of PPT powder compacts are not presented in Fig. 5; however, they are similar to the HT compacts, but the average pore size of PPT compacts is smaller than that of the HT specimens and also presents a broad size distribution of voids. It is evident that the modified powder approach, by reducing the size, size-distribution and degree of hard agglomeration, permits the preparation of more well-compacted powders with more uniform green microstructures. Conversely, the relatively poor packing of HT compacts appears to have a broad pore-size distribution and a sizeable fraction of larger pores remains in the compact. The fact that the extensive hard agglomerates are native to HT powders, should be reflected in the retardation in compaction and lead to numerous larger pores among the hard agglomerates and to smaller pores within the hard agglomerates. This should create a more non-uniform green state with a lower packing density.

3.2. Sintering behaviour

Fig. 6 shows the relation between the sintered density and the calcining temperature for the three processed powders. It is apparent that LT specimens have the highest sintered densities, thereby suggesting that LT powder compacts have a better sinterability than HT and PPT compacts for a given sintering process. This pronounced difference in the packing density and uniformity of the three processed powder compacts is expected to be the reason for such a discrepancy. For a powder compact, it has been pointed out by several researchers that the degree of uniformity of packing would control the uniformity of the pore-size distribution which, in turn, controls the sintering behaviour [13, 14]. That is, the effect of green state on the sintered density shown in Fig. 6 could be strongly related to their packing density and uniformity. Furthermore, these results could also be correlated directly with the state of agglomeration in the starting powders. The lower sintered density for HT and PPT samples implies a higher degree of hard agglomeration of the powders. Namely, the larger and extensive hard agglomerates essentially lead to green compacts with poorer packing and with nonuniform green microstructures. Thus the average pore size is relatively larger and with a broader distribution, which in turn results in a lower sintered density at a given sintering temperature.

As shown in Part I, powders prepared by these chemical routes usually have large surface areas; however, the particle morphologies, especially the state of hard agglomeration, can have a more important impact on their sinterability. It can be seen in Fig. 6 that the densities of sintered compacts from very hard agglomerated HT powders never exceeded 92% theoretical density. In contrast, the magnesia compacts obtained by calcining LT powders at 500–800 °C in air can be sintered to 98%–99% theoretical density, even at temperatures as low as 1300 °C. The enhanced densification for LT specimens is believed to be related to the more uniform green microstructures and to the higher packing densities, resulting from the size and degree of hard agglomerates which were significantly reduced and had a narrower size distribution than its starting powders.

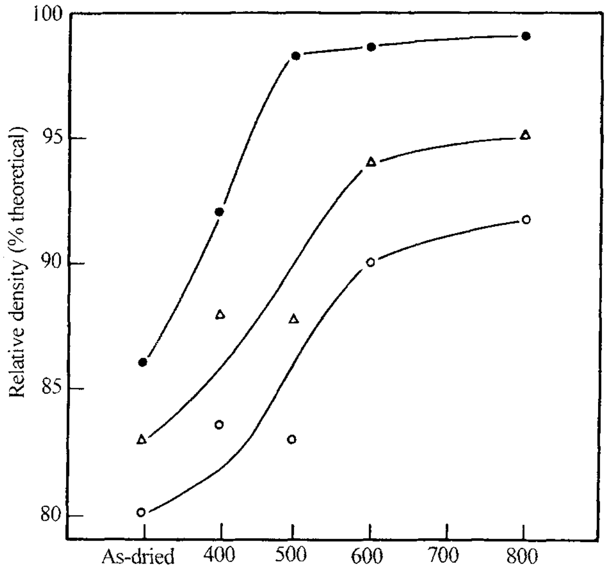

Figure 6 Relative sintered density versus calcining temperature for processed powders sintered at 1300 °C for 6 h in air. Powders were pressed at 166.5 MPa. (○) HT, (●) LT, (△) PPT.

The influence of heterogeneity in the green state of an agglomerated powder compact on the sintered microstructures has been studied and summarized by Lange [3, 14] and Halloran [15]. An important conclusion was that the more aggregated or densely packed regions of a compact tend to densify rapidly and then support local grain growth, whereas large pores survive in regions of more porous packing, and thus densification of a nonuniform green structure should lead to differential densification resulting in abnormal grain growth. Fig. 7 shows the comparison of the sintered microstructures of these processed magnesia powder compacts which were obtained by calcining their as-dried powders at 500 °C in air and then pressing uniaxially at 166.5 MPa. SEM investigations of the polished surface after thermal etching show great differences in microstructures. As seen in Fig. 7a, the HT specimen contains two distinct areas, i.e. dense and locally porous areas, which indicate the heterogeneous microstructural evolution and a sample with about 83% density is obtained. In contrast, Fig. 7b shows dense (98.2%), fine-grained and uniform microstructures formed by sintering the LT powder compact at the same temperature (1300 °C). For the PPT specimen, as shown in Fig. 7c, many irregular voids remain in the sintered body which was less than 88% dense, and with a broad grain-size distribution as in the case of the HT specimen. A lower homogeneity in the sintered microstructures for HT and PPT specimens is essentially associated with the inhomogeneity of their green structures. As shown in Figs 4 and 5, compacts of HT magnesia powders are more poorly packed with a broader distribution of pore size. Thus, the heterogeneous microstructural developments shown in Fig. 7a for HT specimen also imply a reflection of heterogeneity in its green state; that is, suggesting its nonuniform packing structures having denser regions and more porous regions and therefore a broad pore-size distribution has taken place. Namely, during sintering, the smaller pores within hard agglomerates could probably be eliminated and/or shrunk prior to the relatively large inter-aggregated pores. Thus, some densified regions are observed in Fig. 7a in which the large aggregates have smaller intra-aggregated pores that tend to disappear readily during sintering, whereas inter-aggregated areas remain porous.

This differential densification leads to locally inhomogeneous microstructural evolution which seems to be a common phenomenon for the ground gel powder compacts. A similar but more pronounced result is also observed in the sintering alumina ground gel powder compacts [16]. This is believed to be mainly due to the very hard agglomerates within the powders. That is because hard agglomerates can persist during powder consolidation, leading to a nonuniform pore-size distribution in the compacts, which

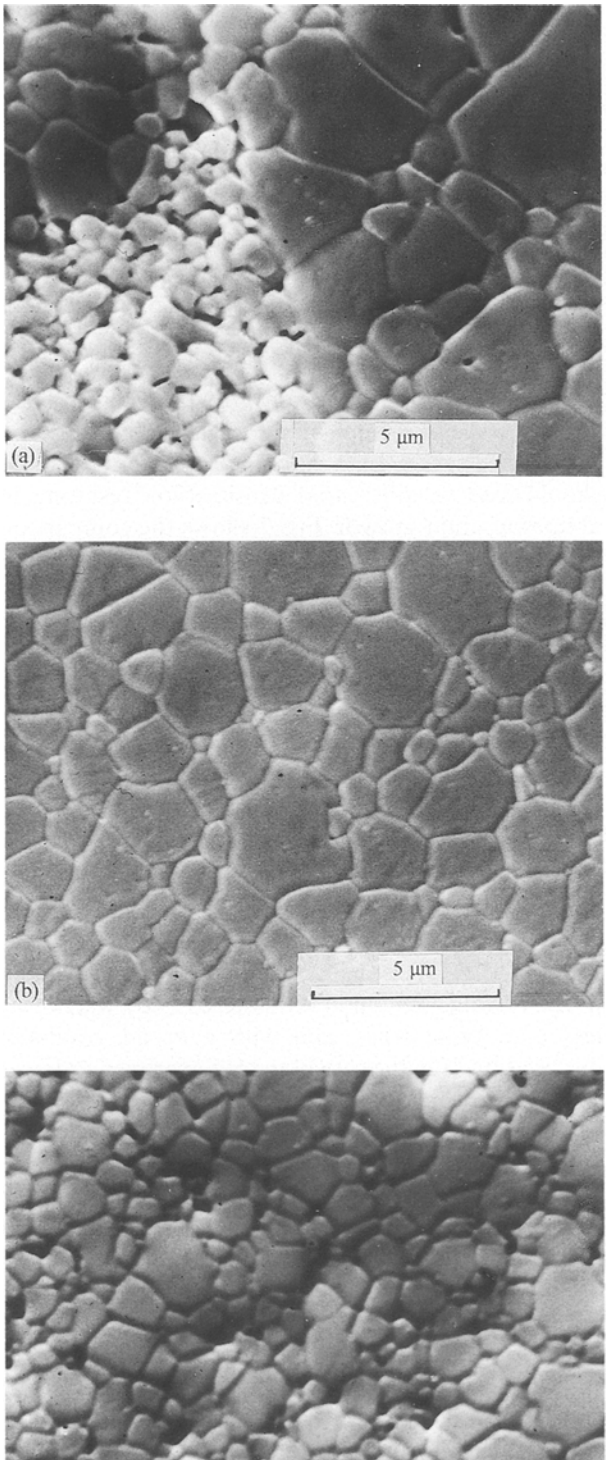

Figure 7 Scanning electron micrographs of (a) HT specimen (with 83% density), (b) LT specimen (with > 98% density) and (c) PPT specimen (with < 88% density) sintered in air for 6 h at 1300 °C.

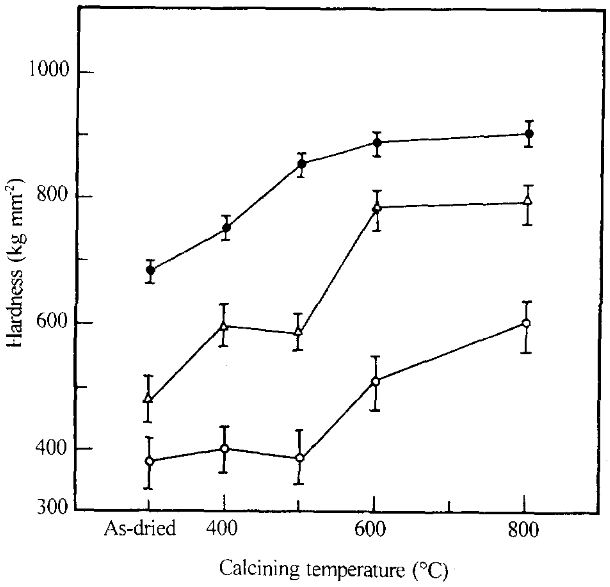

Figure 8 Changes in Vickers hardness of sintered bodies with calcining temperature for the processed powders calcined in air for 2 h. (○) HT, (●) LT, (△) PPT.

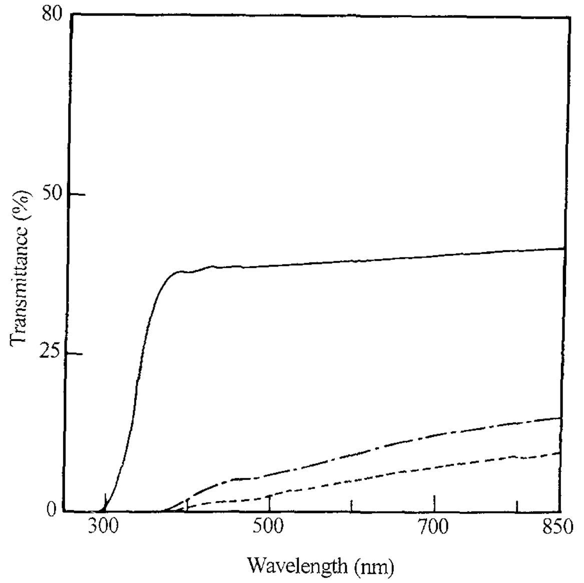

Figure 9 Optical transmittance of magnesia specimens sintered in air at 1300 °C for 6 h (specimens of 0.60 ± 0.08 mm thickness), the corresponding sintered microstructures are shown in Fig. 7. (- - -) HT-500, (——) LT-500, (— - — -) PPT-500.

in turn substantially causes a locally inhomogeneous densification. Fig. 7c shows the sintered microstructures of a PPT specimen that also reflect the disadvantages associated with the use of nonuniform and poorly packed powder compacts. It is suggested that the elimination of smaller intra-agglomerated and intra-aggregated pores occurs; however, the relatively larger inter-agglomerated and inter-aggregated pores remain in the sintered body. Upon examining the microstructures, the HT and PPT specimens apparently exhibit abnormal grain growth, because the denser aggregates support grain growth and thus larger aggregates can initiate unwanted and exaggerated grain growth [14]. However, the microstructural heterogeneity can be efficiently prevented by using the LT powder compacts, mainly due to the fact that the compact has a more uniform packing. It must be recognized that although the soft agglomerates can be readily eliminated by a suspension process in the sol solution, they could be introduced in the subsequent drying and/or calcining steps, due to the tendency of fine particles to reduce their surface free energy [7]. However, the compaction shown in Figs 4 and 5 indicates the less-hard agglomerates of LT powder that were of higher green density and packed more uniformly, so potentially promotes the densification and results in a uniform microstructure. It seems that the effects of hard agglomerates on the heterogeneity of microstructural development during forming and sintering are obviously more pronounced than the soft agglomerates in this study. However, the uniformity of the green compact produced from LT powders, and the absence of observable macrodefects on the sintered body suggest that a uniform high-strength magnesia has been obtained.

Fig. 8 shows the change of Vickers hardness of the sintered body with calcining temperatures. These results are essentially similar to the variation of sintered density as shown in Fig. 6. From Fig. 8, it is seen that the porous and heterogeneous microstructures for HT specimens are responsible for the much lower hardness with more deviation. In contrast, LT specimens have a higher and more uniform hardness. Transmittance of the sintered products was compared as shown in Fig. 9, in which a similar tendency is observed. That is, the dense LT specimen has a higher transmittance, due to the low porosity and fine-grained microstructures that are obtained as shown in Fig. 7b. At wavelengths from 450–850 nm, an LT specimen has an optical transmittance of about 42%. In contrast, the optical transmittance for HT and PPT specimens is relatively lower and increases to 10.0% and 15.7% at 850 nm, respectively, because the key to the translucent materials is closely related to the formation of fine-grained, highly dense and low-porous structures. Thus, as shown in Fig. 7, due to the differential densification in both HT and PPT powder compacts, a higher pore volume and inhomogeneous microstructure should result in their sintered bodies, and consequently these specimens have lower transmittances. In addition, it is reasonable to consider that the purity of LT specimens is higher than that of the HT and PPT specimens, because of avoiding the milling step. This is also available to enhance transmittance of LT specimens.

However, in this study, the observed enhancement in compaction and sinterability for LT specimens is considerable, mainly due to the improvement of powder morphologies, especially the reduction in particle size, size-distribution and degree of hard agglomeration, which are implemental in improving the uniformity of pore-size distribution in the compacts and then promoting the densification.

4. Conclusions

This study indicates that the presence of hard agglomerates must be avoided to achieve a homogeneous microstructure. The homogeneity of the microstructural development during compaction and densification is dependent strongly on the characteristics of the starting powders which varied with different powder processing. It is also emphasized that the state of hard agglomeration within ground gel powders and alkoxide-hydrolysis-derived powder, is indeed a predominant factor affecting the uniformity and microstructural evolution. However, fast sintering of sol–gel-devived powders is a feasible way to prepare dense magnesia, but the first step of the powder route is crucial. The ground gel powders inherently lack an approach for preventing the occurrence of the very hard agglomerated particles. The extensive hard agglomerates often lead to locally inhomogeneous densification, because they should substantially retard compaction and create a nonuniform green state. However, this study demonstrates that the modified powder approach can provide a potential to achieve a dense, high strength and translucent polycrystalline magnesia, by means of a conventional pressing and sintering process at much lower temperature than with conventional magnesia powders, without the use of sintering aids.

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