

Change of internal/pore structure in alumina green body during initial sintering

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A novel characterization method was applied to study the morphological changes of large pores in a ceramic green body during the early stage of densification at 1100 °C for 1–64 h. Large processing pores were present in the green body. They were preserved after densification up to a relative density of 83.9% with their shape and size unchanged significantly. The pore size distribution determined by mercury porosimetry showed the growth of matrix pores of small size, but failed to show the change of large processing pores with densification.

1. Introduction

In the sintering process, pores located in the green body are believed to change their shape, size and concentration [1]. Those that survive become flaws in the sintered body, and behave as the origin of brittle fracture of ceramics. Since the stress to initiate brittle fracture is inversely proportional to the one-half power of the size of pore [2], the reduction of pore size is very important for developing strong ceramics. The reduction in the concentration of pores is also very important. It reduces the probability of fracture under a given stress, and contributes to the improvement of average strength.

A full understanding of the behaviour of large processing pores during sintering is very important. Although the achievement of uniform ceramic green bodies free from large pores is one of the most important objectives in the processing of ceramics [3, 4], virtually all green bodies available today contain a significant concentration of large processing pores. Their behaviour during sintering has been discussed in terms of interfacial energy and the particle configuration surrounding them [5, 6]. The important conclusion reached is that a pore larger than a certain critical size is stable and cannot be removed by sintering. However, there has been little experimental study on this subject.

A full understanding of the behaviour of large pores seems to have been very difficult, due to the obstacles encountered in their characterization. Large pores are characteristically of low concentration, and their direct examination has been almost impossible due to the lack of an adequate analytical tool [7]. Currently available techniques with high resolution do not provide information on features of low concentration, and those adequate for examination of a large volume do not have a high resolution. Commercially available non-destructive methods are only applicable for characterizing large pores with a size under 50 µm which are located in green and partially sintered

bodies. The difficulty increases further in the high-performance ceramics, in which the size and concentration of pores are reduced.

Our new characterization method can remove this difficulty encountered in studying the behaviour of large pores during sintering. In this method, porous opaque specimens are made transparent by an immersion liquid which has a refractive index close to that of the solid phase [8, 9]. The internal structure has been characterized in great detail with a traditional transmission optical microscope, and clear images of processing pores in ceramic green bodies have been reported [10, 11].

The objective of this study was to directly examine the morphological changes of internal/pore structure of a ceramic green and/or sintered body in the initial sintering. Green bodies formed by the powder compaction process were used as models. To provide additional information for the expected unique results, the green and sintered bodies were also examined with conventional SEM and mercury porosimetry. The specimen powder granules used in this study are known to have excellent sintering characteristics and can produce high-strength translucent material by sintering at a temperature as low as 1300 °C. Nevertheless, the present result will show the presence of many large pores. Although these pores left in the sintered body are expected to be smaller than those made with conventional powders, they clearly behave as fracture origins. One of the important insights obtained in this study is that even in one of the best powders currently available, large processing pores are present, and there is still much room for improvement for higher strength in alumina ceramics.

2. Experimental procedure

Active alumina powder granules (TM-DS, Taimei Kagaku, Japan) were used as a starting material. The granules were mould-pressed into pellets

(10 mm ϕ \times 4 mm) at 10 MPa and isostatically pressed at 20 or 300 MPa. For binder removal, the specimen was heated to 600 °C at a heating rate of 1 °C min⁻¹ and kept at this temperature for 2 h in air. The specimen was then sintered at 1100 °C for 1–64 h in air. For examination by the immersion liquid technique, the centre region of the specimen was ground into a thin slab (0.3 mm thick) with sandpaper. After being immersed in bromonaphthalene and made transparent, the slab was examined with an optical microscope (Optiphot, Nikon) in the transmission mode. The fractured surfaces of specimens were also examined by SEM (JSM-T100, Jeol). The pore size distributions of green and sintered bodies were determined with a mercury porosimeter (Model 9310, Micrometrics, USA). Specimens of 2–3 g were dried at 120 °C for 12 h and evacuated for 1 h before measurement. The pore size range of 0.006–60 μ m was examined in 60 steps.

3. Results

Fig. 1 shows observation by the liquid immersion technique of the internal/pore structure of a specimen formed at 20 MPa and sintered for various times. This forming pressure is obviously much lower than that applied in the commercial production of ceramics, but was chosen to demonstrate the presence of abnormally large pores of high concentration. The green body contained many crack-like voids and round features. They are believed to be originated by incompletely fractured granules. In the specimen sintered for 1 h, many crack-like voids are left at the junctions of three granules. Their widths were rather increased and their edges became dull during the densification. Meanwhile, the round feature became less noticeable. In the specimen sintered for 64 h, however, almost no further change was found in the features. Large pores are not eliminated by the densification at least to this stage.

Fig. 2 shows a similar observation for the specimen formed at 300 MPa. This pressure is approximately equal to or even slightly higher than that applied in the commercial production of ceramics. The concentration of pores is much lower than in the previous specimen, and the round feature of complete shape is not found; only a part of the round feature is present in the green body. Nevertheless, many crack-like features are still present at junctions of three granules in this specimen. In addition, spotted features are also found. They are believed to correspond to small isolated pores. The specimen sintered for 1 h has approximately the same structure as the green body. In the specimens sintered for 16 and 64 h, although the observed optical image became less sharp (due probably to the increased light scattering at particle boundaries), crack-like pores are visible. Their size and concentration are not changed markedly from those of the green body.

Fig. 3 shows the cumulative pore volume determined by mercury porosimetry for specimens formed at 20 MPa and sintered for various periods. The majority of pores have a size of 0.1–0.04 μ m in the

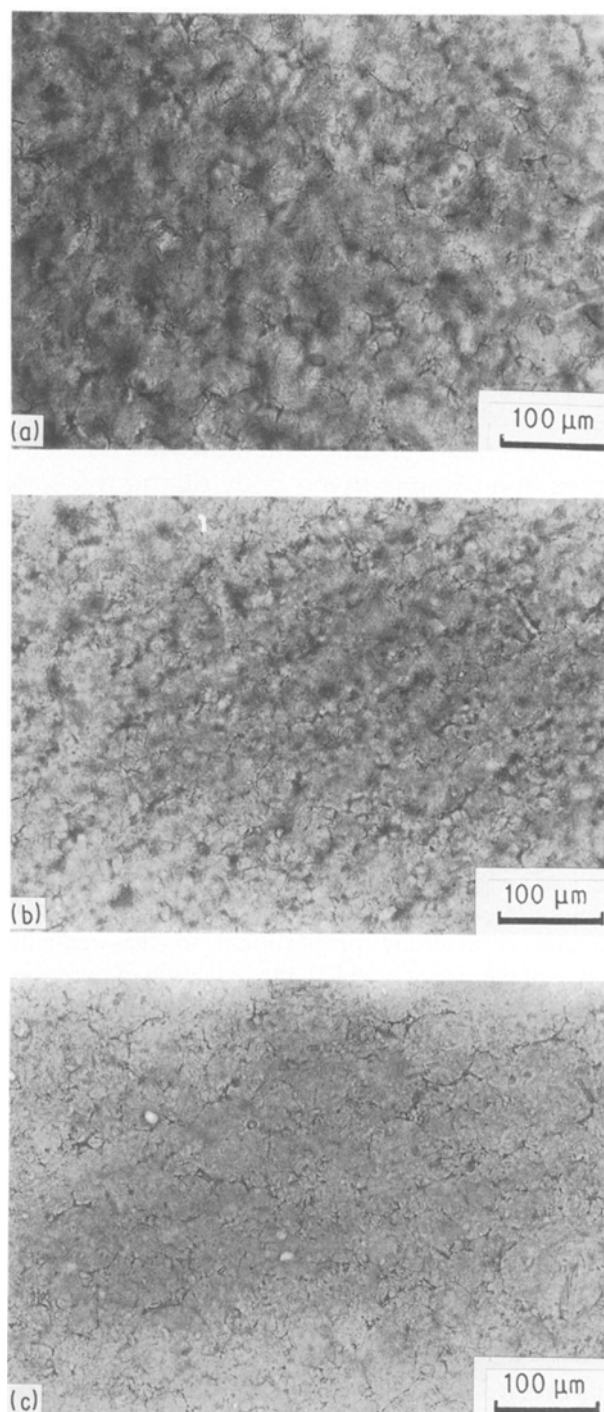


Figure 1 Internal/pore structure of specimens formed at 20 MPa and sintered for various times: (a) green body (RD = 53.7%), (b) sintered body, 1 h (RD = 62.7%), (c) sintered body, 64 h (RD = 72.7%).

green body. Very large pores with size over 0.1 μ m are clearly present, but their total volume is very small. After sintering, these very large pores cannot be detected; they have apparently been removed. With increasing sintering time, the total pore volume decreased and the most frequent pore size increased. At a sintering time between 16 and 64 h, the total pore volume was not changed significantly. However, the most frequent pore size increased markedly.

Fig. 4 shows the cumulative pore volume for specimens formed at 300 MPa and sintered for various periods. Pores with a size over 0.06 μ m were not found

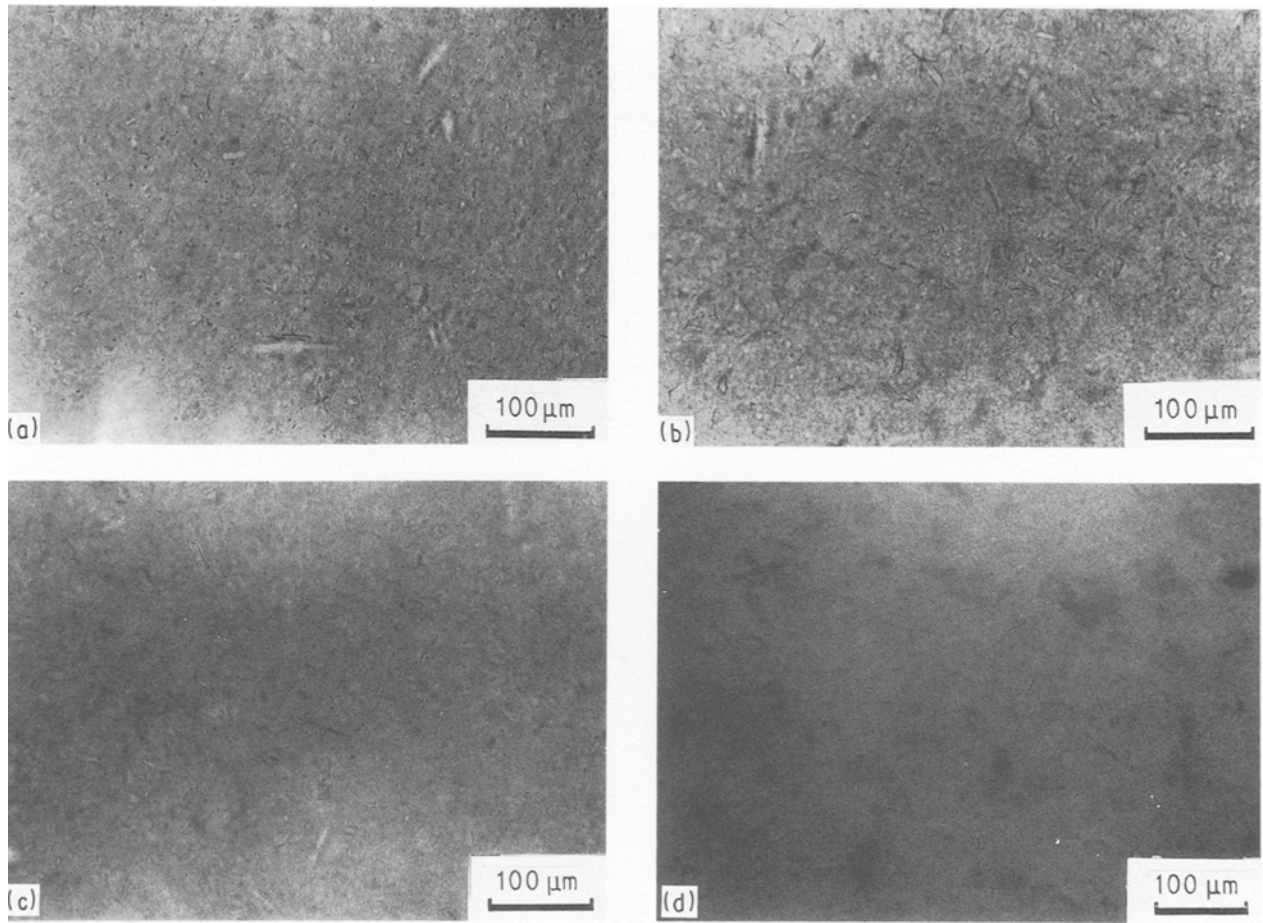


Figure 2 Internal/pore structure of specimens formed at 300 MPa and sintered for various times: (a) green body (RD = 59.3%), (b) sintered body, 1 h (RD = 67.6%), (c) sintered body, 16 h (RD = 75.1%), (d) sintered body, 64 h (RD = 83.9%).

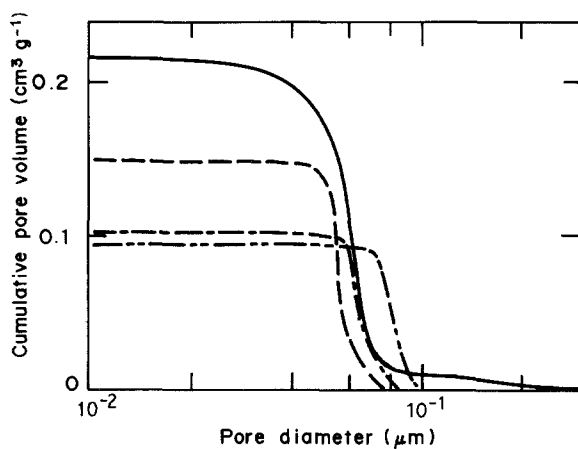


Figure 3 Pore size distributions determined with mercury porosimetry for specimens formed at 20 MPa and sintered for various times: (—) green, (---) 1 h, (- - -) 16 h, (· · ·) 64 h.

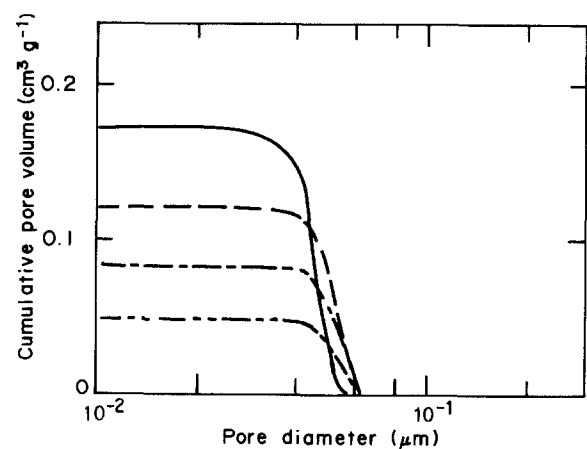


Figure 4 Pore size distributions determined with mercury porosimetry for specimens formed at 300 MPa and sintered for various times: (—) green, (---) 1 h, (- - -) 16 h, (· · ·) 64 h.

in these specimens. The majority of pores have a size between 0.04 and 0.05 μm in the green body, and 0.05 and 0.06 μm in all sintered specimens. The pore size increased slightly in the initial sintering period, but remained almost constant thereafter at this forming pressure.

Fig. 5 shows SEM micrographs of specimens formed at 20 MPa and sintered for various periods. In the green body, the fracture surface shows rounded features. They clearly correspond to the granules used for

the preparation of the present specimens. These features decreased with increasing sintering time, but were not removed completely even after sintering for 64 h.

Fig. 6 shows SEM micrographs of specimens formed at 300 MPa and sintered for various periods. The fracture surface of the green body is much smoother than that of the previous specimen. However, the feature formed by the unfractured granules can still be noted. These features became less noticeable with

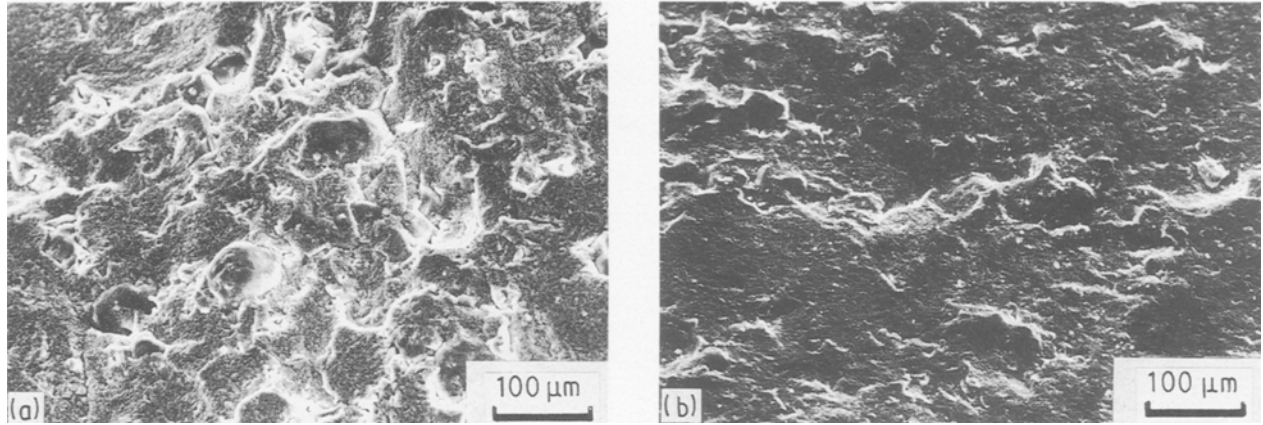
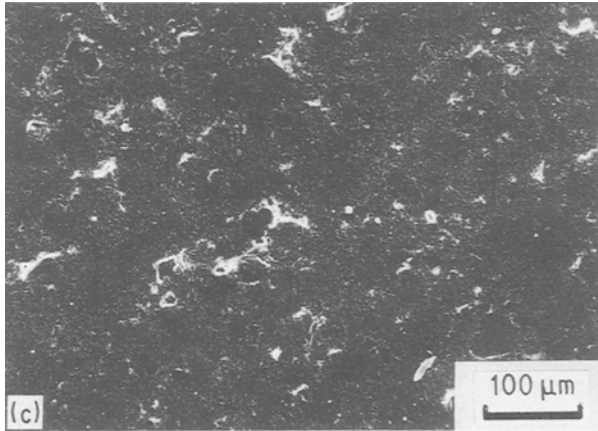


Figure 5 SEM micrographs of specimens formed at 20 MPa and sintered for various times: (a) green body (RD = 53.7%), (b) sintered body, 1 h (RD = 62.7%), (c) sintered body, 64 h (RD = 72.7%).



increased sintering time. The surface is almost perfectly smooth and shows no large feature in the specimen sintered for 64 h.

4. Discussion

Clearly, large processing pores are preserved in the early stage of densification in sintering. That is, once introduced in the green body, large processing pores

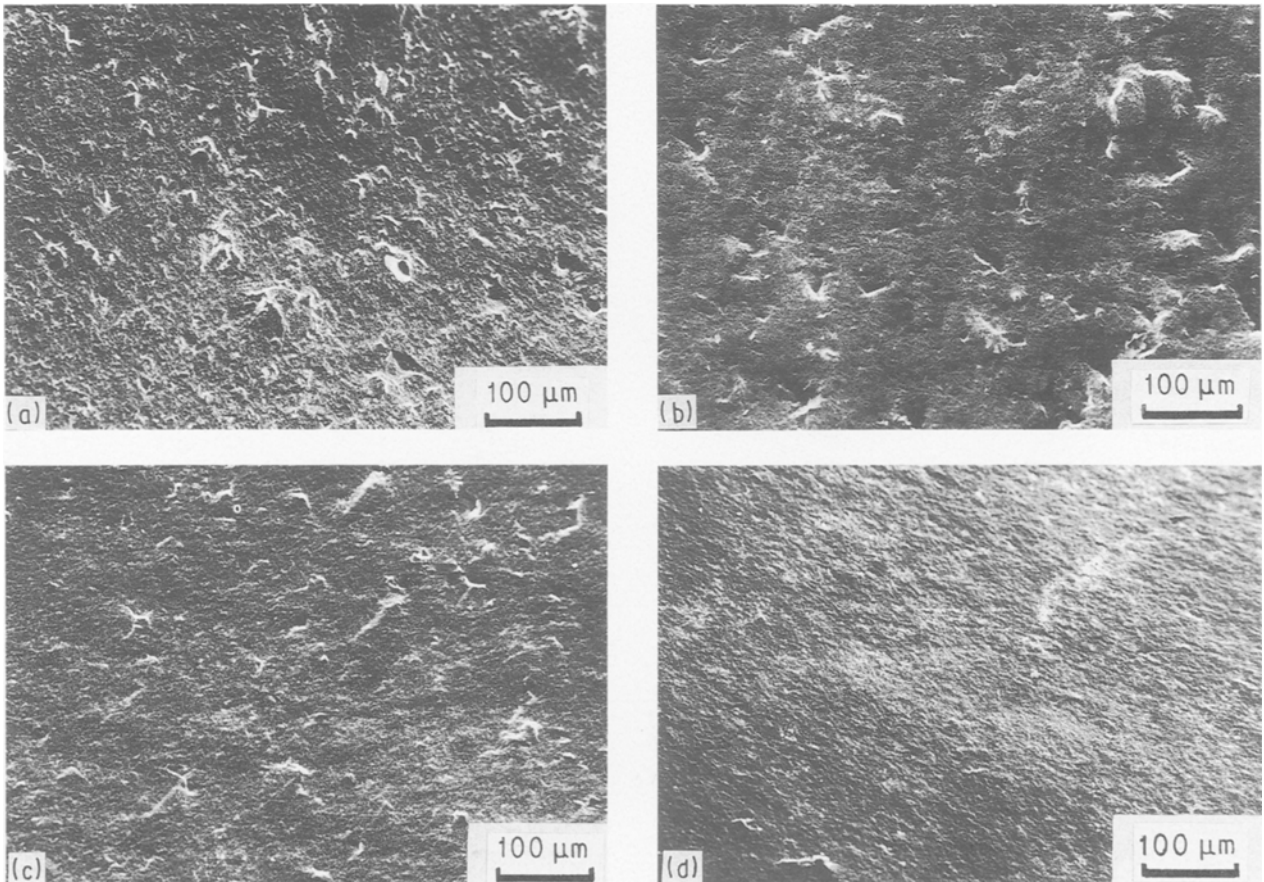


Figure 6 SEM micrographs of specimens formed at 300 MPa and sintered for various times: (a) green body (RD = 59.3%), (b) sintered body, 1 h (RD = 67.6%), (c) sintered body, 16 h (RD = 75.1%), (d) sintered body, 64 h (RD = 83.9%).

cannot be removed at least in this stage of densification. If they persist through the subsequent densification process, they become flaws governing the fracture strength of the whole sintered body. With their exceptionally large size and crack-like shape, they are believed to behave as very detrimental pores which reduce the fracture strength of the sintered body significantly. The presence of large pores in a highly densified body will indeed be shown in a subsequent paper [12] in which a thinned specimen will be examined directly by optical microscopy, and the relation between pore and fracture strength will be discussed. These direct observations of present and subsequent studies strongly show that these pores indeed have a significant effect on the strength of ceramics, and a better processing before firing is needed for their elimination in the sintered bodies.

The results of mercury porosimetry requires discussion. The total pore volumes determined by mercury porosimetry correspond to relative densities of 53.7 and 59.3% for the green bodies formed at 20 and 300 MPa, respectively. These results reflect the reduced pore volume due to the highly packed powder particles at high forming pressure, and this is readily understandable. However, it is not so easy to understand the change of pore size distribution with forming pressure and with densification. The volume of pores for sizes over 1 μm was significant in the green body formed at 20 MPa, and this result is consistent with the direct observation. The absence of corresponding volume after sintering is not consistent, however, with the optical microscopic observation in Fig. 1, which shows the presence of many large pores. A possible explanation for this result is that bottle-necks are formed at the entrance to the large pores in sintering, reducing the apparent pore size [13].

In all specimens, a large portion of the total pore volume represents the matrix pores which occupy the spaces between primary particles. The measured pore size is reasonable for the specimen of sub-micrometre particles used in this study. The growth of matrix pores with densification is also reported in the porosimetric study of Zheng and Reed [14]. They explained the result by the presence of agglomerate particles; rapid sintering of particles in agglomerates make them shrink, providing more space for matrix pores. The same argument holds for the present study. The total volume of large pores is negligibly small in the specimen formed at 300 MPa (Fig. 4). This is consistent with the direct observation in Fig. 2.

The forming pressure clearly affects the growth behaviour of matrix pores in Figs 3 and 4. These results can be explained as follows. Zhao and Harmer [15] showed that the relative densification rate/grain growth rate increased with increasing number of grains surrounding each grain in the powder compact. That is, the higher coordination number of grains in the specimen formed at higher pressure reduces the relative growth rate of pores as shown in the figure. In addition, it is interesting to note the growth of pore size with densification in Fig. 3, particularly the results at 16 and 64 h. They show the growth of pores at approximately constant pore volume. This result

shows that the bottle-neck at the entrance of a pore is removed and pore channels with smooth surfaces are formed.

The stability of large pores in sintering is consistent with the past theoretical arguments of Kingery [1, 5] and Kellett and Lange [6, 16]. According to their discussion, the thermodynamic stability of a pore is governed by the curvature of its surface and varies with the relative sizes of pore and grains. Large pores are characteristically coordinated by many grains, and have a negatively curved surface. The surface energy of this negatively curved surface provides the driving force for pore growth. In contrast, small pores have a positively curved surface and shrink with time.

Although the growth of large pores with sintering is consistent with the thermodynamic argument, an alternative kinetic explanation also seems to be possible. This explanation is based on the differential shrinkage in agglomerated particles and the resultant formation of cracks as presented by Lange and Metcalf [17]. In the present study, granules are considered to be large agglomerates which have a higher particle packing density than their boundary regions. More rapid densification among particles in granules can leave cracks at the boundaries of granules.

The potential of the present characterization technique is that it can yield a successful understanding of the behaviour of large pores during densification. The high concentration of large pores apparently found in this study needs comment. In contrast to the impression one might have from Figs 1 and 2, the size and concentration of processing pores are not as large after the final sintering as in the green state. The size and concentration of processing pores of this specimen are much smaller than those made from conventional raw powders. What made the pore concentration look apparently high is the very large examination volume characteristic of the present technique; large pores located at various depths in the specimen are revealed simultaneously. A comparison of Figs 2 and 4 clearly shows the potential of the present technique. With the conventional SEM, the examination volume is very small, and features with a small concentration are frequently missed. Unlike the other non-destructive methods such as ultrasonic microscopy, the resolutional power of the present technique is clearly high enough for the detailed examinations of processing pores and their behaviour during densification.

Clearly, the matrix and boundary region of the granule must have different optical properties; otherwise they are not visible. The most likely source of this difference is the change of powder packing density between matrix and boundary regions. Boundary regions of a granule are expected to have a low packing density of powder particles. The boundary region must be very thin, since the examination shows that they are visible only when viewed from the tangential direction. The image for the boundary regions became sharper and more noticeable with increasing sintering time and/or density, at least in the initial sintering stage. This result shows the enhancement of non-uniformity through the difference of local sintering

among particles in highly packed and loosely packed regions as discussed above. Other microstructural features became less noticeable with densification. Small pores tended to disappear with densification, which is consistent with the prediction of sintering theory [1, 5, 6, 16].

This technique is suitable for the development of better processing of ceramics, in which the pores needed to be controlled are small not in size but in concentration. The typical size of pore found in fracture origins is 50 μm in the best high-performance ceramics presently available [18]. A single pore of this size in the whole volume of a ceramic body governs its strength and reliability. In the small standard specimen for strength measurement, for example, the strength is governed by the largest pore of concentration as low as one pore per mm^3 .

5. Conclusions

1. Changes of internal/pore structure in alumina green bodies were successfully studied with the liquid immersion technique.

2. Large processing pores were found to be preserved after sintering with little change of their shape.

3. The stability of large pores is consistent with past thermodynamic arguments.

4. Conventional characterization techniques can only partially reveal the characteristics of ceramic green bodies.

5. Improvement of the consolidation process, is needed for the development of better ceramics.

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