JOURNAL OF MATERIALS SCIENCE 28 (1993) 1788–1792

Effect of processing conditions on the characteristics of pores in hot isostatically pressed alumina

K. UEMATSU, M. SEKIGUCHI, J.-Y. KIM, K. SAITO, Y. MUTOH*, M. INOUE*, Y. FUJINO‡
*Department of Chemistry, *Department of Mechanical Engineering, and ‡Department of Planning and Management, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata, Japan*

A. MIYAMOTO
Advanced Technology Research Centre, Nippon Kokan Ltd, Minamiwataridacho 1-1, Kawasakiku, Kawasaki 210, Japan

Effect of processing conditions on the characteristics of residual pores was studied with an optical microscope in hot isostatically pressed translucent alumina ceramics. Green bodies formed by isostatic pressing were sintered at 1300, 1400 and 1600 °C and then hot isostatically pressed at a temperature 50 °C below the respective sintering temperature for 1 h at 100 MPa. All specimens were fully dense within experimental accuracy (± 0.1%), and the grain size increased with increasing sintering/hot isostatic pressing temperatures. A variety of pores were found in all specimens. The distribution of pores was uniform at various locations within the specimen. The pore population decreased with increasing pore size, but was finite in the size range exceeding 84 μm. The pores in this range increased with increasing sintering/hot isostatic pressing temperature. Except for these large pores, the pore population was similar under all processing conditions.

1. Introduction

In the processing of ceramics, the control of residual pores has been one of the major objectives. Significant improvement of properties such as fracture strength, electrical breakdown, and transmittance of light, etc. [1–3], is expected to result from the reduction in the size and concentration of pores. In many of the excellent previous studies of processing, however, processing conditions are related to the average characteristic of pores, such as porosity (relative density) [4–7] or average pore size [8]. Our knowledge of pore-size distribution and the effect of processing on pore characteristics is very limited.

Hot isostatically pressed alumina provides an opportunity to examine the effect of processing conditions on the pore characteristics in ceramics. Its translucency allows the application of optical microscopy to examine residual pores in the transmission mode. This analytical tool is capable of evaluating all pores with the size range from over 100 μm down to near sub-micrometre over the entire volume of a specimen of reasonable size, i.e. approximately 50 mm^3. This capability is superior to other sophisticated non-destructive techniques [9–15] for the present objectives. One possible shortcoming of the optical microscopy is that it provides only silhouettes of features present in the specimen, leaving the additional task of identification of these features. However, this causes no difficulty in the present study. The majority of features found in this study will be shown to be pores, because they can be removed almost entirely by hot isostatic pressing at higher temperature [16].

The objective of this research was to clarify the characteristics of pores with the size range from over 100 μm down to 0.5 μm in a typical high-performance ceramic, and relate them to the processing conditions. The basic characteristics of isostatically pressed high-density alumina ceramics are well understood [17–20].

2. Experimental procedure

Active alumina powder granules (TM-DS, Taimei Kagaku Kogyo, Minamiminowa, Kamiinagun, Nagano, Japan) were used as the starting material. The granules were moulded into bars (15 mm × 15 mm × 80 mm) at 20 MPa and isostatically pressed at 300 MPa. After heating at 600 °C for 2 h in air to remove the binder, the specimens were sintered at 1300, 1400 or 1600 °C for 1 h in air to eliminate open pores. A commercial apparatus (QIH-9, NKK-ASEA, Tokyo, Japan) was used for hot isostatically pressing the sintered specimens at a temperature 50 °C below the respective sintering temperatures (heating rate 10 °C min^{-1}) at 100 MPa for 1 h. A thin slab

0022–2461

(~0.5 mm) was cut from each specimen normal to the longitudinal direction, and both surfaces were polished with successively finer diamond pastes. After finishing with 1/4 μm diamond powder, the translucent specimen had an approximate size of 0.5 mm × 10 mm × 10 mm. An optical microscope (Optiphot, Nikon, Tokyo, Japan) in transmission mode was used for characterizing the pores. The objective lens of the microscope was traversed at a fixed interval (10 μm at × 600, 25 μm at × 200, and 50 μm at × 100) from the top to bottom surfaces to focus pores located at various depths in specimen. Hundreds of micrographs were taken to cover the entire volume of the specimen. The size of each pore was represented by its maximum apparent diameter as determined from the micrograph using a calibrated scale. Microstructures of the specimen were also examined with SEM (STM-T100, Jeol, Tokyo, Japan) on polished and thermally etched surfaces. The average grain size was determined by the standard line intercept method. Bulk density was determined by Archimedes' method with distilled water as the immersion liquid. The internal structure of the green body was characterized by the new immersion liquid technique [21–23] with bromonaphthalene as the immersion liquid. The green body was thinned to 0.3 mm on sand paper after the binder was removed, and made transparent by the immersion liquid. The same optical microscope as used above was applied for the examination of the internal structure.

3. Results

Visual inspection showed that the thinned specimen had excellent transparency except for some parts of the surface regions. The transparency tended to increase with decreasing sintering/hot isostatic pressing temperature. Isolated opaque regions less than 0.5 mm thick were present at some edges and corners of all specimens. These regions were probably formed by the contamination, and were not subjected in the subsequent evaluation. Other parts of the specimen were homogeneous.

Table I shows the characteristics of the specimens. All specimens are fully dense (100% ± 0.1%) within experimental accuracy. The grain size increased with increasing sintering/hot isostatic pressing temperature. The minimum grain size (1.05 μm) achieved in this study is one of the finest of all reported alumina ceramics [24].

Fig. 1 shows the microstructures of a specimen. No pore was found on the polished and thermally etched surfaces as expected for a specimen of full density. The microstructure was uniform and consisted of equiaxed grains. There was no sign of abnormal grain growth.

TABLE I Characteristics of specimens

Sintering temp. (°C)	HIP temp. (°C)	Grain size (μm)	Relative density (%)
1300	1250	1.05	100
1400	1350	2.39	100
1600	1550	5.85	100

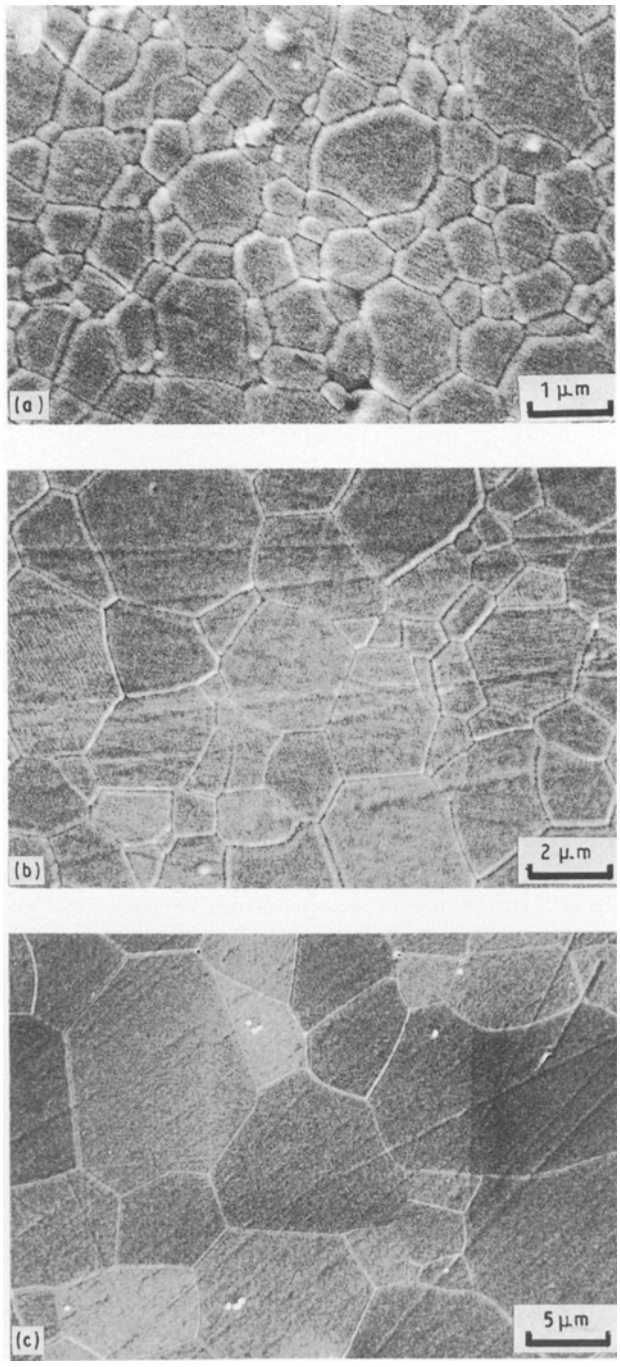

Figure 1 Microstructure of a specimen examined by SEM, after (a) sintering at 1300 °C and HIP at 1250 °C, (b) sintering at 1400 °C and HIP at 1350 °C, (c) sintering at 1600 °C and HIP at 1550 °C.

Fig. 2 shows examples of transmission optical microscopic observations. All micrographs show many small features of particle-like shape. Most of these features are identified as pores in a separate study [16]. The largest pore found in the upper half of Fig. 2b has an elongated shape and its size is approximately 40 μm. Some exceptional micrographs show much larger pores. Exceptionally large pores tended to have rather irregular shapes and complicated structure. At the magnification used (× 200), an area of 0.29 mm × 0.43 mm is examined in one field. A pore with size down to 12 μm can be reliably characterized at this magnification. The volume given by this area times the thickness of specimen is examined in one series of observations.

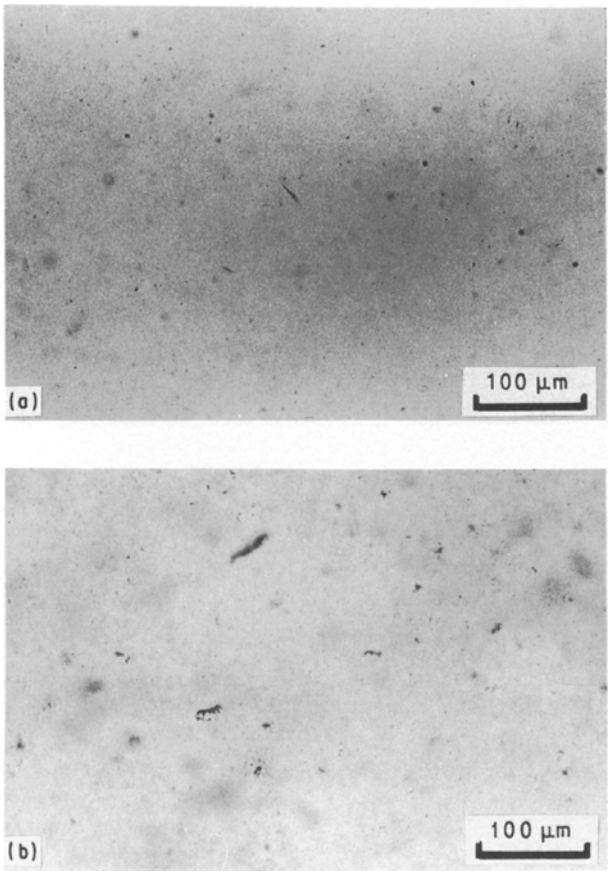

Figure 2 Optical microscopic examination of pores, after (a) sintering at 1300 °C and HIP at 1250 °C, (b) sintering at 1600 °C and HIP at 1550 °C.

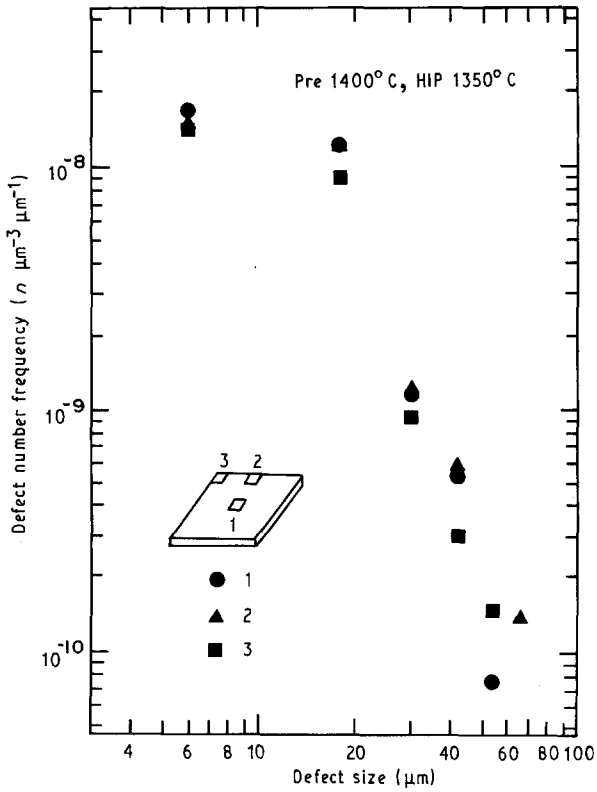

Figure 3 Defect-size distributions at various positions in high-density translucent alumina prepared by hot isostatic pressing.

Fig. 3 shows the pore-size distributions at the corner, edge and centre regions of the specimen which was sintered at 1400 °C and hot isostatically pressed at 1350 °C. The positions examined are shown schematically in the figure. The population of pores decreases approximately linearly with increasing pore size at all positions in this plot. The size distributions of pores were approximately the same for these positions, and can be expressed by a straight line, except for the smallest pore. Note that the frequency for the smallest pores has a large uncertainty, because they are too small to be evaluated accurately at the magnification applied (× 200). Except for this datum point, the pore-size distributions were the same as the detailed pore-size distribution for the entire specimen shown next. Similar results were found also in other specimens, showing uniform pore distribution throughout the volume in all specimens.

Fig. 4 shows the pore-size distributions determined by combining the observation at low magnification with that at high magnification. A much larger examination volume than that in Fig. 3 gives more detailed average information over the entire specimen. The population of these large pores tended to increase with increasing sintering/hot isostatic pressing temperature, but that of smaller pores is rather insensitive to the temperature. The maximum sizes of pores found in these specimens were 108, 150 and 180 μm, for those sintered at 1300, 1400 and 1600 °C, and hot isostatically pressed at a temperature 50 °C below these temperatures, respectively.

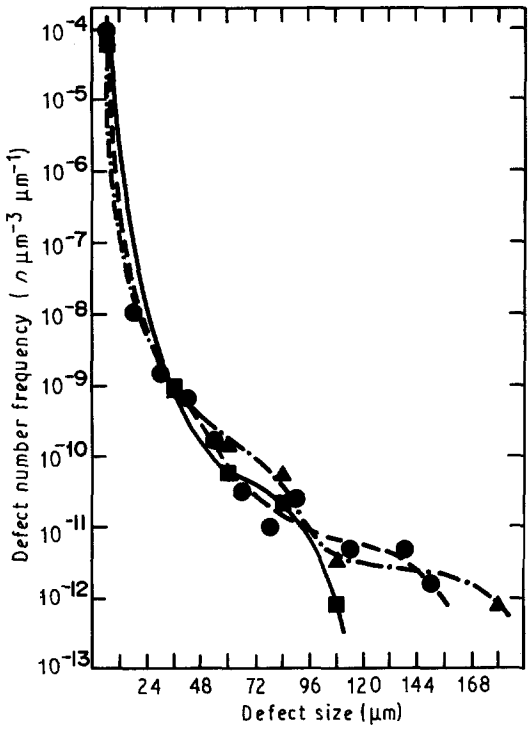

Figure 4 Defect-size distribution in high-density translucent alumina prepared by hot isostatic pressing. (■) Preheated at 1300 °C, HIP 1250 °C; (●) preheated at 1400 °C, HIP 1350 °C; (▲) preheated at 1600 °C, HIP 1550 °C.

Fig. 5 shows the internal structures for the surface and centre regions of the green body. Both regions contain sharp crack-like pores. Their shape suggests that they were voids left at the boundaries of deformed and partially fractured granules. The concentrations of these voids were similar in the surface and centre

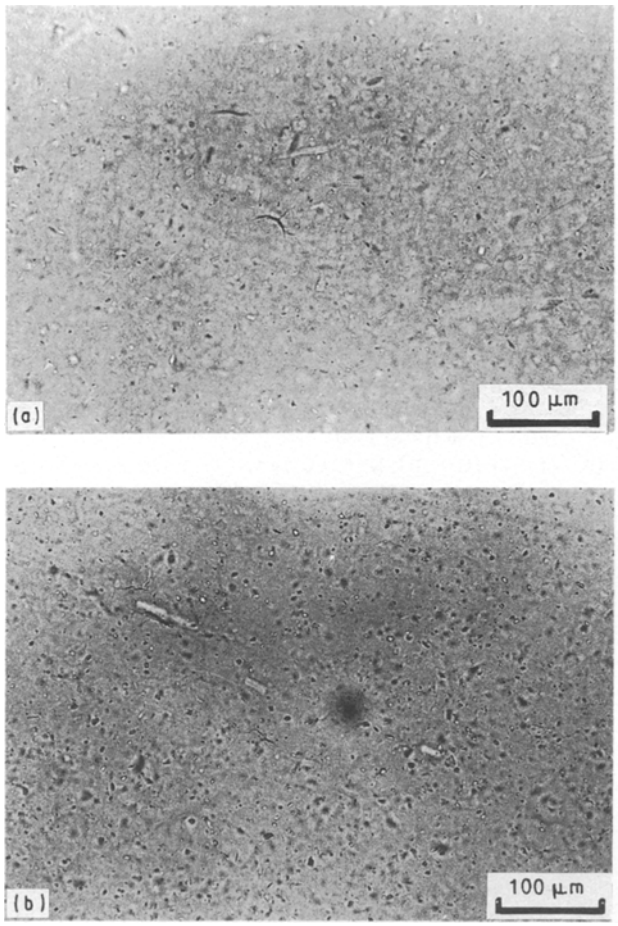

Figure 5 Internal structures for the surface and centre regions of a green body. (a) Surface region, (b) central region.

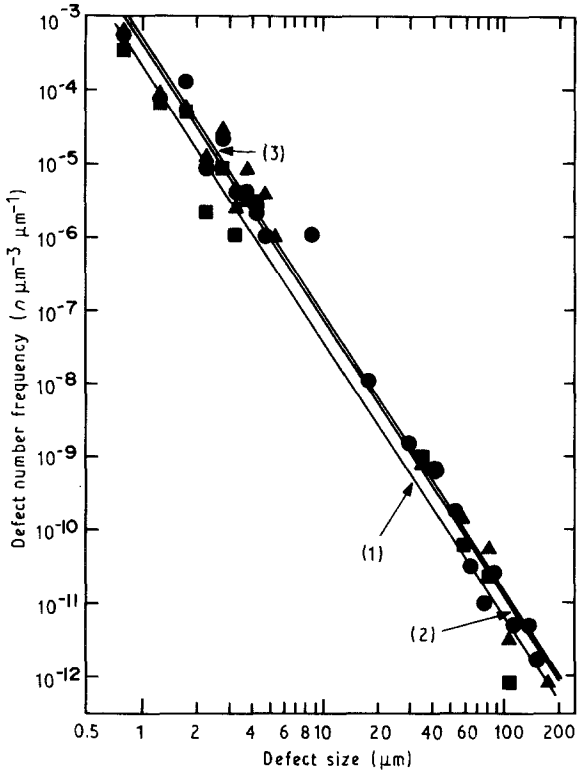

Figure 6 Replot of the defect-size distribution of Fig. 6 on a logarithmic scale. (1) (■) Preheated at 1300 °C, HIP 1250 °C; (2) (●) Preheated at 1400 °C, HIP 1350 °C; (3) (▲) Preheated at 1600 °C, HIP 1550 °C.

regions of the specimen. Other features of internal structure were also similar for these regions.

4. Discussion

Large pores with a size exceeding 80 μm are present even in the hot isostatically pressed high-density alumina. Pores and precipitates of second phase are the two major defects possible in ceramics. However, the majority of these defects is found to be pores as mentioned earlier and will be presented in a subsequent paper [16], almost all defects found in the specimen were successfully removed by hot isostatic pressing at tempertures equal to or slightly higher than the sintering temperature. If defects are precipitates, they must remain after this treatment.

The defect-size distribution is re-plotted on a logarithmic scale in Fig. 6. In this plot, data of all specimens are expressed as straight lines of approximately the same slope. The result of Fig. 3 is consistent to this plot, except the datum for the pore of the smallest size, for which the result in Fig. 3 contains significant uncertainty.

The likely source of large pores found in this study is the crack-like voids in the green body shown in Fig. 5. These voids were also commonly found in our previous study under all forming conditions [21–23]. Even the isostatic pressing at 600 MPa could not remove these pore completely.

The behaviour of pores during sintering was discussed thermodynamically [25–28]. These studies showed that pores larger than the critical size grew during the sintering period. For the pore to shrink, its size had to be less than the critical value which is comparable to the grain size of the matrix. Because the void size represented by its length is tens of micrometres in Fig. 5, and the grain of the matrix phase was much smaller, as shown in Table I, no shrinkage of pores is expected for large pores in the present system. A large pore grows monotonically with grain growth during sintering, and the pore size left in the sintered specimen is expected to increase with increasing sintering temperature. In our recent studies [29, 30], we reported direct evidence supporting this expectation for the initial stage of densification.

Once they are formed, the removal of these large pores is known to be difficult even with hot isostatic pressing [5]. Clearly, a green body without these crack-like voids is vital for producing high-performance ceramics. This may not be easy for ceramics produced through the powder compaction process, however. We often found similar large pores [31, 32] in zirconia and silicon nitride green bodies prepared by the powder compaction process.

The linearity of Figs 3 and 6 shows that the pore-size distribution follows the empirical form $q(x) = Qx^{-n}$. The constants obtained in the present specimens were $n = 3.76$ for all specimens, and $Q = 2.13 \times 10^{-4}$, 4.07×10^{-4} and 5.13×10^{-4} for specimens sintered at 1300, 1400 and 1600 °C, respectively. This form is the same as that used in the theoretical treatment of the strength–pore size distribution relationship of Gee [33]. The form is different from that

determined through fracture statistics analysis. The size distribution of pores reported by Matsuo and Kitakami [34] has a maximum and somewhat resembles the log-normal distribution. The discrepancy between these results is understandable. The former study reports the distribution for all pores, whereas the latter reports the distribution of pores which is the most detrimental for fracture.

The same pore-size distribution was found for various positions in the specimen at least for sizes between 12 and 66 μm. This result is consistent with the internal structure of a green body as shown in Fig. 5. The same void concentration at the surface and centre regions of the green body suggests that its density was approximately constant throughout.

This uniform density distribution in green body is, however, rather surprising. Abe *et al.* [35] reported the presence of significantly non-uniform density distribution in an isostatically pressed ceramic green body. The density was highest at the surface and decreased inwards into the specimen. Because high density is favourable for densification in normal sintering [36], the non-uniformity in the green body may create heterogeneity in our sintered body and is preserved even after hot isostatic pressing. Without further information, we cannot identify the cause of the uniform pore distribution in the present specimen. Our tentative opinion is that the excellent granule characteristics are responsible for achievement of homogeneous pore distribution in both the green and final bodies.

References

1. F. F. LANGE, "Fracture Mechanics of Ceramics, I", edited by R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum, New York, 1974) p. 3.
2. N. M. ALFORD, K. KENDALL, W. J. CLEGG and J. D. BIRCHALL, *Adv. Ceram. Mater.* **3** (1988) 113.
3. F. M. ERNSBERGER, *ibid.* **3** (1988) 161.
4. F. F. LANGE, *J. Amer. Ceram. Soc.* **72** (1989) 3.
5. J. SUNG and P. S. NICHOLSON, *ibid.* **71** (1988) 788.
6. B. J. KELLETT and F. F. LANGE, *ibid.* **71** (1988) 7.
7. K. G. EWSUK and G. L. MESSING, *J. Mater. Sci.* **19** (1984) 1530.
8. G. G. LONG, S. KRUEGER and R. A. PAGE, *J. Amer. Ceram. Soc.* **74** (1991) 1578.
9. D. R. JOHNSON, M. A. JANNEY and R. W. McCLUNG, "Nondestructive Testing of High Performance Ceramics" (American Ceramic Society, Westerville, Ohio, USA, 1987) p. 19.
10. J. G. SCHROTH and A. P. DRUSCHITZ, *J. Amer. Ceram. Soc.* **72** (1989) 1292.
11. D. E. YUHAS and L. W. KESSLER, "Materials Characterization", Materials Research Society, Vol. 15 (Plenum, New York, 1983) p. 413.
12. K. A. HARDMAN-RHYNE and N. F. BERK, *J. Amer. Ceram. Soc.* **69** (1986) C285.
13. K. G. FRASE and K. A. HARDMAN-RHYNE, *ibid.* **71** (1988) 1.
14. E. R. GENERAZIO, D. J. ROTH and D. B. STANG, *ibid.* **72** (1989) 1282.
15. M. D. WEEKS and J. W. LAUGHNER, "Advances in Ceramics", Vol. 21 (American Ceramic Society, Westerville, Ohio, USA, 1987) p. 793.
16. M. MIYASHITA, J.-Y. KIM, N. UCHIDA and K. UEMATSU, MRS Symp. Proc. Vol. 251 (1992) p. 151.
17. K. UEMATSU, K. ITAKURA, N. UCHIDA, K. SAITO, A. MIYAMOTO, and T. MIYASHITA, *J. Am. Ceram. Soc.* **73** (1990) 74.
18. K. ITAKURA, N. UCHIDA, K. UEMATSU, K. SAITO, A. MIYAMOTO and T. MIYASHITA, *J. Ceram. Soc. Jpn Inter. Ed.* **96** (1988) 1560.
19. M. SEKIGUCHI, K. ITAKURA, J.-Y. KIM, Z. KATO, N. UCHIDA, K. UEMATSU, K. SAITO and A. MIYAMOTO, *Seramikkusu-Ronbunshi* **97** (1989) 1486.
20. K. UEMATSU, K. ITAKURA, M. SEKIGUCHI, N. UCHIDA, K. SAITO and A. MIYAMOTO, *J. Amer. Ceram. Soc.* **72** (1989) 1239.
21. K. UEMATSU, J.-Y. KIM, N. UCHIDA, Z. KATO and K. SAITO, *Seramikku-Ronbunshi* **98** (1990) 1515.
22. K. UEMATSU, J.-Y. KIM, M. MIYASHITA, N. UCHIDA and K. SAITO, *J. Amer. Ceram. Soc.* **73** (1990) 2555.
23. K. UEMATSU, M. MIYASHITA, M. SEIKGUCHI, J.-Y. KIM, N. UCHIDA and K. SAITO, *J. Amer. Ceram. Soc.*, in press.
24. A. ROOSEN and H. K. BOWEN, *ibid.* **71** (1988) 970.
25. J. ZHENG and J. S. REED, *ibid.* **72** (1989) 810.
26. W. D. KINGERY, in "Ceramic Processing before Firing", edited by G. Y. Onoda and L. L. Hench (Wiley, New York, 1978) pp. 291.
27. W. D. KINGERY and B. FRANCOIS, in "Sintering and Related Phenomena", edited by G. C. Kuczynski, N. A. Hooton and C. F. Gibbon (Gordon and Breach, New York, 1976) pp. 471.
28. B. J. KELLETT and F. F. LANGE, *J. Amer. Ceram. Soc.* **72** (1989) 725.
29. K. UEMATSU, M. MIYASHITA, J.-Y. KIM, N. UCHIDA, *J. Amer. Ceram. Soc.*, **75** (1992) 1016.
30. J.-Y. KIM, M. MIYASHITA, N. UCHIDA and K. UEMATSU, *J. Mater. Sci.*, **27** (1992) 6609.
31. J.-Y. KIM, M. MIYASHITA, M. INOUE, N. UCHIDA, K. SAITO and K. UEMATSU, *ibid.* **27** (1992) 587.
32. M. INOUE, J.-Y. KIM, Z. KATO, N. UCHIDA, K. UEMATSU and K. SAITO, in "Transactions of the Materials Research Society of Japan" (Uchida-Rokakuho, Tokyo, Japan, 1990) p. 192.
33. M. G. GEE, *Mater. Sci.* **26** (1984) 85.
34. Y. MATSUO and K. KITAKAMI, in "Fracture Mechanics of Ceramics", Vol. 7, edited by R. C. Bradt, A. G. Evans, D. P. H. Hasselman and F. F. Lange (Plenum, New York, 1986). p. 223.
35. O. ABE, S. KANZAKI and H. TABATA, *Seramikku-Ronbunnshi* **97** (1989) 12.
36. O. ABE, S. AOKI, S. KANZAKI and H. TABATA, *ibid.* **97** (1989) 432.

Received 16 September 1991
and accepted 2 September 1992