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Sintering behaviour of highly agglomerated ultrafine zirconia powders

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The sintering behaviour of highly agglomerated ultrafine zirconia powders can be described by a combination of mechanisms such as neck formation and shrinkage, fissure formation and growth, pore growth, grain growth, pore-rearrangement shrinkage, and pore entrapment. There exist two optimum sintering temperatures : one is due to the competition between neck formation and shrinkage, fissure formation and pore growth; the other is due to the competition between pore shrinkage and pore entrapment, both resulting from grain growth. It is also found that an increase of green density, which is caused either by a different consolidation pressure, a different preparation method, or a different calcination temperature, results in a decrease of sintered bulk density. This can be explained by the state of agglomeration and the uniformity of powder packing.

1. Introduction

Agglomerate-free powders have been the goal of powder processing for a long time. Many researchers [1–8] have demonstrated the improved performance of agglomerate free powders which can be sintered to nearly full density at relatively low temperatures. However, it is difficult to employ conventional forming methods such as dry pressing to shape the agglomerate-free powders. Therefore, it is beneficial to study fully the sintering behaviour of agglomerated powders.

Ceramic powders are known to agglomerate especially when they are very fine. The state of agglomeration is different if the method of preparation and processing is varied. Powders made from alkoxide, oxychloride, and many other methods appear different in the degree of agglomeration, the strength of the agglomerate, the packing of agglomerate and surface activity. Powders with different processing also show different agglomeration, e.g. water-washed ZrO_2–Y_2O_3 gels produce hard agglomerates, whereas further washing with ethyl alcohol produces soft agglomerates [9]. The state of agglomeration affects the pore size distribution of powder compacts after pressing, and thus affects the sintering behaviour of the powders.

Rhodes [1] and Reeve [10] showed that a dense agglomerate could pull away from the surrounding matrix, leaving a lenticular crack where the agglomerate was partially detached from the matrix. This type of pore may never close, causing densification to halt at some finite level below theoretical density.

Kingery and Francois [11] recognized that pores will grow if their coordination number R is larger than a critical number R_c. Only those pores with $R < R_c$ can disappear during sintering. As grain growth occurs, R will decrease. Lange [12] showed that grain growth and rearrangement processes could reduce the coordination number of pores and allow further densification. Since higher sintering temperatures allow higher rates of grain growth, high end-point densities can be achieved. However, lower sintered bulk densities are obtained if the sintering temperature is raised too high. This is usually explained by pore entrapment due to grain growth.

Recently some research activities [12, 13] have dealt with the influence of aggregates on sintering behaviour. However, the crystallite sizes of the aggregate/agglomerate used were relatively large. The purpose of the present paper is to examine the progress of the bulk density of highly agglomerated ultrafine powder compacts during sintering at different sintering temperature, for powders of different states of agglomeration.

2. Experimental procedures

Zirconia powders partially stabilized with 3 mol % Y_2O_3 were prepared by the oxychloride and alkoxide methods. For the oxychloride method, $ZrOCl_2 \cdot 8H_2O$ and YCl_3 of suitable proportions were weighed and added to deoinized water to form a solution of 0.3 M concentration. The solution was then added slowly to an NH_4OH solution of pH 9.35. To maintain the pH at 9.35, additional NH_4OH solution was added to the solution continuously. After reaction, the turbid solution was filtered and washed with deionized water three times to remove chlorine ions. Then the filtered powder was washed with ethyl alcohol three times and dried.

In the case of the alkoxide method, $Zr(OC_3H_7^n)_4$ (n represents normal) was dissolved in 1-propanol to form a solution of 2 M concentration then $Y(NO_3)_3 \cdot 5H_2O$ was mixed with the propanol solution of $Zr(OH_3H_7^n)_4$. Next, an HNO_3 solution of pH 0.5 was added to the propanol solution and heated to

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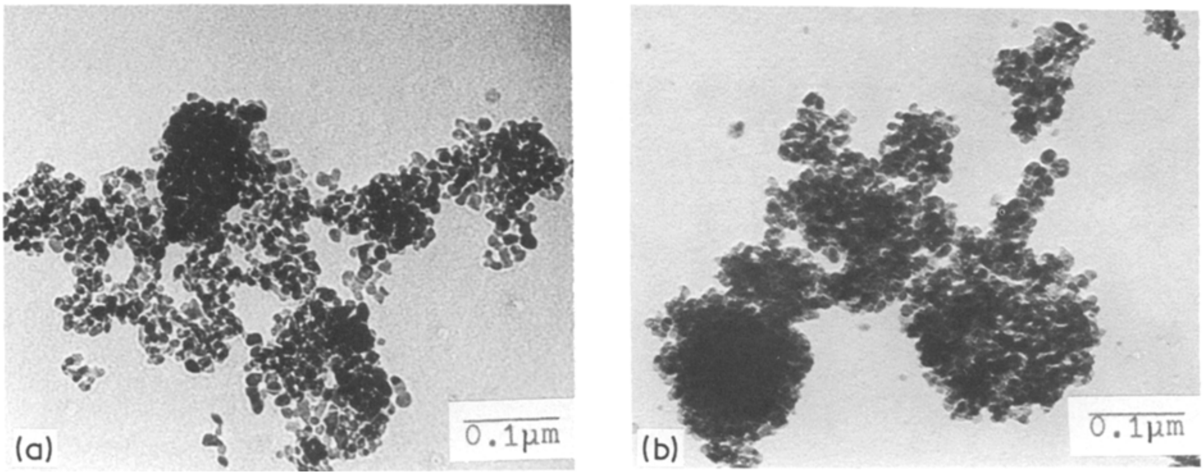


Figure 1 TEM pictures of ZrO_2–3 mol % Y_2O_3 powders, prepared by (a) oxychloride method, (b) alkoxide method, calcined at 600° C for 1 h then ball-milled for 10 h.

50° C to form a clear solution. The resulting propanol solution was then slowly added to NH_4OH solution of pH 9.35. Similarly, additional NH_4OH solution was added to keep the pH at 9.35. After reaction, the turbid solution was filtered and washed with deionized water three times, then with ethyl alcohol three times and dried. For simplicity, powders prepared by oxychloride and alkoxide methods will be called oxychloride and alkoxide powders, respectively, in the following sections.

The dried alkoxide powder was calcined at 600° C for 1 h, whereas the dried oxychloride powder was calcined for 1 h at 550, 600, 650, 700 or 800° C. All the calcined powders with the addition of 1 wt % polyvinyl alcohol were ball-milled in a plastic bottle with zirconia balls and deionized water for 10 h. The ball-milled powders were dried, milled again with pestle and mortar, and were pressed in a die under 175 MPa pressure to form pellets of 1.5 cm diameter and 1 mm thickness.

The pellets were held at 400° C for 1 h and then sintered in an air atmosphere for different periods of time at different temperatues. There were two samples for each sintering condition. The bulk densities of the sintered pellets were measured by the Archimedes method. The microstructures of the sintered pellets were investigated with SEM. The crystal phases were determined by X-ray diffraction.

Both oxychloride and alkoxide powder after calcination were observed with transmission electron microscopy (TEM). The surface areas of both powders were determined by the BET method. The particle size distributions of agglomerated powders were determined with a centrifugal particle size analyser.

3. Results

3.1. Powder characteristics

TEM pictures of oxychloride and alkoxide powders which were calcined at 600° C for 1 h and ball-milled in water for 10 h and dried are shown in Fig. 1. The crystallite sizes of both powders appear to be about 10 nm. Both powders are highly agglomerated. This is further confirmed by the particle size distribution of both powders. Fig. 2 shows that the agglomerate size distribution of oxychloride powder calcined at 600° C is coarser than that of alkoxide powder processed under similar conditions. The surface area measured by the BET method is 212 $m^2\,g^{-1}$ for calcined alkoxide powder and 81 $m^2\,g^{-1}$ for calcined oxychloride powder. The equivalent spherical crystallite size is about 12.1 nm for oxychloride powder, very close to what was determined by TEM, and about 4.6 nm for alkoxide powder, which is lower than what is observed by TEM. The green densities of the powder compacts pressed under 175 MPa are 2.32 $g\,cm^{-3}$ for alkoxide powder and 2.82 $g\,cm^{-3}$ for oxychloride powder. The crystal structures of both powders calcined at 600° C are determined to be the tetragonal phase. If the theoretical density of the tetragonal phase is taken as 6.10 $g\,cm^{-3}$, the green densities pressed at 175 MPa are 38.0 and 46.25% of theoretical density, respectively, for alkoxide and oxychloride powders calcined at 600° C. All the results suggest that oxychloride powders have a higher degree of agglomeration than alkoxide powders after being calcined at 600° C and ball-milled.

The crystallite sizes of oxychloride powders calcined at 550, 600, 650, 700 and 800° C are about 7, 10, 11, 12 and 17 nm, respectively, as investigated by TEM. The mean agglomerate sizes are determined to be 1.8, 2.1, 1.1, 1.4 and 1.4 μm from their agglomerate

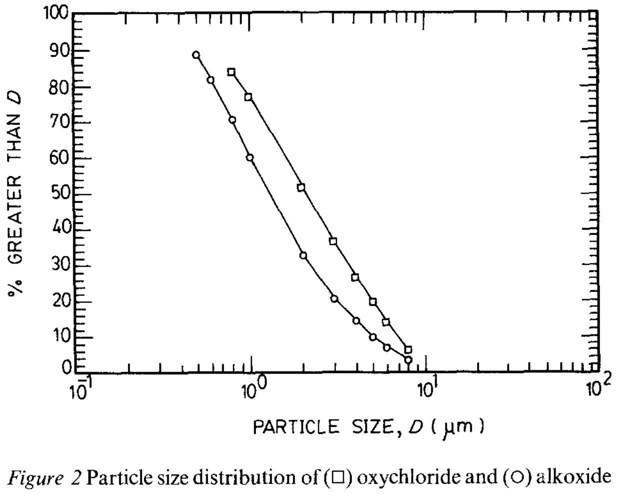


Figure 2 Particle size distribution of (□) oxychloride and (○) alkoxide powders calcined at 600° C for 1 h and ball-milled for 10 h.

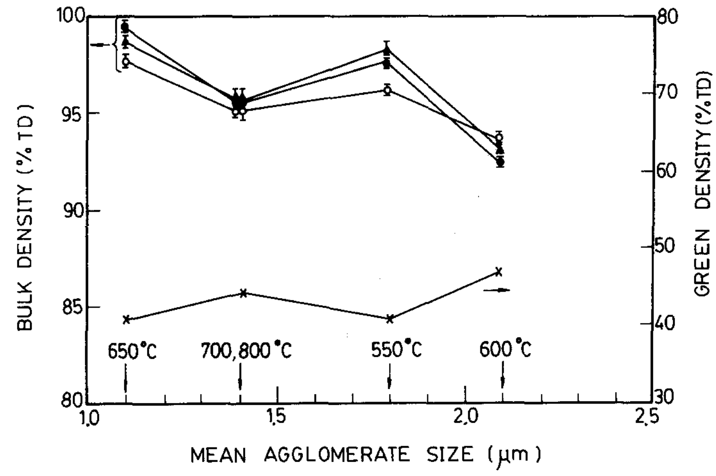


Figure 3 Bulk density and green density (175 MPa) against mean agglomerate size for oxychloride powders calcined at 550, 600, 650, 700, and 800° C for 1 h. Samples were sintered at (○) 1250, (▲) 1350 and (●) 1450° C for 5 h. TD = theoretical density.

size distribution, and the green densities of powder compacts pressed at 175 MPa are 2.47, 2.82, 2.46, 2.70 and 2.75 g cm^{-3} for oxychloride powders calcined at 550, 600, 650, 700 and 800° C, respectively. Fig. 3 indicates the variation of green density with mean agglomerate size. There is no simple relationship among calcination temperature, mean agglomerate size and green density. Compacts pressed with powders calcined at 650° C have the smallest green densities and those calcined at 600° C have the largest green densities. All powders after calcination appear to be the tetragonal phase.

3.2. Sintering kinetics

Fig. 4 illustrates the sintered bulk density against sintering time data for powder compacts prepared by the oxychloride method and calcined at 600° C for 1 h. It is shown that the bulk density reaches 5.78 g cm^{-3} at 1450° C in 1 h, drops to 5.56 g cm^{-3} when sintered for 3 h, then increases again to 5.57 and 5.72 g cm^{-3} for 5 and 10 h sintering, respectively. The decrease of bulk density from 1 to 3 h sintering at 1450° C is very significant. The appearances of these samples are quite different. The surface is smooth after 1 h and has small bulges on the surfaces for 3, 5 and 10 h samples. Fig. 4 also shows the sintered bulk density against time data for powder compacts prepared by the oxychloride method at 1350° C. The bulk density of the compact increase to 5.57 g cm^{-3} in 1 h, then to 5.69, 5.71 and 5.80 g cm^{-3} for 3, 5 and 10 h sintering, respectively. No drop of bulk density is observed in the progress of sintering at this temperature. It should be noted that the increase of bulk density from 3 h sintering to 5 h sintering is only 0.02 g cm^{-3} (average rate = 0.01 g cm^{-3} h^{-1}), whereas that from 5 to 10 h sintering is 0.1 g cm^{-3} (average rate = 0.02 g cm^{-3} h^{-1}). It is very unusual that the long-time sintering rate is larger than the short-time sintering rate. The surfaces of samples sintered at 1350° C contain bulges too. However, they are much smaller than those on 1450° C samples. The samples sintered at 1250° C for 5 h do not contain bulges.

The bulk density sintered for 5 h at different sintering temperatures for oxychloride powder calcined at 600° C is shown in Fig. 5. It illustrates that the sintered density decreases from 5.72 to 5.57 g cm^{-3} as the sintering temperature increases from 1250 to 1450° C

Fig. 6 illustrates the bulk density against sintering time data of powder compacts prepared by the alkoxide method and calcined at 600° C for 1 h, showing that the bulk density sintered at 1300° C increases to 5.82, 5.92, 5.98 and 5.99 g cm^{-3} for 1, 3, 5 and 10 h

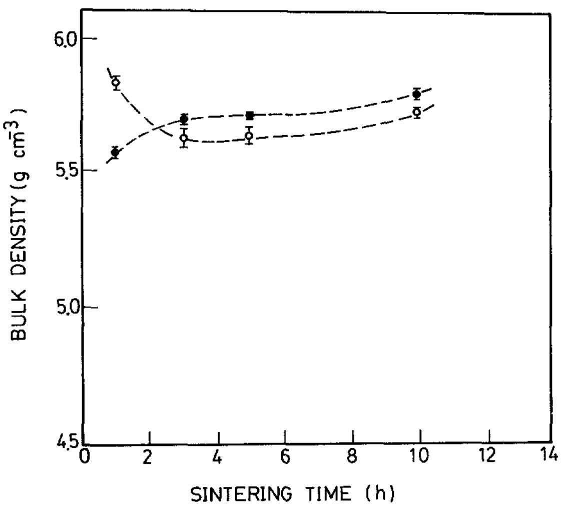


Figure 4 Bulk density against sintering time of oxychloride powder calcined at 600° C for 1 h, and sintered at (○) 1450 and (●) 1350° C.

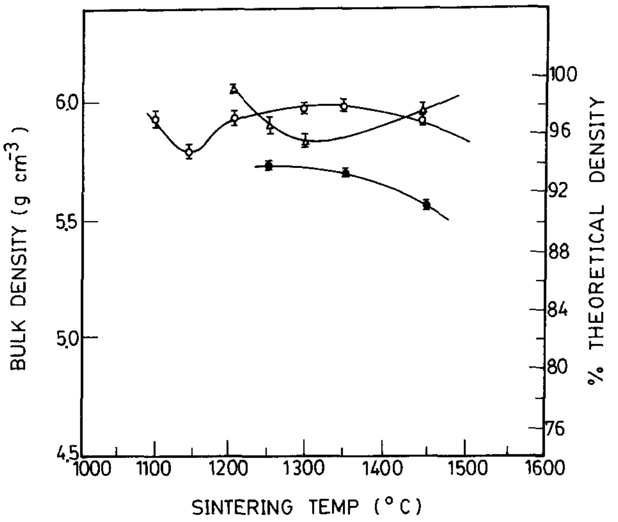


Figure 5 Bulk density against sintering temperature for powder compacts calcined at 600° C for 1 h. Samples were sintered at each temperature for 5 h. (●) Oxychloride, 175 MPa; (○) alkoxide, 175 MPa; (△) alkoxide, 140 MPa.

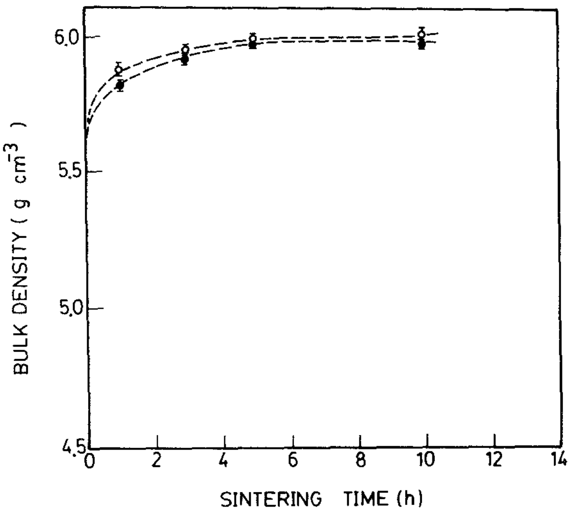


Figure 6 Bulk density against sintering time of alkoxide powders calcined at 600° C for 1 h and sintered at (○) 1350 and (●) 1300° C.

sintering, respectively. The bulk density increased quickly in the early stage of sintering and then slows down, which is similar to what is commonly observed. Samples sintered at 1350° C show a similar trend. All samples appear smooth.

The bulk densities of alkoxide powder compact pressed at 175 and 140 MPa and sintered at different temperatures for 5 h are shown in Fig. 5. It illustrates that the bulk density does not monotonically increase with sintering temperature; the bulk densities drop at 1150 and 1450° C for 175 MPa samples and drop at 1200° C for 140 MPa samples. A decrease of bulk density at relatively high temperature is often observed, but that at relatively low temperature is seldom reported.

The bulk densities of samples sintered for 5 h at 1250, 1350 and 1450° C from oxychloride powder calcined at different temperatures are shown in Fig. 3. There is no simple relationship between calcination temperature and sintered bulk density. However, two interesting points should be noted: first, the higher the green density, the lower the sintered bulk density; second, the higher the green density, the higher the trend of reduction of the sintered bulk density with sintering temperature, i.e. the tendency is the smallest for samples calcined at 650° C and the largest for 600° C samples.

3.3. Microstructural observations

The microstructures shown in Figs 7 a to d are observed from fractured surfaces of oxychloride samples calcined at 600° C for 1 h and sintered at 1450° C for 1, 3, 5 and 10 h, respectively. Fig. 7a shows the non-uniform distribution of pores in a sample sintered for 1 h at 1450° C. The grain size is uniform, approximately 0.45 μm. Fig. 7b, sintered for 3 h at

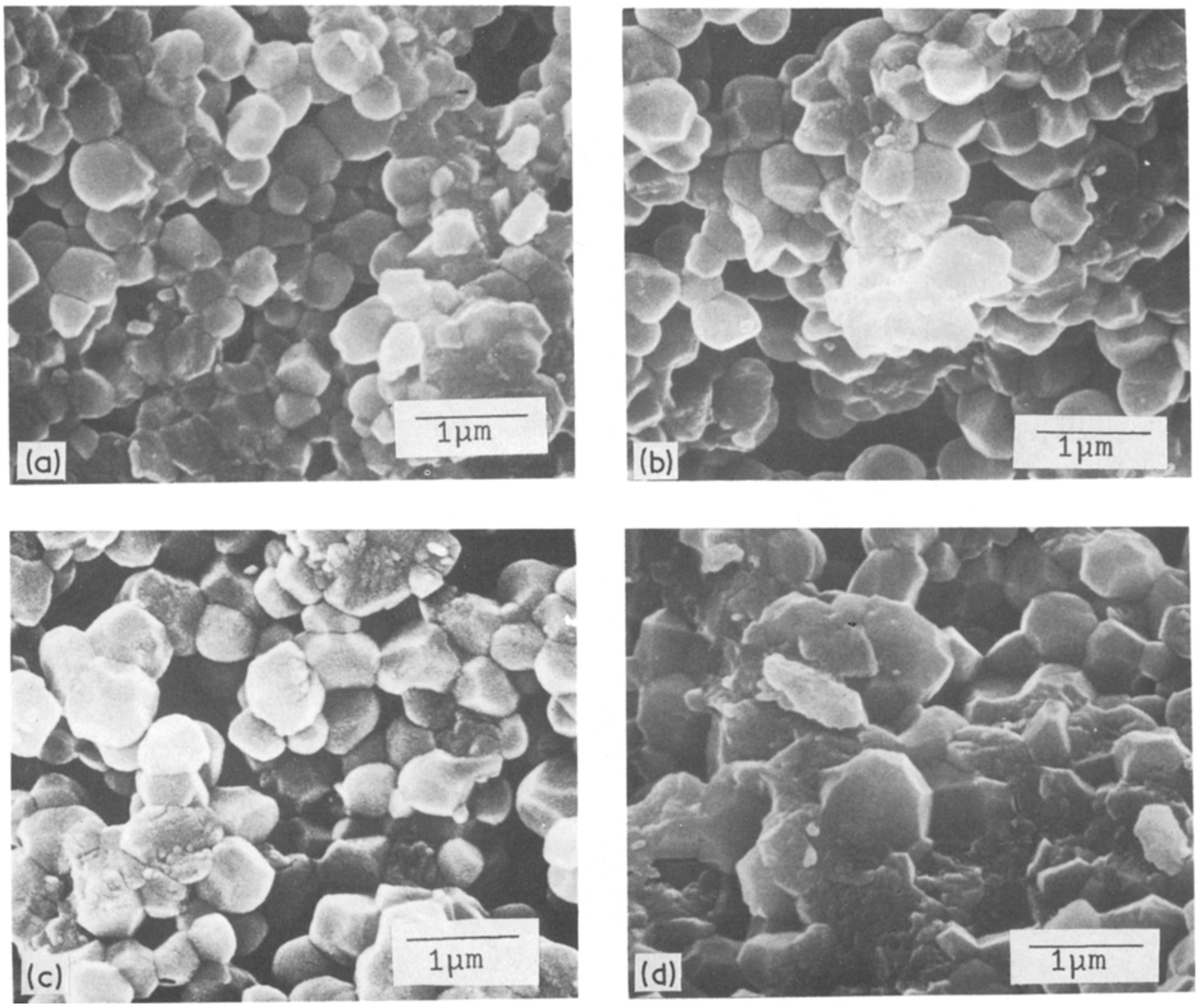


Figure 7 Microstructures of oxychloride powder calcined at 600° C for 1 h and sintered at 1450° C for (a) 1, (b) 3, (c) 5 and (d) 10 h.

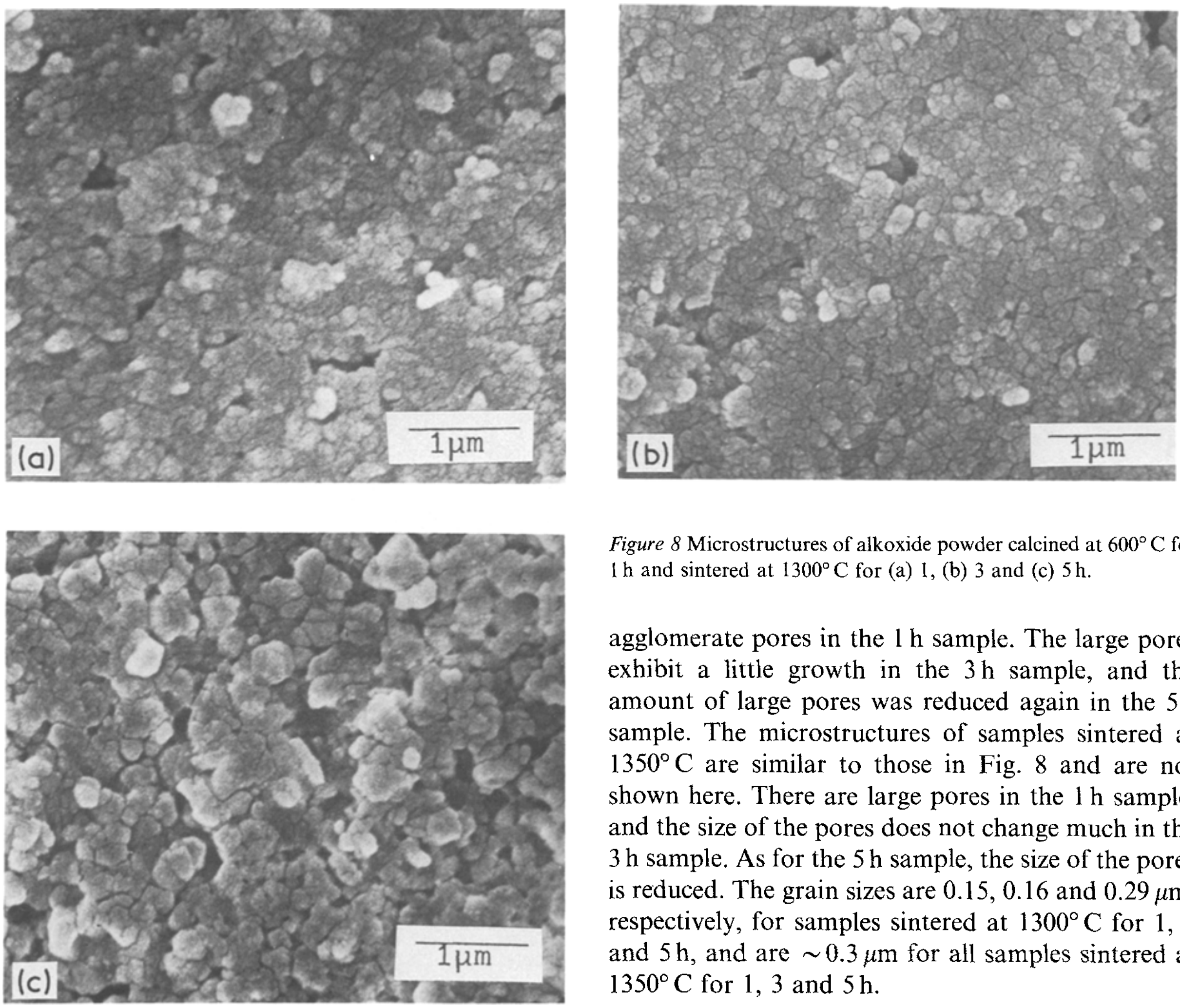


Figure 8 Microstructures of alkoxide powder calcined at 600° C for 1 h and sintered at 1300° C for (a) 1, (b) 3 and (c) 5 h.

1450° C, exhibits more large pores than the 1 h sample. The grain size, about 0.5 μm, does not show too much grain growth. Fig. 7c illustrates the microstructure of a sample sintered for 5 h at 1450° C, showing that the amount of large pores seems less than that in the 3 h samples; the distribution of grain size consists of two parts, one remaining almost the same size without growth as in the 3 h sample (i.e. ~ 0.5 μm), the other growing to 0.7 to 0.9 μm. Fig. 7d, a sample sintered for 10 h at 1450° C, shows that there are fewer large pores and more large grains than in the 5 h samples.

The characteristic features of the microstructures of oxychloride samples calcined at 600° C for 1 h and sintered at 1350° C are similar to those in Fig. 7 and will not be shown. The fracture surface of a sample sintered for 1 h at 1350° C contains large pores that are widely distributed. As compared with that sintered at 1450° C for 1 h, the distribution of pores is similar, whereas the grain size is smaller, ~ 0.38 μm. The volume fraction of pores reduces continuously for samples sintered at 1350° C for 3, 5 and 10 h. The degree of pore growth does not seem high. The grain sizes of samples sintered at 1350° C for 3, 5 and 10 h are ~ 0.40, ~ 0.40 and 0.50 μm, respectively. The rate of grain growth is not high.

Fig. 8 illustrates the microstructures for alkoxide powder compacts which were calcined at 600° C for 1 h and sintered at 1300° C for 1, 3, and 5 h, showing that there are large pores which are mainly inter-agglomerate pores in the 1 h sample. The large pores exhibit a little growth in the 3 h sample, and the amount of large pores was reduced again in the 5 h sample. The microstructures of samples sintered at 1350° C are similar to those in Fig. 8 and are not shown here. There are large pores in the 1 h sample, and the size of the pores does not change much in the 3 h sample. As for the 5 h sample, the size of the pores is reduced. The grain sizes are 0.15, 0.16 and 0.29 μm, respectively, for samples sintered at 1300° C for 1, 3 and 5 h, and are ~ 0.3 μm for all samples sintered at 1350° C for 1, 3 and 5 h.

3.4. Effect of consolidation pressure

Oxychloride powder calcined at 600° C for 1 h was employed to study the effect of the consolidation pressure. Powder compacts dry-pressed under various conditions were sintered at 1450° C for 5 h. The resulting bulk densities and green densities are shown against consolidation pressure in Fig. 9. The green density generally increases with consolidation pressure. The green density obtained at 105 MPa is higher than that obtained at 140 MPa. This is because the compacts pressed at 105 MPa were all broken; thus they were reground and repressed at 105 MPa. Fig. 9 shows that the sintered bulk density decreases with increasing green density no matter how the green density was obtained. This is opposite to what is usually observed.

Alkoxide powder calcined at 600° C for 1 h was also employed to study the effect of consolidation pressure. Two consolidation pressures were applied, i.e. 140 and 175 MPa. The powder compacts were sintered for 5 h at various temperatures. The sintered bulk density has been plotted against sintering temperature in Fig. 5. The green densities after pressing at 140 and 175 MPa are 31 and 38% of theoretical density, respectively. It is seen that the bulk density decreases with sintering temperature in the low temperature range and then increases again. The bulk density curve moves toward the higher sintering temperature range, if the green density decreases (i.e. the consolidation pressure decreases).

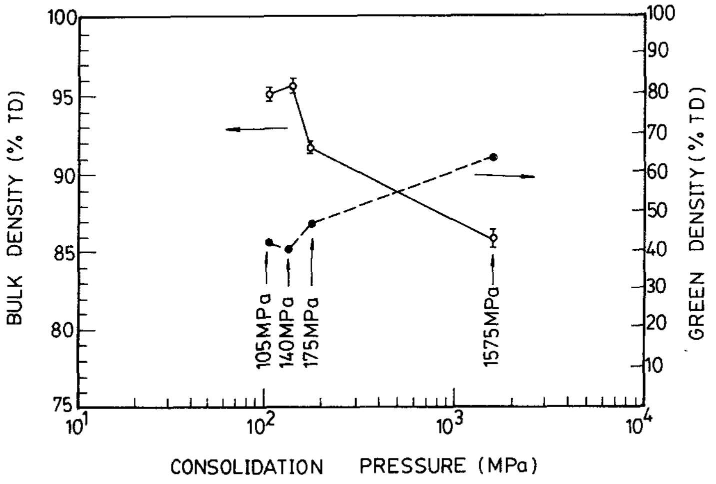


Figure 9 (○) Bulk density and (●) green density against consolidation pressure for oxychloride powders calcined at 600° C for 1 h and sintered at 1450° C for 5 h.

4. Discussion

4.1. Sintering behaviour of highly agglomerated ultrafine powders

The sintering behaviour described in the previous section appears different from that generally reported in some respects. However, this can be explained if the mechanisms which usually occur during sintering are considered.

It is well known that neck formation and shrinkage, fissure formation and growth, pore growth, grain growth, pore rearrangement and pore entrapment can happen during the sintering of highly agglomerated ultrafine powders. Although these processes may occur in the entire period of sintering, there are always only one or two dominating in a certain period. Therefore, sintering may be divided into several stages and described as follows.

4.1.1. First stage: neck formation and shrinkage

In the beginning of the sintering process, compacts of agglomerated powders contain a lot of contact area between particles within agglomerates or among agglomerates. Since the contact areas have negative curvature, materials transfer to the contact areas and necks form. If mechanisms allow particle centres to approach each other, shrinkage occurs. Areas with a high density of contacts shrink faster than those with a low density of contacts. In general, shrinkage occurs in the entire compact, so that density continues to increase with time as shown in Fig. 10 (Region I). The kinetics may be described by suitable equations derived from sintering [14–22].

4.1.2. Second stage: fissure formation and growth

Since the shrinkage is greater in areas of high neck density than in those of low neck density, tensile stress may build up in the bonds between these areas as sintering proceeds. The tensile stress [22] built up is estimated to be

$$\sigma_t = (n_1 - n_2)\, \gamma \, \mathrm{d}A'$$

where n_1, n_2 are the neck densities of two neighbouring areas, i.e. the numbers of necks per unit volume; γ is the surface energy per unit area, and $\mathrm{d}A'$ is the change in area produced by a single neck. This tensile stress may be more or less relieved by the redistribution or movement of atoms caused by the increased diffusion coefficient resulting from tensile stress. If the tensile stress is not relieved fast enough as compared with its build-up, it will reach the critical level of tensile strength of the material and cause the bond to break. Thus separations or fissures are formed between areas with different neck densities. After fissure formation, the constraint previously imposed by the broken part is removed. The continuing shrinkage of both parts enlarges the separation and causes the fissure to grow. When fissure formation and growth occurs, the sintering rate slows down. For areas without separation shrinkage continues to occur, but the total shrinkage rate is decreased as shown in Regions I to II of Fig. 10.

The formation of fissures depends on the sintering temperature, which affects the rate of neck formation, the rate of tensile stress build-up, and the rate of stress relief.

4.1.3. Third stage: pore growth

As sintering proceeds, neck areas continue to increase and the neck curvature decreases. Therefore, the driving force of densification also decreases. Mass rearrangement in the region of interagglomerate pores

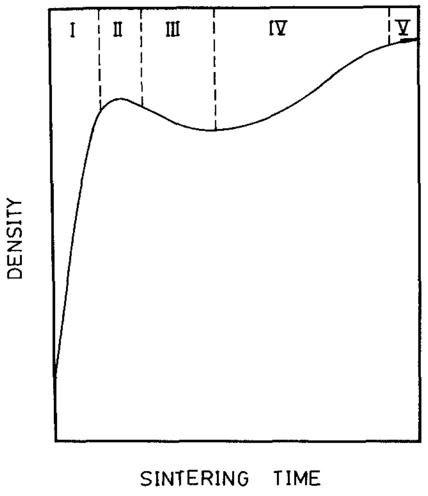


Figure 10 A schematic diagram of the possible bulk density against sintering time curve for highly agglomerated ultrafine powder.

overcomes densification in the neck areas. In the interagglomerate pore region, a critical coordination number R_c exists that defines the transition from convex ($R > R_c$) to concave ($R < R_c$) surfaces. In the general situation, surfaces tend to move toward their centres of curvature. Thus pores with convex surfaces can grow and cause a reduction of bulk density.

In highly agglomerated ultrafine powder compacts, the coordination number R of the pores easily exceeds R_c. These large pores will grow. If the degree of pore growth is high, the total shrinkage will show a negative densification, i.e. the compact expands as shown in Region III of Fig. 10. In addition, pore growth and de-densification are also enhanced by the coalescence of trapped gas [23, 24].

4.1.4. Fourth stage: grain growth and pore rearrangement shrinkage

As sintering proceeds, the porosity in high-density areas continues to decrease. The inhibition of grain boundary movement due to the pores decreases and causes grain growth. Grain growth changes the coordination number R of the large pores, and R becomes lower than R_c again. After rearrangement the pore surfaces change from convex to concave. Pore shrinkage occurs and the density of the compact increases again, as shown in Region IV of Fig. 10. Gupta [25] showed for a number of different powders that the bulk density, after some sintering schedules, is proportional to grain size. Lange [12] also suggested that grain growth is important in obtaining high-density ceramics. On the other hand, if there are gas-filled pores within compacts, the gas diffusing along grain boundaries leaves the compact, thus permitting a higher driving force for densification and causing the observed increase in bulk density.

4.1.5. Fifth stage: pore entrapment

As the porosity drops, the rate of grain growth may become fast enough to cause pore entrapment within the grains. When this happens, the densification rate drops and approaches zero as shown in Region V of Fig. 10. The bulk density may reach an end-point for practical sintering times.

The sintering stages described above suggest the dominant mechanisms which occur in different time periods. In different powder systems and different temperature ranges the stages may combine and some features disappear. Some stages may not even show up. The mechanisms which dominate in different stages may also change their order. For example, the degree of fissure formation, pore growth and grain growth may not be large enough as compared with neck formation and shrinkage so that Stages II, III and IV combine together and show a slow densification after Stage I. This is the case shown in the 1350° C data of Fig. 4, which is what is usually observed.

4.2. The effect of sintering temperature

It is generally accepted that a higher sintering temperature results in a higher sintered bulk density unless the temperature becomes so high that pores become entrapped within grains. In sintering highly agglomerated ultrafine powder, however, fissure formation and pore growth take place to such an extent that a higher temperature causes a lower sintered bulk density. According to our experimental observations, it is suggested that fissure formation and pore growth are very extensive for oxychloride powders calcined at 600° C and sintered at 1450° C. The decrease of bulk density from the 1 h value to the 3 h value (Fig. 4) is mainly caused by pore growth. Comparing Figs 7a and b, it is evident that pore growth occurs during the period from 1 to 3 h at 1450° C. Other evidence of pore growth is the appearance of bulges on the surfaces of samples sintered at 1450° C for 3, 5 and 10 h. The samples sintered at 1450° C have a lower bulk density than those sintered at 1350° C for time periods longer than 3 h (Fig. 5). The microstructures suggest that the degree of pore growth as well as that of fissure formation and growth is much lower for samples sintered at lower temperatures such as 1350 and 1250° C. This is supported by the appearance of the sintered samples. There are only very small bulges on the surfaces of samples sintered at 1350° C, and no bulges for those sintered at 1250° C. Furthermore, there was no observed reduction of bulk density during sintering at 1350 and 1250° C (Fig. 4). Because of the lesser pore growth at lower temperatures, the bulk densities for samples sintered at 1250° C are higher than for those sintered at 1350 and 1450° C (Fig. 5).

During the later stage of sintering at 1450° C, there was a significant increase of the sintering rate in the 5 to 10 h period. This suggests that new mechanisms became operative. From microstructural observations, the grain size increased slowly from the 1 to the 3 h period and abruptly from the 3 to the 5 h period. It is reasonable to argue that mechanisms related to grain growth caused the change of the densification rate. It is believed that the pore rearrangement proposed by Lange [12] is the mechanism. Grain growth changes the number of grains surrounding pores. The reduction of the coordination number of grains around pores, as well as the change of pore surface from convex to concave, take time to reach equilibrium. Thus pore shrinkage due to a reduction of the coordination number of pores usually occurs over a longer time period. This explains the increase of the densification rate during the period from 5 to 10 h at 1350° and 1450° C as compared to that from 3 to 5 h for oxychloride samples calcined at 600° C (Fig. 4). The increase of densification rate could also be caused partly by the diffusion of gas out of the compact, thereby increasing the driving force for densification.

For alkoxide powders sintered at 1300 and 1350° C, the variation of sintered bulk density with time is similar to what is commonly observed, i.e. the bulk density increases quickly in the early stage then slows down in the late stage. From microstructural observations (Fig. 8), there was an essentially continuous decrease of pore volume and an increase of grain size without abnormal behaviour. No bulges were observed on the surfaces of the sintered samples. Thus it may be reasoned that the degree of pore growth is much lower in alkoxide samples than in oxychloride samples, if both powders are calcined at 600° C. The different sintering behaviour of oxychloride powders and alkoxide powders will be discussed in the next section.

Although the degree of pore growth is low in alkoxide powder compacts, it may still affect the sintering behaviour. For alkoxide powder compacts, fissure formation and pore growth are believed to be the cause of the reduction of sintered bulk density at 1150° C (Fig. 5). The increase of bulk density above 1200° C is caused by grain growth and pore rearrangement shrinkage, and the decrease of bulk density at 1450° C is thought to be a result of pore entrapment within the grains.

It is well demonstrated [1, 2] that complete densification can be achieved at relatively low temperature if all of the particles have the same packing density. In the present study, a high bulk density can also be obtained at relatively low temperature, e.g. 1100° C for an alkoxide powder compact (Fig. 5). However, it is very difficult to achieve the theoretical density. The problem of sintering highly agglomerated ultrafine powders mainly reside in the different requirements for prevention of fissure formation and removal of interagglomerate pores. To prevent the formation of fissures during sintering, the sintering temperature should be relatively low so that the rate of stress build-up is lower than the rate of strength build-up. At this level of sintering temperature, however, the removal of interagglomerate pores, which is possible through grain growth and pore rearrangement processes, is inhibited. The bulk density increases continuously with time without the occurrence of de-densification, but finally reaches an end-point density due to the presence of interagglomerate pores.

To remove the interagglomerate pores, the sintering temperature should be high enough so that grain growth occurs in the later stage of sintering. The reduction of coordination number for pores will cause pore rearrangement shrinkage. However, at this high temperature, it is usually observed that the formation of fissures is extensive. Furthermore, the growth of interagglomerate pores occurs long before the process of pore removal, which is caused by grain growth and pore rearrangement, becomes operative. This adds to the difficulty of removing interagglomerate pores, because it takes longer for grains to grow to what is required for pore rearrangement and shrinkage to happen. In this situation, the grain size for interagglomerate pores to shrink is much larger than that required if no pore growth has occurred. Therefore, the possibility of entrapping pores within the grains is increased. The bulk density reaches an end-point density due to pore entrapment.

There exists an optimum sintering temperature arising from the competition between densification caused by neck formation and shrinkage and de-densification caused by the formation and growth of fissures and pores. The optimum temperatures, which lie below 1100° C for alkoxide compacts and below 1250° C for oxychloride compacts, are suggested to be determined by these competition mechanisms.

There may also exist another optimum sintering temperature caused by the competition between pore shrinkage and pore entrapment, both induced by grain growth. The optimum temperature of between 1350 and 1450° C for alkoxide powder compacts is thought to be the result of such competition. As for oxychloride powder compacts, the optimum may occur at a temperature higher than 1450° C.

Even for powder compacts sintered at optimum temperatures, it is impossible to obtain full density because of the different requirements for different mechanisms to complete densification.

4.3. The effect of agglomeration

The sintering behaviours of oxychloride powders are affected very significantly by their calcination temperatures. Fig. 3 shows that not only the absolute sintered density but also its variation with sintering temperature are changed after calcining the oxychloride powder at different temperatures. The sintered bulk density against sintering temperature curve is not directly related to the calcination temperature. The powder calcined at 650° C has the highest sintered density, whereas that calcined at 600° C has the lowest sintered density. Those calcined at 550, 700 and 800° C lie between them. From TEM investigations, powders calcined at 550, 600, 650, 700 and 800° C consist of crystallites of sizes increasing with calcination temperature. Thus, it is believed that the change of sintering behaviour does not arise from differences of crystallite size. Fig. 3 shows the mean agglomerate size of powders calcined at different temperatures. It is interesting to note that the powder calcined at 650° C has the smallest mean agglomerate size, whereas that calcined at 600° C has the largest mean agglomerate size, and those calcined at 550, 700 and 800° C lie between them. Furthermore, it is interesting that the green densities of powder compacts pressed at 175 MPa are 40.5, 46.2, 40.3, 44.3 and 45.0% of theoretical density for powders calcined at 550, 600, 650, 700 and 800° C, respectively. The sintered bulk density as shown in Fig. 3 seems directly related to the green density. The lower the green density, the higher the sintered bulk density and the smaller the trend of decreasing sintered bulk density with sintering temperature.

It is not clear why increasing the calcination temperature does not result in a simple trend of agglomeration. However, it is clear that the state of agglomeration and the uniformity of powder packing affect the sintering behaviour of ultrafine powder compacts. For samples pressed at the same consolidation pressure, the green density may increase with the amount of hard agglomerate in the powder. The higher the amount of hard agglomerate, the less uniform is the packing and the more large interagglomerate pores exist. From the sintering behaviour discussed previously, all these situations cause significant fissure formation and pore growth, and thus result in a lower sintered bulk density and a higher trend of reduction of sintered bulk density with increasing sintering temperature.

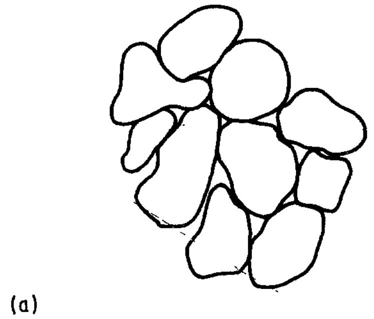
As described previously, when both powders were calcined at 600° C, oxychloride samples showed extensive pore growth during sintering at high temperatures, whereas alkoxide samples showed only a small degree of pore growth during sintering. The different sintering behaviour of these two powders can also be explained by differences in their state of agglomeration. From particle size distribution measurements (Fig. 2) it is shown that the agglomerate distribution of oxychloride powder is coarser than that of alkoxide powder if both powders are calcined at 600° C. The green density of the powder compact consolidated at 175 MPa is 46.2% of theoretical density for oxychloride powder calcined at 600° C and 38% of theoretical density for alkoxide powder. These two data in combination suggest that an alkoxide powder compact, which contains less hard agglomerates, is more uniform in its state of agglomeration than oxychloride. However, the sintered bulk densities of the alkoxide powder compacts are higher than those of the oxychloride powder compacts. The state of agglomeration seems more important than the green density in sintering highly agglomerated ultrafine powders.

4.4. The effect of consolidation pressure

For oxychloride powder calcined at 600° C, i.e. the most highly agglomerated powder investigated in this study, the effect of consolidation pressure is to change the green density. As shown in Fig. 9, an increase of consolidation pressure from 140 to 1575 MPa raises the green density, and causes a reduction of the sintered bulk density after sintering at 1450° C for 5 h. On the other hand, when the consolidation pressure decreases to 105 MPa but is followed by grinding and repressing at 105 MPa, the green density increases as compared with 140 MPa, and the sintered bulk density decreases. Therefore, it is clear that no matter how the consolidation pressure is achieved, if the consolidation raises the green density it reduces the sintered bulk density after sintering for 5 h at 1450° C. It has been shown that there is a high degree of fissure formation and pore growth during sintering in oxychloride powder calcined at 600° C and sintered at 1450° C. The increase in green density with consolidation pressure may result in a less uniform packing of agglomerate and thus more extensive pore growth and lower sintered bulk density.

Agglomerates are usually made up of smaller and more densely packed subunits, which were called "domains" by Lange [12]. Domains pack together to form an agglomerate. Fig. 11a is a schematic diagram of packed agglomerates. There are three classes of pores: (i) pores within domains, (ii) pores between domains, and (iii) interagglomerate pores. The pore size and size distribution may be described as in Fig. 11b. The effect of increasing pressure is to reduce the pore size and size distribution and to increase the green density. If the agglomerates are hard, the effect of pressure may not be to change much of the interagglomerate pore distribution, but to reduce the interdomain pores to a much higher extent by slight rearrangement and the deformation of domains. For domain pores, pressure may shift their size toward smaller pore size but not to affect their distribution too much. The effect of consolidation on the total pore size distribution of hard agglomerates may be illustrated as in Fig. 11c; the total pore size distribution changes toward a bimodal one. A bimodal pore size distribution means less uniformity in powder packing, and may enhance fissure formation and pore growth.

For alkoxide powders consolidated at 175 and 140 MPa the green densities are 38 and 31% of theoretical, respectively. The sintered bulk density against sintering temperature is illustrated in Fig. 5. Both curves show similar changes of bulk density with respect to sintering temperature, except that the bulk density curve for powder compacts consolidated at lower pressure, i.e. 140 MPa, shifts to the higher sintering temperature region. According to the previous argument, a lower consolidation pressure results in a lower green density and more uniform powder packing; it needs a higher temperature for neck formation, fissure formation and pore growth to occur, so that the whole density curve shifts toward a higher temperature region.



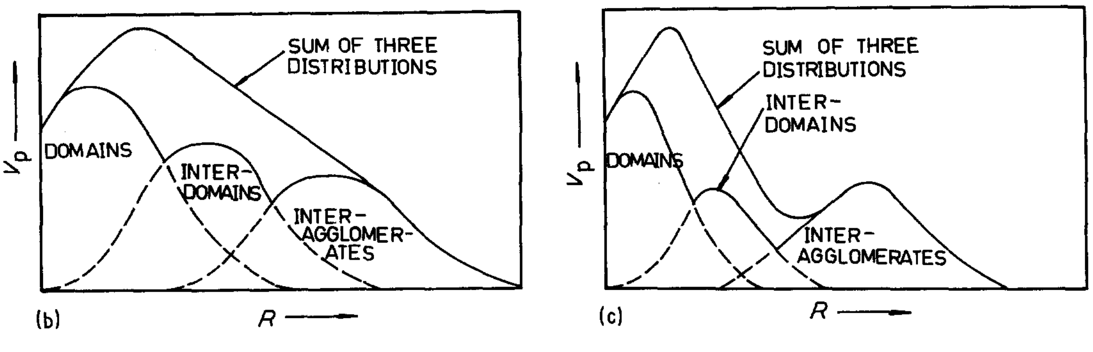


Figure 11 (a) A schematic diagram of packed agglomerate, after Lange [12]. (b) Pore volume distribution of a powder, after Lange [12]. V_p represents pore volume. (c) Change of pore volume distribution of powder compact after increasing consolidation pressure.

5. Conclusions

The sintering behaviour of highly agglomerated ultrafine zirconia powders can be described by a combination of mechanisms such as neck formation and shrinkage, fissure formation and growth, pore growth, grain growth, pore rearrangement shrinkage, and pore entrapment.

In highly agglomerated ultrafine powders, it is often found that the bulk density decreases in a certain period of time during sintering. This phenomenon can be explained by fissure formation and pore growth.

Fissure formation and pore growth can occur extensively in sintering highly agglomerated ultrafine powder, especially at high sintering temperatures. Thus a higher sintering temperature does not necessarily result in higher sintered density.

There are optimum sintering temperatures in sintering highly agglomerated ultrafine powder compacts. One is due to the competition between neck formation and shrinkage, fissure formation, and pore growth. The other is due to the competition between pore shrinkage and pore entrapment, both resulting from grain growth.

In sintering highly agglomerated ultrafine powder compacts, an increase of green density is not necessary for the sintered bulk density to increase. If an increase of green density results in a less uniform powder packing, it usually causes a decrease of sintered bulk density. Any processing parameters such as preparation method, calcination temperature and consolidation pressure which affect the state of agglomeration, the uniformity of powder packing and the green density may affect the sintering behaviour of powder compacts.

References

1. W. H. RHODES, *J. Amer. Ceram. Soc.* **64** (1) (1981) 19.
2. M. F. YAN and W. W. RHODES, *Mater. Sci. Eng.* **61** (1983) 59.
3. T. VASILOS and W. RHODES, in "Ultrafine-grain Ceramics" (Syracuse University, Syracuse, New York, 1970) p. 137.
4. P. H. RIETH, J. S. REED and Q. W. NAUMANN, *Amer. Ceram. Soc. Bull.* **55** (8) (1976) 717.
5. *Idem, ibid.* **55** (8) (1976) 727.
6. D. W. JOHNSON, D. J. NITTI and L. BERRIN, *ibid.* **51** (12) (1972) 896.
7. C. GRESKOVICH and K. N. WOODS, *ibid.* **52** (5) (1973) 473.
8. E. A. BARRINGER and H. K. BOWEN, *J. Amer. Ceram. Soc.* **65** (12) (1982) C199.
9. K. HABERKO, *Ceram. Int.* **5** (1979) 148.
10. K. D. REEVE, *Amer. Ceram. Soc. Bull.* **42** (8) (1963) 452.
11. W. D. KINGERY and B. FRANCOIS, in "Sintering and Related Phenomena" (Gordon and Breach, New York, 1967) p. 471.
12. F. F. LANGE, *J. Amer. Ceram. Soc.* **67** (2) (1984) 83.
13. F. W. DYNYS and J. W. HALLORAN, *ibid.* **67** (9) (1984) 596.
14. G. C. KUCZYNSKI, *Trans. AIME* **185** (1949) 169.
15. N. CABRERA, *ibid.* **188** (1950) 667.
16. W. D. KINGERY and M. BERG, *J. Appl. Phys.* **25** (1955) 1205.
17. R. L. COBLE, *J. Amer. Ceram. Soc.* **41** (2) (1958) 55.
18. *Idem,* "Kinetics of High Temperature Processes" (Wiley, New York, 1958) p.147.
19. D. L. JOHNSON and I. B. CUTLER, *J. Amer. Ceram. Soc.* **46** (11) (1963) 541.
20. D. L. JOHNSON, *J. Appl. Phys.* **40** (1969) 192.
21. R. L. COBLE, *ibid.* **41** (1970) 4798.
22. H. E. EXNER, *Rev. Powder Metall. Phys. Ceram.* **1** (1–4) (1979) 1.
23. T. K. GUPTA and R. L. COBLE, *J. Amer. Ceram. Soc.* **51** (9) (1968) 525.
24. B. FRANCOIS, R. DELMAS, G. CIZERON and W. D. KINGERY, *Mem. Sci. Rev. Met.* **64** (1967) 1079.
25. T. K. GUPTA, *J. Amer. Ceram. Soc.* **55** (5) (1972) 276.

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