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Effect of agglomerates in ZrO_2 powder compacts on microstructural development

J. L. SHI, J. H. GAO, Z. X. LIN, D. S. YAN
Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding Xi Road, Shanghai 200050, Peoples' Republic of China

Ultrafine zirconia powders were prepared by a coprecipitation and spray-drying method. Agglomerates may be fragmented or present in green bodies after compaction. The effect of agglomerates on sintering and microstructural development was studied and it was found that the agglomerate content in compacts was a major factor affecting the microstructure development and the sintered densities. The interaction between agglomerates themselves, and between agglomerates and the primary particle matrix is discussed. It is argued that the hard agglomerates in the powder from the water-washed coprecipitates are formed by oxo-bridging between non-bridging hydroxyl groups present in the zirconium hydroxide structures due to the effect of hydrogen bonding in the aqueous system. The substitution of organic –OR groups for the non-bridging hydroxyl groups removes this hydrogen-bonding effect between the zirconium hydroxide units and thus eliminates the cause of agglomeration.

1. Introduction

Powders of very fine particle size do not always show good sinterability as predicted by the classic sintering theories [1–4], because of the formation of agglomerates in the fine powders. The effects of agglomeration on sintering and microstructural development have been extensively reported in the literature [5–7], and it has been proposed that they may be classified into two categories, namely the interaction between agglomerates when the agglomerate content in a powder compact is high (all primary particles are agglomerated) and interaction between agglomerates and the primary particle matrix when the agglomerate content is low. The effect of the interaction between agglomerates has been discussed by Lange [8] theoretically, and by Shi *et al.* [9] through careful experimentation. The interaction between agglomerates has also been discussed by Lange and Metcalf [10] theoretically and schematically, but in Lange's experiments, only deliberately prepared large agglomerates of several millimetres in size were embedded in the primary particle matrix, and so the conclusions drawn are not totally relevant to real systems. In the present study, zirconia powders having very fine particle sizes were prepared by different treatments to develop naturally different contents of agglomerates, and the sintering behaviour of these powders was investigated and discussed.

2. Experimental procedure

Superfine, fully stabilized cubic zirconia(+ 7 mol % yttria) powders were prepared by a coprecipitation and spray-drying method using zirconium oxychloride and yttria as starting materials in the manner described elsewhere in detail [11]. The powders used in the experiments were obtained by different treatments of the coprecipitates. The P-0 powder was prepared using only distilled water washing, whilst the P-2 and P-6 powders were obtained with ethanol washing two or six times following the water washing, respectively. The P-0 and P-6 powders are expected to contain hard and soft agglomerates, respectively, and the P-2 powder may have a complicated response to agglomeration behaviour during compaction. Powders were calcined at from 420–1000 °C for 25 min.

The sintering behaviour of these green samples was studied by determining the pore-size distributions and sintered densities of the bodies at different stages of sintering, as well as microstructural observation with the SEM. The pore sizes of the compacts and the sintered bodies were measured by mercury-porosimetry (Model 9210) and found to lie in the range 30 μm–3 nm. The agglomerate contents in the compacts were recalculated from the pore-size distribution data on the basis of separate pore-size distribution ranges corresponding to the agglomerates and primary particles [12].

3. Results

3.1. Pore-size distribution and agglomerate content before and after compaction

3.1.1. Pore-size distribution in powders

Fig. 1 shows the typical pore-size distribution of the spray-dried zirconia powder calcined at 600 °C. Three types of pore are present in the powder: (a) inter-primary particle pores of size < 0.1 μm, (b) inter-agglomerate pores in the range 0.1–5 μm and (c) the largest pores (inter-secondary agglomerate pores) of 5–35 μm. The presence of agglomerates in the powder

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is clearly shown. As all very fine primary particles (10–40 nm [12]) can be made into agglomerates by spray-drying, it can be assumed that the agglomerate content in the spray-dried powders is close to 100%.

3.1.2. Compaction behaviour of powder P-2

The P-2 powders (obtained by ethanol washing twice) calcined at different temperatures were compacted at 100 MPa and their pore-size distributions determined as shown in Fig. 2. The pore-size distributions of the compacts differ appreciably from those of the powders. This is evident mainly from the elimination of inter-secondary agglomerate pores and by the reduction in inter-agglomerate pore size and volume, as is also shown in Fig. 3. Assuming that the initial powder is 100% agglomerated, the agglomerate contents in the compacts from powders were calculated from pore-size distribution data and are given in Table I. The data shown in the table indicate that the agglomerate contents at and below 800 °C are less than 25%, while the content is 100% at 1000 °C.

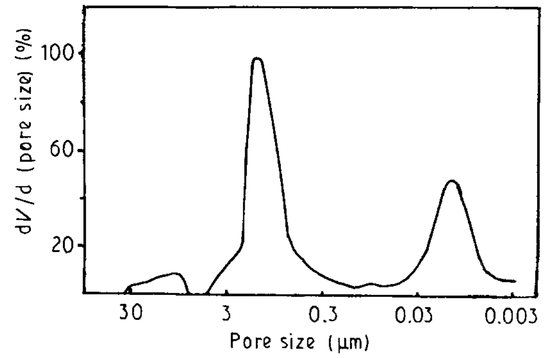


Figure 1 Pore-size distribution of the spray-dried powder P-2 calcined at 600 °C.

Fig. 4 shows the pore-size distributions of P-2 powder at different pressures, and Fig. 5 shows the relation between agglomerate content and pressure. Agglomerate content decreases rapidly with increasing pressure and approaches zero at 200 MPa implying complete elimination of agglomerates. It can be seen that inhomogeneity (large pores in the compacts) occurs at 500 MPa of the inhomogeneous distribution of the compaction stresses in the green sample during uniaxial dry-pressing, although the inter-agglomerate pores have been eliminated at that pressure.

3.1.3. Compaction behaviour of powders P-0 and P-6

The pore-size distributions of powder P-0 and P-6 compacts at 100 MPa are shown in Fig. 6. It can be seen that washing the precipitates six times leads to the formation of soft agglomerates in the powder which are fragmented completely at a pressure as low as 100 MPa. In contrast, the agglomerates in only water-washed and spray-dried powder, P-0, are hard and basically unaffected at a pressure of 100 MPa (nearly 100% agglomerated), and are apparently still not affected even at 500 MPa.

TABLE I The agglomerate content, C_{agg}, in the compacts of the powder P-2 calcined at different temperatures

	Calcination temperature (°C)			
	420	600	800	1000
C_{agg} (vol %)	8.80	19.0	21.1	100[a]

[a]Calculated value is 122%, but 100% is used.

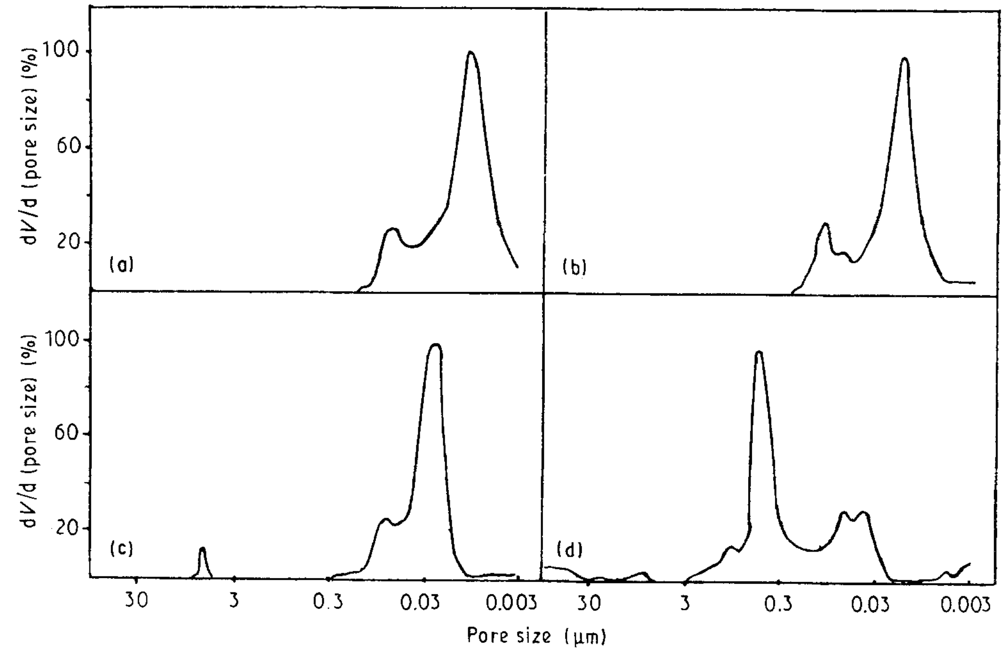


Figure 2 Pore-size distributions of the compacts at 100 MPa for powder P-2 calcined at (a) 420, (b) 600, (c) 800 and (d) 1000 °C.

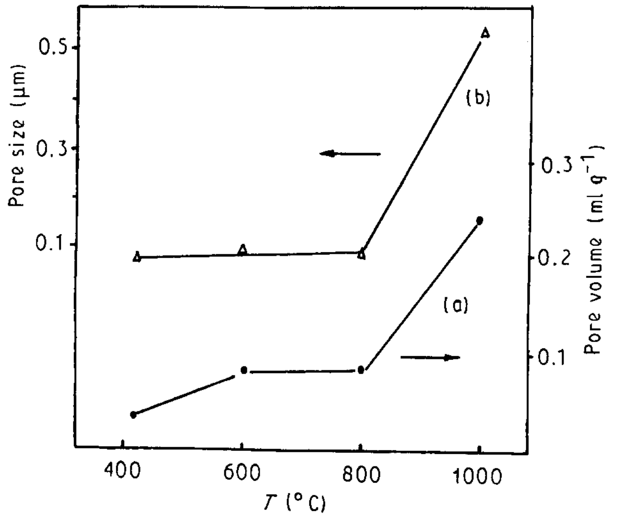


Figure 3 Temperature dependence of (a) inter-agglomerate pore volume and (b) the pore size in P-2 powder compacts at 100 MPa.

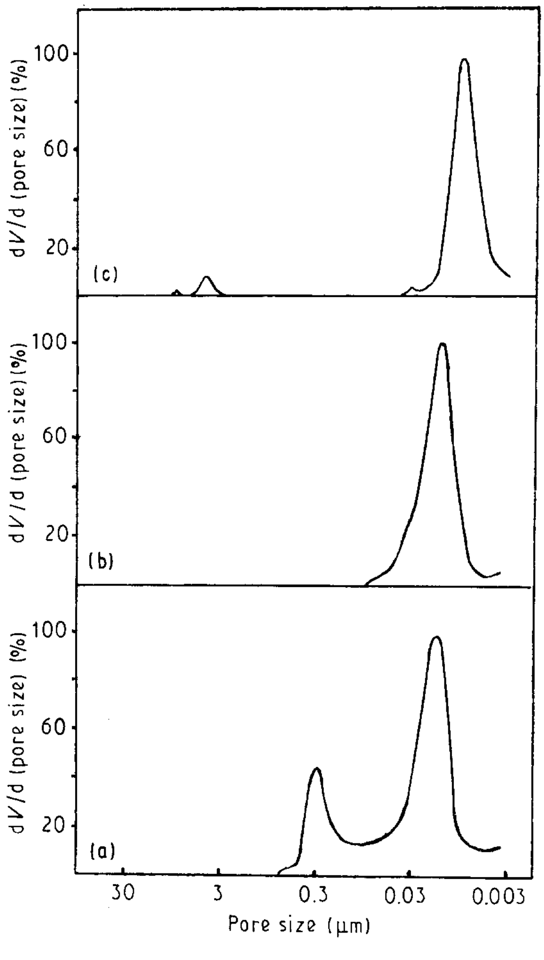


Figure 4 Pore-size distributions of P-2 powder compacts formed at (a) 50, (b) 200, (c) 500 MPa (calcined at 600 °C).

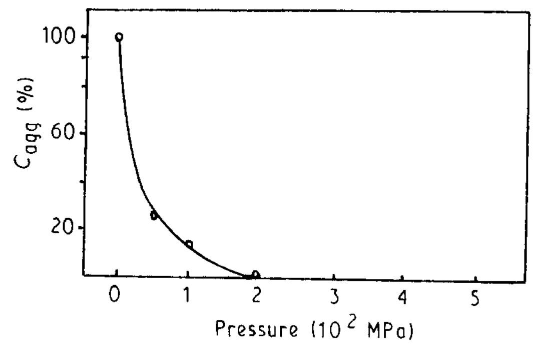


Figure 5 Agglomerate content as a function of compaction pressure for P-2 powder calcined at 600 °C.

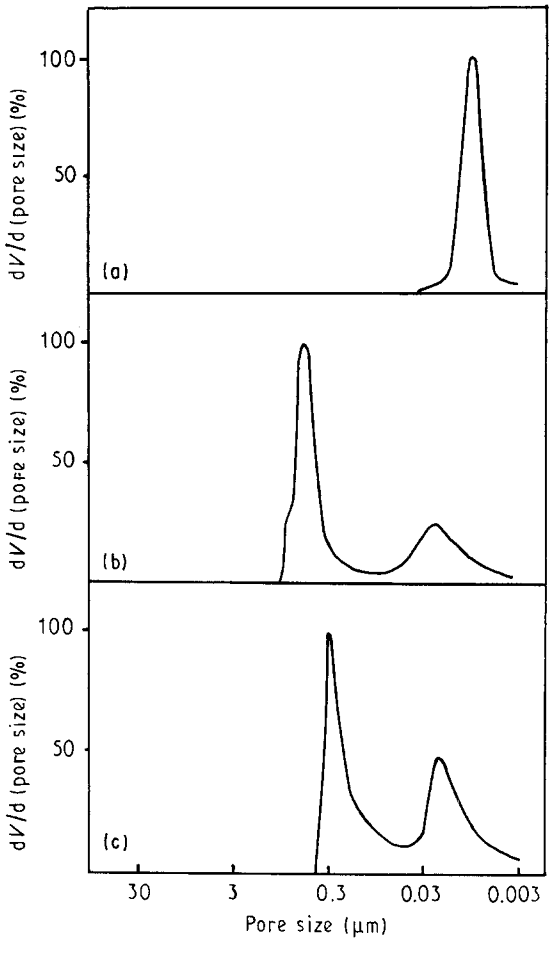


Figure 6 Pore-size distributions of the powder compacts of (a) P-6 at 100 MPa; (b) P-0 at 100 MPa, and (c) P-0 at 500 MPa.

3.2. Sintering behaviour and microstructure of P-2

3.2.1. Pore-size distributions in sintered bodies

Pore-size distributions (for open pores only) of the sintered bodies from powder P-2 calcined at 600 °C and compacted at 100 MPa at different sintering temperatures are shown in Fig. 7. Two peaks in the distributions appear in the body sintered at 1100 °C: one for the larger size range (secondary pores) and another for the smaller size (primary pores), both grew to larger sizes after sintering at 1100 °C. Grain growth during densification is responsible for the growth of the primary pores; and larger secondary pores may not be affected at such a low temperature so the enlargement of secondary pores is due to the densification of agglomerates. As sintering proceeds at higher temperatures, 1250 and 1400 °C, the secondary pores remain but their volume decreases, and the primary pores are diminished substantially as shown

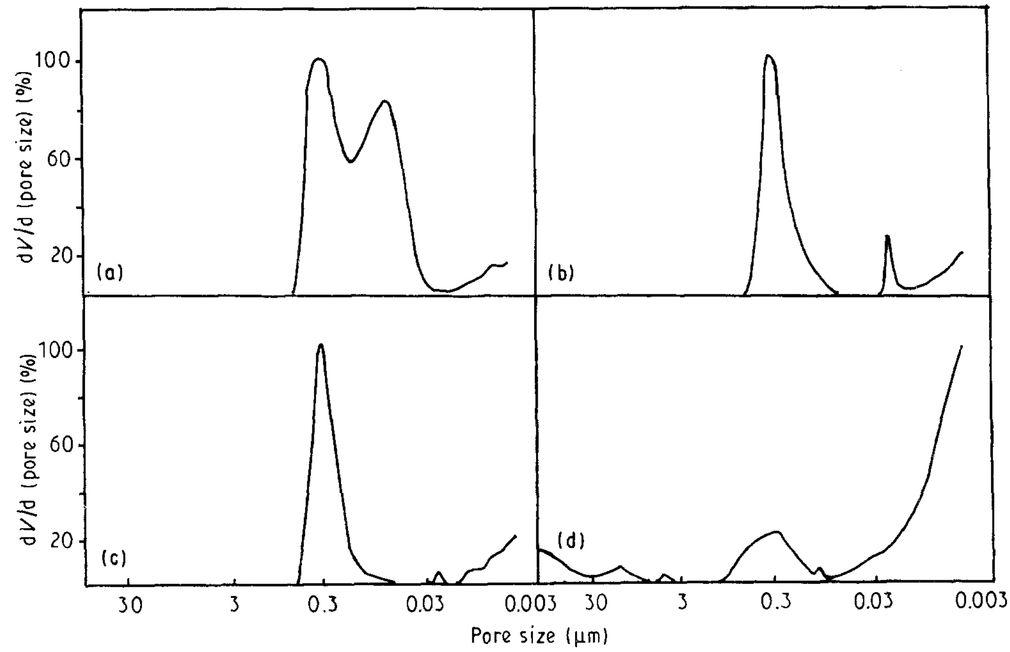


Figure 7 Pore-size distributions of the sintered bodies at (a) 1100, (b) 1250, (c) 1400 and (d) 1600 °C, of P-2 powders (calcined at 600 °C) compacted at 100 MPa.

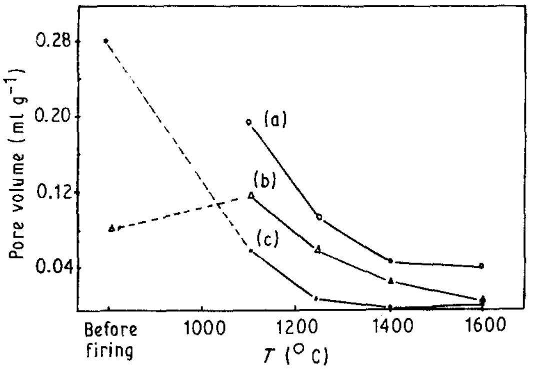


Figure 8 Pore volume versus sintering temperature for P-2 powder compacts (600 °C, 100 MPa): (a) total pore volume; (b) inter-agglomerate pore volume; and (c) inter-primary particle pore volume.

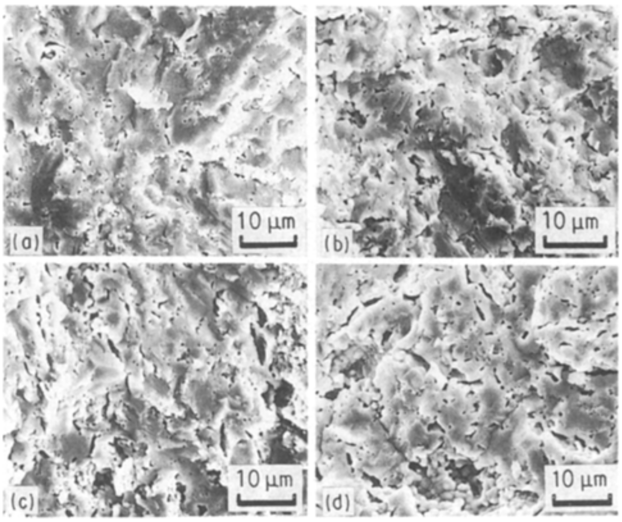


Figure 9 Microstructure of the fractured surfaces of the sintered bodies at 1600 °C for P-2 powder calcined at (a) 420, (b) 600, (c) 800 and (d) 1000 °C formed at 100 MPa. Densities: (a) 5.80 g cm^{-3}, (b) 5.75 g cm^{-3}, (c) 5.57 g cm^{-3}, (d) 5.42 g cm^{-3}.

in Fig. 8 by their volume. At 1600 °C, the pore-size distribution shows both diminution of secondary pores and the generation of very small pores and large pores of about 10 μm, but the total pore volume is not changed basically.

3.2.2. Microstructural development as a function of calcination temperature

Microstructures of sintered bodies at 1600 °C for the powders P-2 calcined at various temperatures from 420–1000 °C are shown in Fig. 9. The agglomerate contents in the compacts increase with increasing calcination temperature, and lead to increasing pore content and pore size in the sintered bodies, as observed in Fig. 9. Powder calcined at low temperatures (420 °C, for example) shows smaller and some round pores in the sintered sample but those at higher temperatures give larger and crack-like pores in addition to the smaller and round ones, corresponding to the inhomogeneity in the compacts (800 and 1000 °C, Fig. 2). The microstructures of the sintered bodies are related to the agglomerate content in the compacts. High agglomerate contents in compacts may lead to the retarded densification because of the high content and large size of the secondary pores, thus resulting in high porosity and large pore size in sintered samples. The sintered densities for each temperature are also shown in Fig. 9.

3.2.3. Effect of forming pressure

As illustrated in Fig. 10, at 50 MPa, because a considerable amount of large secondary pores remains in the sample, the sintered microstructures reflect such a feature leading to low density, as shown in Fig. 10. At 200 MPa, all agglomerates are fragmented with no secondary pores left in the green sample, so no crack pores are observed. Compaction at a rather high pressure, 500 MPa, results in inhomogeneity in the green sample and the formation of large cracks in sintered samples with lower density.

3.3. Sintering behaviour and microstructure of powders P-0 and P-6

Powder compact containing no agglomerates at 100 MPa (P-6) is very sinter reactive and a density of 97.5% theoretical is reached at 1250 °C, 2 h, as shown by its microstructure in Fig. 11a, but that containing large amounts (almost 100%) of hard agglomerates (P-0) is not densified effectively even at 1600 °C (about 80% theoretical), and the large inter-agglomerate pores are not removed, as illustrated in Fig. 11b, below.

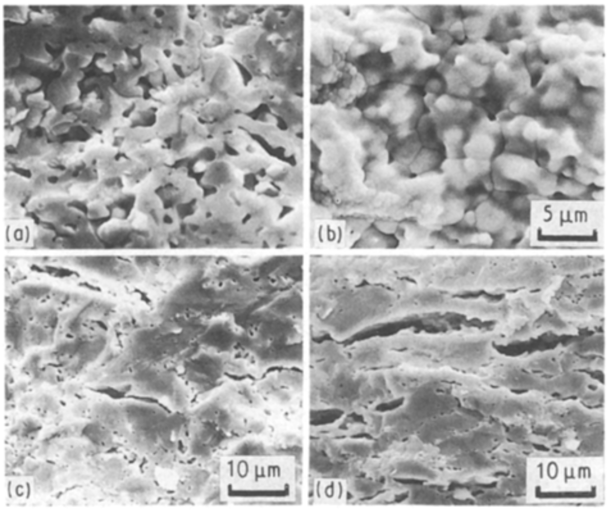


Figure 10 Microstructure of the fractured surfaces of the sintered bodies at 1600 °C for P-2 powder (600 °C) compacted at (a) 50, (b) 200, (c) 320 and (d) 500 MPa. Densities: (a) 5.30 g cm^{-3}, (b) 5.70 g cm^{-3}, (c) 5.58 g cm^{-3}, (d) 5.20 g cm^{-3}.

4. Discussion

4.1. Effect of agglomerates on microstructural development

It has been shown that the compacts of the powder P-2 calcined at 1000 °C and P-0 at 600 °C are composed of 100% agglomerates and the pores formed after sintering are the results of the interaction between agglomerates, as illustrated in Fig. 11b; a large amount of inter-agglomerate pores remaining in the microstructure after sintering, are difficult to remove because of their larger sizes. No interaction between agglomerates and primary particle matrix occurs in them.

For powder P-2 calcined at and below 800 °C, the agglomerate content is less than 25% after compaction at 100 MPa with also a much smaller secondary pore size. Because of this low agglomerate content, the interactions between agglomerates and primary particle matrix play a significant role affecting the microstructure development during sintering in addition to the possible interaction between agglomerates. The secondary pores persist at 1400 °C while the primary pores are practically eliminated, as shown in Fig. 7. By 1600 °C most secondary pores are eliminated while the remaining pores in the range 0.1–5 µm and the large pores at about 10 µm occurring in the sintered body resulting from the interaction between agglomerates and matrix are difficult to remove.

Compacts obtained at 200 MPa of P-2 and 100 MPa of P-6 contain no secondary pores, so no interactions either between agglomerates themselves or between agglomerates and the matrix occur during sintering. The microstructures formed are free from crack-like pores and the sintered densities are high, especially for P-6 powder which can be sintered at only 1250 °C.

Fig. 12 is a schematic drawing illustrating the effect of agglomerates in compacts on microstructure development. Non-agglomerated powder compacts (Fig. 12a) densify much faster than agglomerated powder compacts, partially agglomerated ones of relatively small inter-agglomerate pore size (Fig. 12b) need high temperature for the removal of such pores, and totally agglomerated ones of relatively large inter-ag-

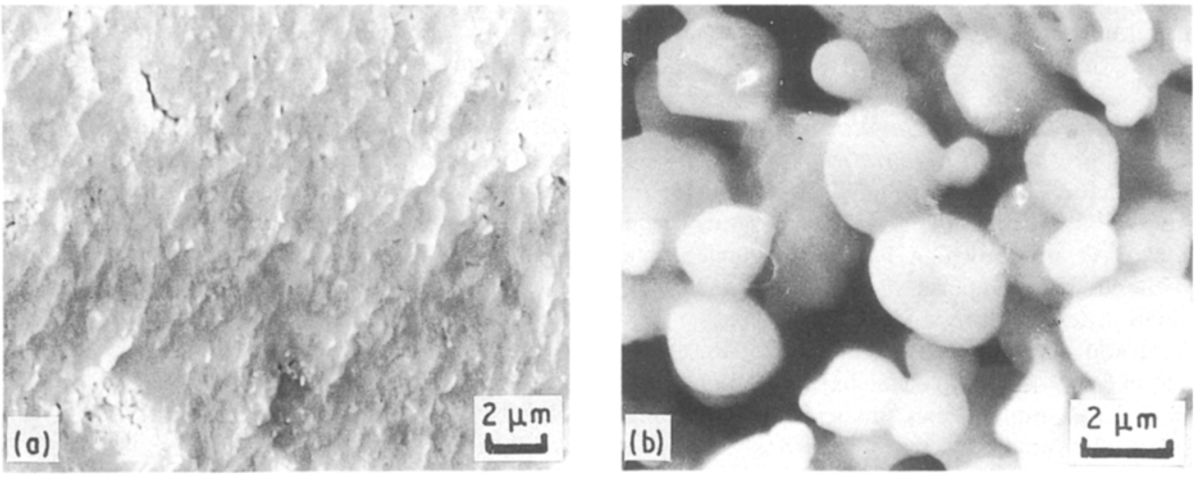


Figure 11 Microstructure of the fractured surfaces of (a) P-6, 600 °C, 100 MPa, sintered at 1250 °C and (b) P-0, 600 °C, 100 MPa, at 1600 °C.

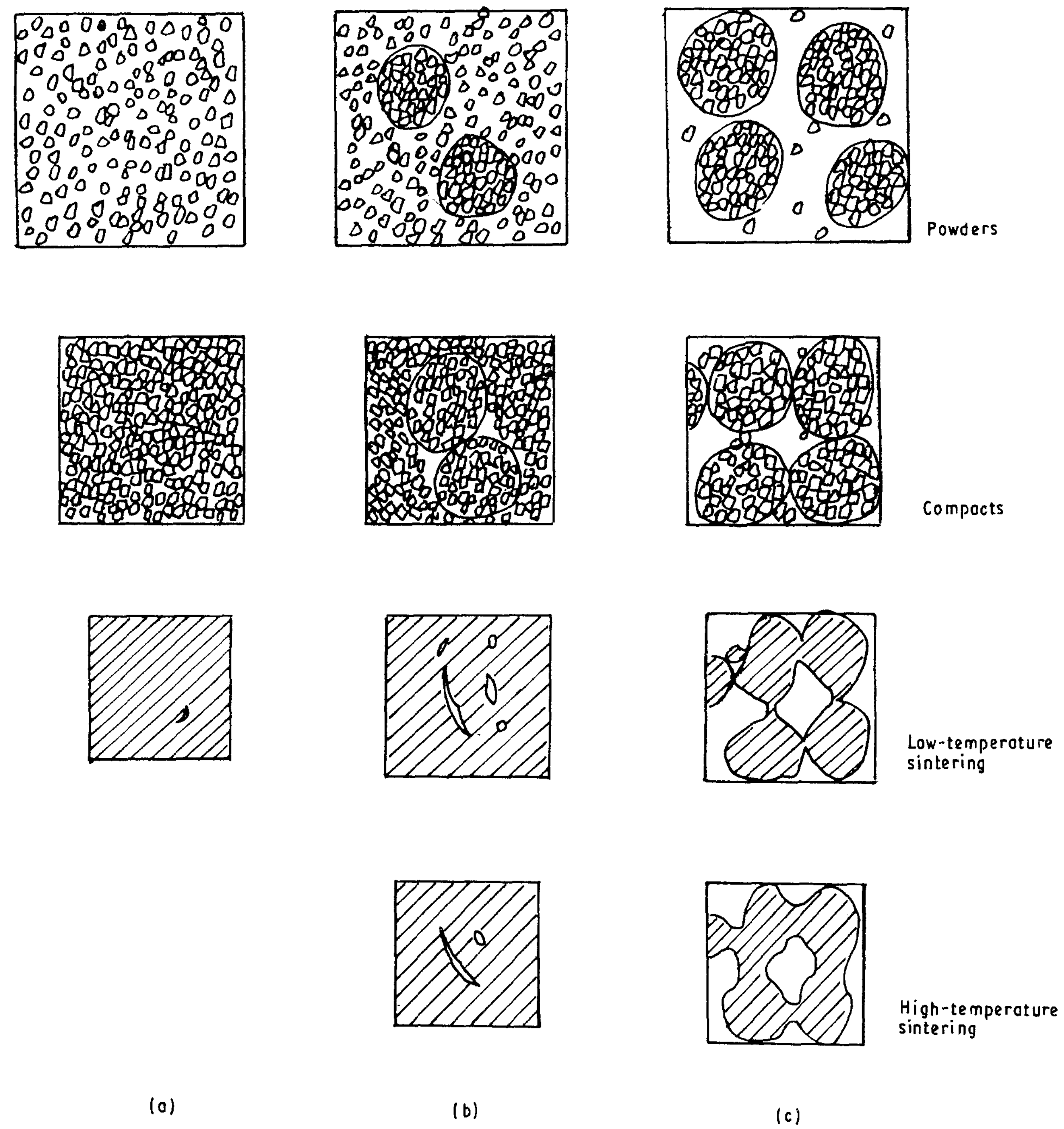
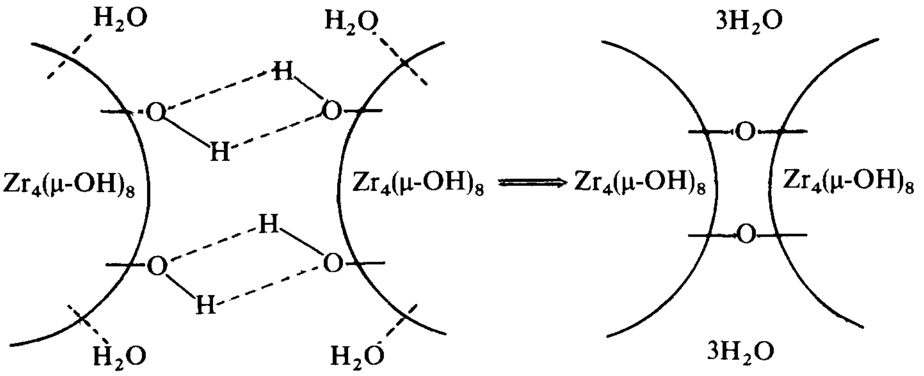


Figure 12 Schematic drawings of the processes of agglomerate influence on the microstructural development for (a) non-agglomerated powder compacts, (b) partially agglomerated compacts and (c) fully agglomerated compacts.

glomerate pore size (Fig. 12c) can only develop porous microstructures even at high enough temperatures.

4.2. Formation of hard agglomerates for the coprecipitated powder

The effect of the agglomerates in water-washed coprecipitates of zirconia powders has been proposed to be due to the loss of hydroxyl groups in the zirconium hydroxide structure (the structure has been proved to be: $[Zr_4(\mu\text{-OH})_8(OH)_8 \cdot nH_2O] \cdot mH_2O$, μ-OH is an unremovable oxo-bridging structural hydroxyl group between zirconium atoms, OH is the non-bridging structural hydroxyl group, nH_2O is the chemically coordinated water and mH_2O is physisorbed water), by Jones and Norman [13] and due to the hydrogen bonding between the chemically coordinated water on zirconium hydroxide particle surfaces by Readey and Lee [14]. The effect of the ethanol washing on the agglomeration and sintering behaviour discussed recently by Kaliszewski and Heuer [15] is to remove such coordinated water. The present authors believe that agglomerates so formed are still not hard because the loss of the chemically coordinated water may not cause the formation of strong oxo-bridging between zirconium hydroxide particles only by nature of the relatively high surface tension of water. The essential agglomeration occurs during the process of the formation of oxo-bridging between the non-bridging hydroxyl groups in the zirconium hydroxide structures [13], due to the effect of the hydrogen bonding between non-bridging hydroxyl groups in the structure unit



Such a loss of non-bridging hydroxyl groups can lead to the substantial oxo-bridging between the zirconium hydroxide structure units and the strong agglomeration during calcination and between zirconia particles. The substantial number of –OR groups for the hydroxyl groups and other water components like chemically coordinated water and physisorbed water [13] in the molecular structures can change the hydrous zirconium structure into $[Zr_4(\mu\text{-}OH)_8(OR)_8 \cdot nROH] \cdot mROH$ and clear up the hydrogen bonding between the structure units and made the coprecipitates closer to the zirconium alkoxide $[Zr(OR)_4] \cdot mROH$ in nature. So the substitution of –OR groups for the non-bridging –OH is the key process in the prevention of strong agglomeration [16], because the decomposition of –OR group is accompanied by a carbonation and oxidation (burning) process, as observed by the one of the authors.

5. Conclusion

Agglomerate content and size in the powder are important factors in microstructural development and densification. The oxo-bridging between non-bridging hydroxyl groups in zirconium hydroxide structure units is believed to be the cause of hard agglomerates. The complete alcohol substitution of –OR groups for non-bridging –OH can lead to the formation of soft agglomerate and agglomerate-free compacts at 100 MPa, while only water-washed powder contains hard agglomerates unfragmented even at 500 MPa. Lower temperature calcination of the zirconia powder partially washed with alcohol in the coprecipitates favours lower agglomerate contents and smaller inter-agglomerate pore sizes, and thus leads to finer microstructures and higher sintered density than the powder calcined at higher temperatures. Inter-agglomerate interaction is the major factor affecting sintering when the agglomerate content is high, resulting in porous microstructures. Interactions between agglomerates and the primary particle matrix led to the formation of crack-like voids in microstructures when the agglomerate content was low. These factors have to be taken into account when considering the microstructure and properties of the final sintered bodies.

References

1. G. C. KUCZYUSKI, N. A. HOOTON and C. F. GIBSON (Eds), "Sintering and Related Phenomena" (Gordon and Breach, New York, 1967).
2. G. C. KUCZYUSKI (Ed.), "Sintering and Related Phenomena", Materials Science Research, Vol. 6 (Plenum Press, New York, 1973).
3. W. D. KINGERY (Ed.), "Ceramic Fabrication Processes", Part IV (Technology Press Cambridge, MA, Wiley, New York, 1958).
4. R. L. COBLE, *J. Appl. Phys.* **32** (1961) 787.
5. D. E. NIESZ and R. B. BENNETT, in "Ceramic Processing Before Firing", edited by G. Y. Onada Jr and L. L. Hench (Wiley, New York, 1978) pp. 63–71.
6. J. S. REED, T. CARBONE, C. SCOTT and S. LUKERIEWISA, in "Processing of Crystalline Ceramics", edited by H. Palmour III, R. F. Davis and T. M. Hare (Plenum, New York, 1987) pp. 171–180.
7. W. H. RHODES, *J. Amer. Ceram. Soc.* **64** (1981) 19.
8. F. F. LANGE, *ibid.* **65** (1982) 83.
9. J. L. SHI, J. H. GAO, Z. X. LIN and T. S. YEN, *ibid.* **74** (1991) 994.
10. F. F. LANGE and M. METCALF, *ibid.* **68** (1985) 369.
11. J. L. SHI, J. H. GAO and Z. X. LIN, *J. Chinese Ceram. Soc.* **17** (1989) 417.
12. J. L. SHI, PhD thesis, Shanghai Institute of Ceramics (1989).
13. S. L. JONES and C. J. NORMAN, *J. Amer. Ceram. Soc.* **71** (1988) C-1909.
14. M. J. READEY, R. R. LEE, J. W. HALLARAN and A. H. HEUER, *ibid.* **72** (1990) 1499.
15. M. S. KALISZEWSKI and A. H. HEUER, *ibid.* **73** (1990) 504.
16. K. HABERKO, *Ceram. Int.* **5** (1979) 148.

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