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Influence of Granules Characteristics and Compaction Pressure on the Microstructure and Mechanical Properties of Sintered Alumina

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ABSTACT

The influence of granules characteristics and compaction pressure on the microstructure and mechanical properties of sintered alumina was studied as a function of slurry dispersion state. The characteristics and the compaction behavior of the spray dried alumina granules considerably affected the microstructure as well as the mechanical properties of the sintered body. In the green bodies formed with granules prepared with a dispersed slurry, the granules with dimple clearly existed and caused pore defects in sintered body. These dimples were clearly present even in the green body prepared at 180 MPa. The pores between the granules were not removed during pressing and sintering, and remained in the sintered body. In contrast, in the granules fabricated from a flocculated slurry, the destroy of granules at the contact points was observed with increasing pressure. Sintered bodies fabricated with fewer defects showed strength increase. For the sample fabricated with flocculated slurry, the pores at the boundaries of granules were small and more irregular shape compared with those of dispersed slurry.

Key words: Flocculated slurries, Spray-dried, Alumina, Granule, Weibull distribution

1. Introduction

In ceramic powder processing, the microstructure and properties of final products are sensitive to the various factors in each processing step. Spray drying is commonly utilized to dry a milled slurry and to produce granules in mass-production because of its superior productivity. However, many investigators have clarified that the major source of pore defects in sintered body is granule.[1-9] For instance, it has been pointed out that flocculates state of powders in a slurry affect the characteristics of granules, densification and properties of green and sintered bodies. [5,8,10,11] It is evident that the control of flocculation or dispersion in a slurry is crucial for the fabrication of alumina ceramics with high performance capabilities. Pore defects are the major concern in the processing of advanced engineering ceramics.[12,13] The major source of these pore defects can be related to the structure and characteristics of the granules used. Dimples in granules and the incomplete adhesion between granules result in the formation of void spaces at their center and boundaries in green bodies.[14-16] Therefore, the characteristics of granules, including compaction behavior, has to be properly controlled in order to eliminate the detrimental features in green bodies and to improve the strength and reliability of sintered bodies. Uematsu *et al.*[17,18] show that removal of large pores (over 100 μm in diameter) may be difficult even in the final stage of densification. Shinohara *et al.*[20] showed that the coalescence of pores, with limited shrinkage during densification and grain growth in the late intermediate to final stage of sintering, was responsible for the preservation or development of the large pores. Finally, large pores are distributed in the sintered body and cause the decrease in the strength of ceramics. It is thus very important to reduce the detrimental features such as pores or void space fromed at the centers and boundaries of granules in green bodies.

In this study, the influence of slurry flocculation on the microstructure and properties of granules, green and sintered bodies was examined for alumina ceramics. High resolution scanning electron microscopy was used to examine the details of the microstructural change of alumina granules, prepared from flocculated and dispersed slurries, in green bodies during cold isostatic pressing.

2. Experimental

The high-purity alumina (99.997%) powders with submicrometer particle size (AKP-20, Sumitomo Chemical Co., Tokyo; average particle size was 0.53 μm) were used in this study. The alumina powder (100 kg) was ground and dispersed by using an attrition mill after stirring in the ion exchange water (45 kg) with and without polycarboxylic acid ammonium salt (0.8 kg, Celuna D-305, Chukyo Yushi Co. Ltd., Nagoya, Japan) as a dispersant. Each slurry was

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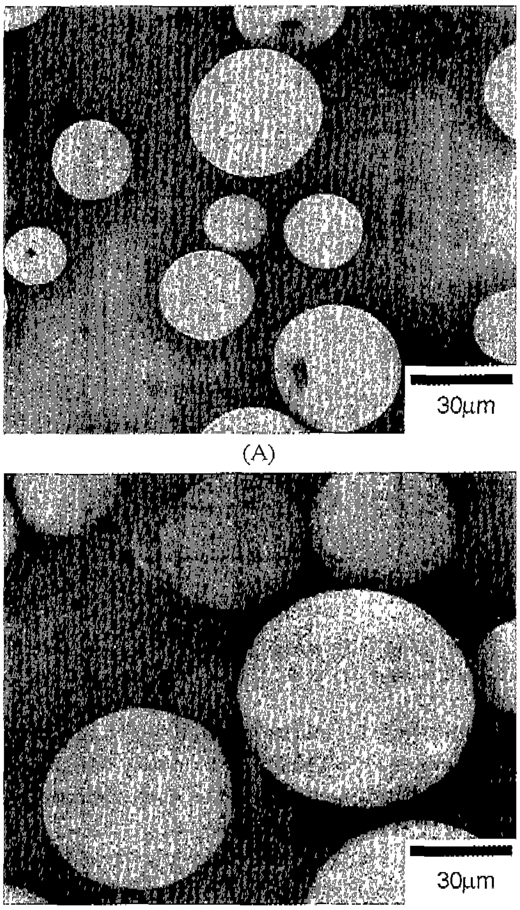
mixed with a binder (1.388 kg, Celuna WF-804, Chukyo Yushi Co. Ltd., Nagoya, Japan and 1.808 kg, WF-610, Chukyo Yushi Co. Ltd., Nagoya, Japan) and lubricants (0.78 kg, Serosol 920, Chukyo Yushi Co. Ltd., Nagoya, Japan), then successively dried and granulated with a spray dryer with inlet flow gas temperature of 150°C. The granules was sieved with a 100 μm screen, packed in a mold, and uniaxially pressed at 9.8 MPa to form green bodies (80 mm×80 mm×12 mm). Then the green bodies were cold isostatically pressed at 100 MPa and 180 MPa. Sintering was carried out in an electric furnace at 1500°C and 1600°C for 2 h at a heating rate of 150°C/h. The microstructures of spray-dried granules and the green body fracture surfaces were observed by SEM (JSM-6340F, JEOL, Ltd., Tokyo, Japan). Sintered densities were determined by the Archimedes method using water as an immersion medium. Microstructure observation was made on polished and thermally etched surfaces of sintered bodies by using scanning electron microscope (SEM) (JSM-T300, JEOL, Japan). For optical microscopic examination in the transmission mode,[14,15,19,20] thin specimens of thickness 50 μm were prepared. Both surfaces were polished with diamond paste of 1.0 μm and the internal structures were examined with an optical microscope (ORTHOLUX, Leitz, Wetzlar, Germany). The flexural strength was measured for 22 specimens (3 mm×4 mm×40 mm) with the method specified by JIS R 1601 using a four-point bending technique with an inner and outer spans of 10 and 30 mm, respectively, and a cross head speed of 0.5 mm/min.

3. Results

Figure 1(A) and (B) show the structure of spray-dried alumina granules fabricated from dispersed and flocculated slurries. It is obvious that the granules fabricated from a dispersed slurry are irregularly shaped and mostly contain dimples, as shown in Fig. 1(A). On the other hand, the granules prepared from a flocculated slurry are essentially spherical and no dimples are observed (Fig. 1(B)). Comparison of the photomicrographs clearly showed that the granule size was larger for the granules from flocculated slurry than from dispersed slurry.

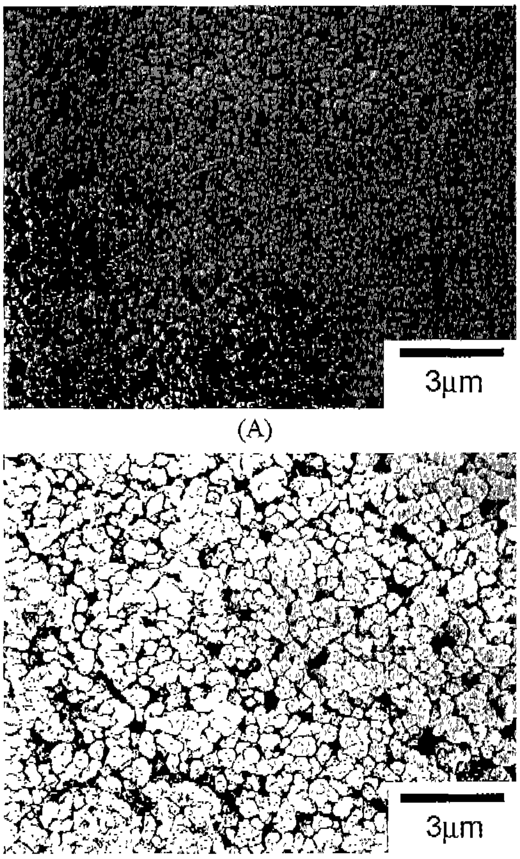
Figure 2 shows the microstructure of the granules taken on the surface of them at high magnification. It is clear that the powder particles in the granules made from a dispersed slurry are tightly packed (Fig. 2(A)), whereas the particles



(A)

(B)

Fig. 1. Comparison of spray-dried alumina granules fabricated from (A) dispersed and (B) flocculated slurry.



(A)

(B)

Fig. 2. Surface morphology of granule fabricated from (A) dispersed and (B) flocculated slurry.

in the granules made from a flocculated slurry are relatively loosely packed (Fig. 2(B). The structure of powder packing in these alumina granules are well coincident with those found in the silicon nitride granules made from dispersed and flocculated slurries.[5)]

Figures 3 and 4 show the fracture surfaces of green compacts formed with the different granules after cold isostatic pressing at 100 MPa and 180 MPa, respectively. The difference in compaction of the granules is clear between those from dispersed and flocculated slurries. In the green body formed at 100 MPa with granules prepared from a dispersed slurry (Fig. 3(A)), the traces of granules, with the dimples, are clearly visible (shown by arrow). With increasing a compaction pressure to 180 MPa (Fig. 3(B)), the deformation and fracture of the granules are promoted although many of the boundaries are still clear between the traces of granules. Dimples also persist in unfractured granules. In green bodies made with granules prepared from a flocculated slurry, on the other hand, boundaries between the granules are far better adhered with powder particles than those in compacts made with granules fabricated from a dispersed slurry (Fig. 4(A)). It appears that the fracture of granules are promoted at the contact points and the traces of granules almost disappear with increasing an applied pressure (Fig. 4(B)).

Figure 5 shows the change in the density of specimens sintered at 1500 and 1600°C as a function of the cold isostatic compaction pressure. The density clearly tends to increase with the sintering temperature and the compaction pressure. When sintered at 1500°C, the relative density as lower than 98% for all samples pressed at each forming pressure regardless of the slurry flocculation state.

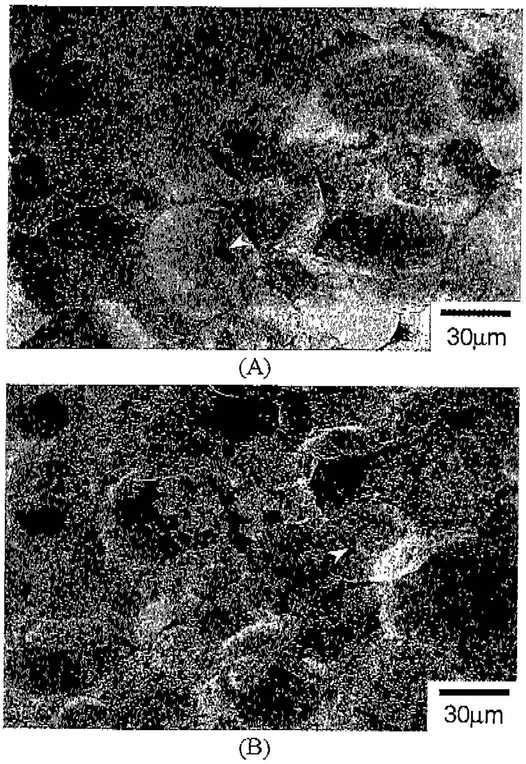


Fig. 3. SEM of micrographs of fracture surfaces of alumina green body fabricated from dispersed granules with cold isostatic pressures of (A) 100 MPa and (B) 180 MPa.

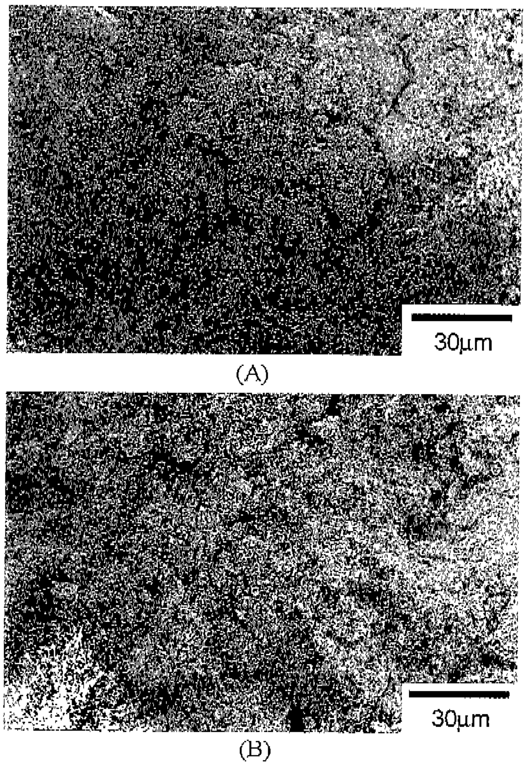


Fig. 4. SEM of micrographs of fracture surfaces of alumin green body fabricated from flocculated granules with col isostatic pressures of (A) 100 MPa and (B) 180 MPa.

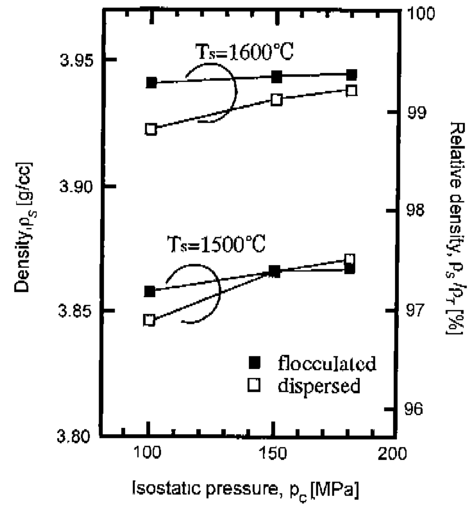
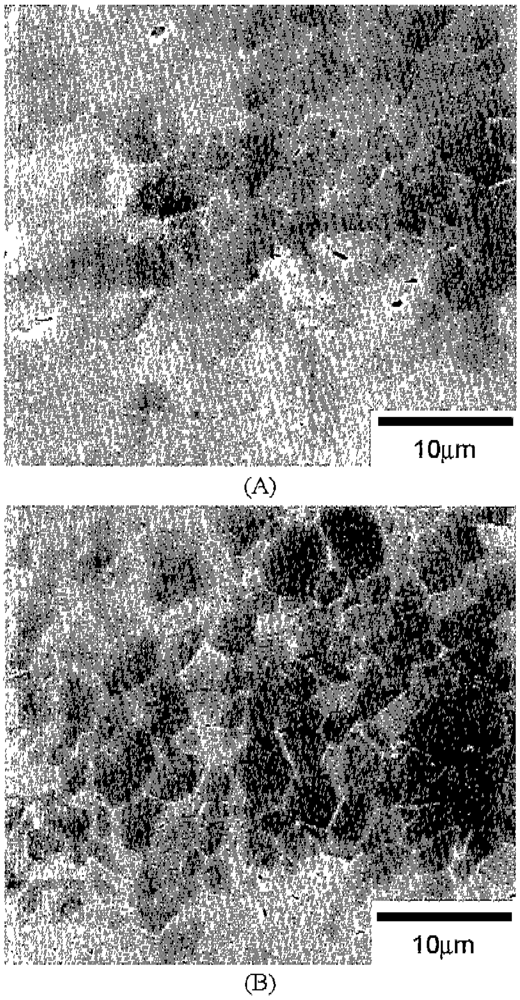


Fig. 5. Effect of cold isostatic pressure on relative density o sintered bodies at 1500°C and 1600°C.

Figure 6 shows SEM micrographs taken on the polished and thermally etched surface of the specimens isostatically pressed at 180 MPa and sintered at 1600°C for 2 h. The pores are remained mostly at grain boundaries in a sample prepared from a dispersed slurry, shown in Fig. 6 (A). These



(A)

(B)

Fig. 6. SEM observation of microstructure of sintered bodies at 1600°C fabricated from (A) dispersed and (B) flocculated granules with cold isostatic pressure of 180 MPa.

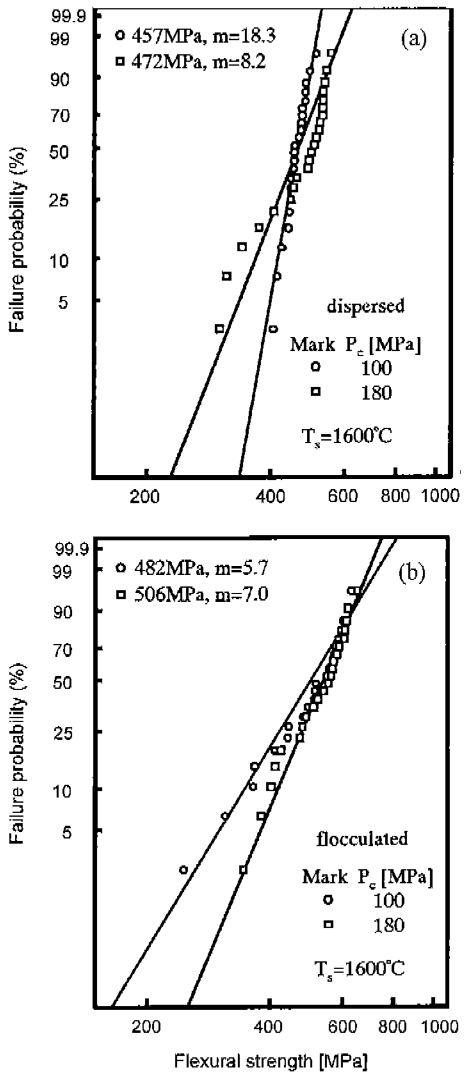


Fig. 7. Weibull plots of the flexural strength for specimens made with (A) dispersed and (B) flocculated granules.

pores originate from voids caused by the incomplete deformation and adhesion of powder particles in collapsed dimples at the centers and boundaries of granules in the green body. A small difference was found in the microstructure of a sintered body. Fairly uniform microstructure was noted in the sample made from flocculated slurry (Fig. 6 (B)).

Figure 7 shows the Weibull distribution curves of the fracture strength for specimens fabricated from the different granules by sintering at 1600°C. As shown, the strength was clearly higher for the specimens made from a flocculated slurry (482 and 506 MPa for isostatic pressures at 100 and 180 MPa, respectively) than for those from a dispersed slurry (457 and 472 MPa). Calculated Weibull modulus was the highest for the specimen made from a dispersed slurry and formed at 100 MPa although the average strength was the lowest.

Figures 8 and 9 show the internal microstructure of sintered bodies observed by an optical microscope in the transmission mode. The traces of granules and dark shadows are clearly visible in the specimen fabricated from a dispersed slurry and formed at the pressure of 100 MPa (Fig. 8(A)). The shadows exist at both the centers and boundaries of the traces of granules. With increasing the forming pressure to 180 MPa, the boundaries between granules in the sintered body became less clear although many but small shadows are distributed rather uniformly throughout the system. For specimens made from a flocculated slurry, large dark shadows with round and irregular shapes are also found (Fig. 9), although the number of them is clearly smaller than that of shadows found in the sintered body fabricated with granules from a dispersed slurry. The traces of granules are unclear in these specimens. The shadows are still visible in the sintered body fabricated with high forming pressure (Fig. 9(B)), although the size of them become clearly small. It has been reported[1,3,18)] that the dark shadows corresponded to pores and/or low density regions in sintered bodies and the size distribution of them affected the strength of ceramics.

Fractographical analysis performed on the fracture sur-

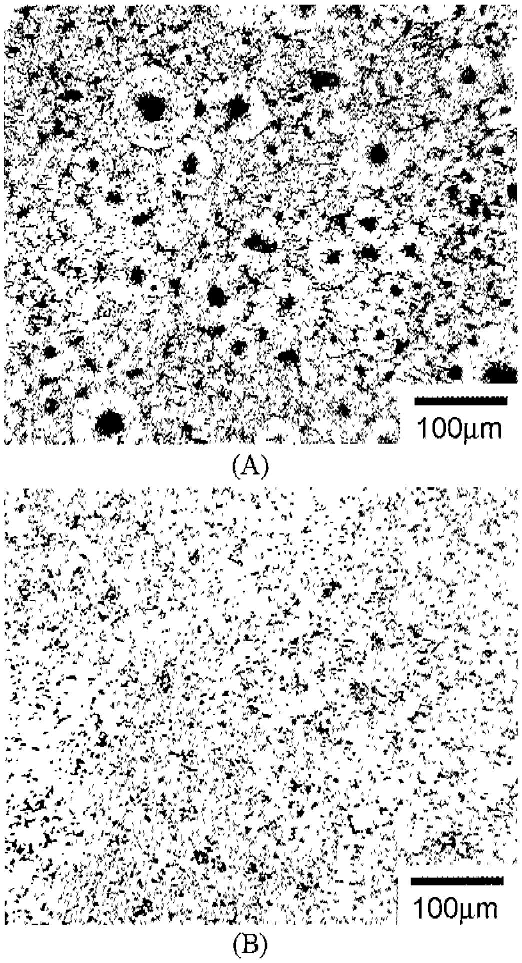


Fig. 8. Optical microscopic examination on the effect of cold isostatic pressure on pore structure in sintered alumina ceramics fabricated from dispersed granules. (A) 100 MPa and (B) 180 MPa.

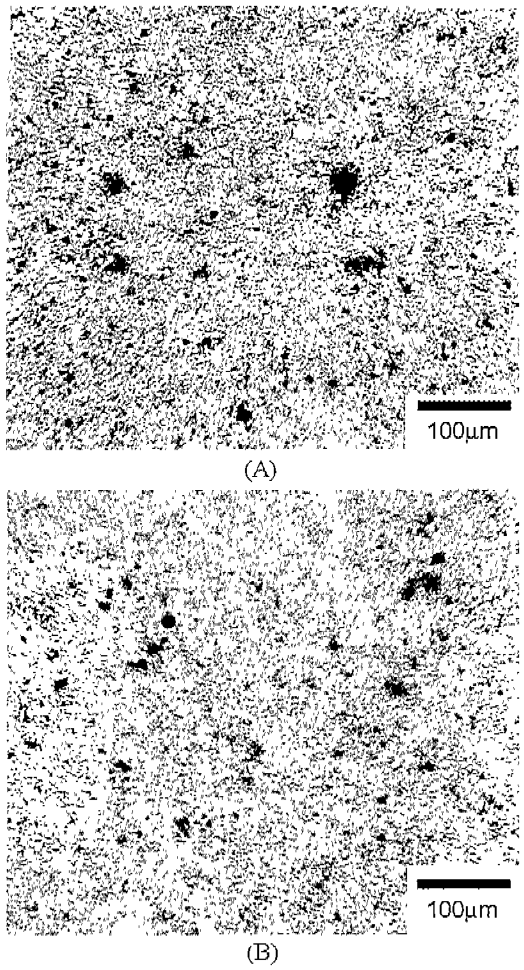


Fig. 9. Optical microscopic examination on the effect of cold isostatic pressure on pore structure in sintered alumina ceramics fabricated from flocculated granules. (A) 100 MPa and (B) 180 MPa.

face of the specimens revealed that large voids were responsible fracture origins. Figure 10 shows the typical fracture origins found in sintered bodies fabricated with granules made from a flocculated slurry. These micrographs are taken for specimens which showed relatively low strength. Large voids are found as fracture origins in these specimens and are responsible for the degradation of alumina ceramics.

4. Discussion

The dimples in alumina green bodies were confirmed by high resolution scanning electron microscopy. The large pores of approximately round shape were developed from dimples in granules, which were used for the production of this ceramics through the powder compaction process. Pores of more or less irregular shape were formed from the low density regions at the boundaries of granules. These pores developed from the dimples and boundaries of granules must be the fracture origin in this study. It was recognized that a fracture origin was an internal pore mainly from fracture surface observation after the strength examination. It was indicated that these pores were fracture origin in the sample made from dispersed slurry at 100 MPa and the weibull modulus increased with the decline of the average strength. This is because the sample made at 100 MPa contained many large pores, and the size of fracture origin was controlled to be uniform by these pores.

This paper investigated the influence of the characteristics of granules on the microstructure and the strength of sintered bodies manufactured in the commercial scale. Removing the large pores by conventional pressureless sintering is very difficult. As our opinion, the granules should be round shape, soft and deformable without dimples. This is an important factor in improving the mechanical properties of high reliability ceramics.

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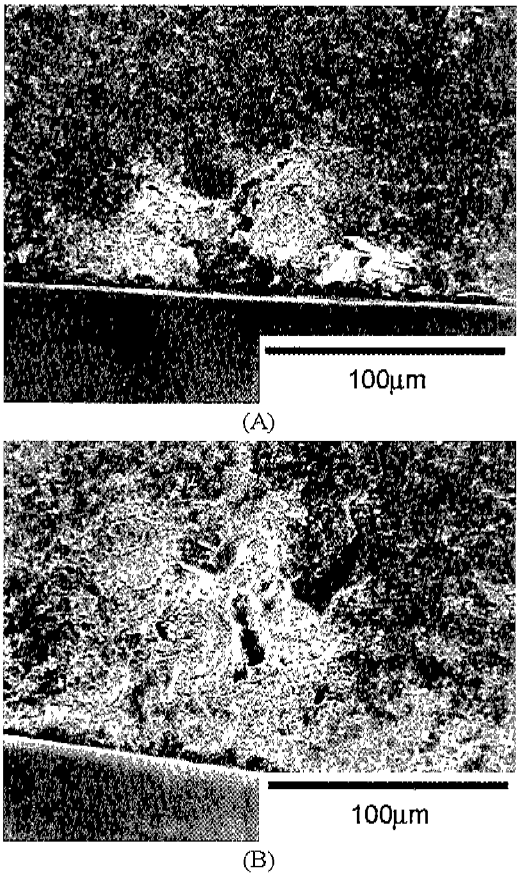

Fig. 10. An example of fracture origin in sintered bodies fabricated from flocculated granules with cold isostatic pressures of (A) 100 MPa and (B) 180 MPa.

REFERENCES

1. K. Uematsu, M. Sekiguchi, J.-Y. Kim, K. Saito, Y. Mutoh, M. Inoue and Y. Fujino, "Effect of Processing Conditions on the Characteristics of Pore in Hot Isostatically Pressed Alumina," *J. Mater. Sci.*, 28(11), 1788-92 (1993).
2. N. Shinohara, M. Okumiya, T. Hotta, K. Nakahira, M. Naito and K. Uematsu, "Effect of Seasons on Density, Strength of Alumina," *Am. Ceram. Soc. Bull.*, **78**(2), 81-84 (1999).
3. T. Hotta, K. Nakahira, M. Naito, N. Shinohara, M. Okumiya and K. Uematsu, "Origin of Strength Change in Ceramics Associated with the Alteration of Spray Dryer," *J. Mater. Sci.*, 14(7), 2974-79 (1999).
4. M. Kitayama and J. A. Pask, "Formation and Control of Agglomerates in Alumina Powder," *J. Am. Ceram. Soc.*, **79**(8), 2003-11 (1996).
5. H. Takahashi, N. Shinohara, K. Uematsu and J. Tsubaki, "Influence of Granule Character and Compaction on the Mechanical Properties of Sintered Silicon Nitride," *J. Am. Ceram. Soc.*, **79**(4), 843-48 (1996).
6. W. J. Walker, Jr., J. S. Reed and S. K. Vema, "Influence of Granule Character on Strength and Weibull Modules of Sintered Alumina," *J. Am. Ceram. Soc.*, **82**(1), 50-56 (1999).
7. H. J. Lim, D. H. Cho, M. K. Kim, S. M. Han and M. Iwasa, "The Evaluation of Mechanical Properties for Alumina Ceramics," *J. Kor. Ceram. Soc.*, **33**(3), 339-47 (1996).
8. H. Takahashi, N. Shinohara and K. Uematsu, "Influence of Spray-dry Slurry Flocculation on the Structure of Sintered Silicon Nitride," *J. Ceram. Soc. Jpn.*, **104**(1), 59-62 (1996).
9. W. J. Walker, Jr., J. S. Reed and S. K. Verma, "Influence of Slurry Parameters on the Characteristics of Spray-dried Granules," *J. Am. Ceram. Soc.*, **82**(7), 1711-19 (1999).
10. J. H. Park, M. I. Hwang, D. H. Kim, H. U. Choi and Y. N. Kim, "The Fabrication and Characteristics of Porous Alumina Ceramics by Pressureless Powder Packing Forming Method: I. Alumina," *J. Kor. Ceram. Soc.*, **36**(6), 662-70 (1999).
11. H. C. Park, J. W. Kim, U. K. Paik and S. C. Choi, "Effect of Green Microstructure on Sintered Microstructure and Mechanical Properties of Reaction-bonded Silicon Carbide," *J. Kor. Ceram. Soc.*, **36**(1), 97-105 (1999).
12. R. W. Rice, "Fracture Mechanics of Ceramics, Vol.1," Ed. by R. C. Bradt, D. P. H. Hasselman and F. F. Lange, Plenum, New York, pp. 323 (1974).
13. A. G. EVANSE, "Structural Reliability; A Processing-dependent Phenomenon," *J. Am. Ceram. Soc.*, **65**(3), 127-37 (1982).
14. K. Uematsu, "Immersion Microscopy for Detailed Characterization of Defects in Ceramic Powders and Green Bodies," *Powder Technology*, **88**(2), 291-98 (1996).
15. K. Uematsu, M. Miyashita, J. Y. Kim, Z. Kato and N. Uchida, "Effect of Forming Pressure on the Internal Structure of Alumina Green Bodies Examined with Immersion Liquid Technique," *J. Am. Ceram. Soc.*, **74**(9), 2170-74 (1991).
16. M. Miyashita, J. Y. Kim, Z Kato, N. Uchida and K. Uematsu, "Effect of Compaction Pressure on the Internal Structure of Sintered Alumina," *J. Ceram. Soc. Jpn.*, (*in Jpn.*), **100**(11), 1357-60 (1992).
17. K. Uematsu, M. Miyashita, J. Y. Kim and N. Uchida, "Direct Study of the Behavior of Flaw-forming Defect in Sintering," *J. Am. Ceram. Soc.*, **75**(4), 1016-18 (1992).
18. Y. Iwamoto, H. Nomura, I. Sugiura, J. Tsubaki, H. Takahashi, K. Ishikawa, N. Shinohara, M. Okumiya, T. Yamada, H. Kamiya and K. Uematsu, "Microstructure Evolution and Mechanical Strength of Silicon Nitride Ceramics," *J. Mater. Res.*, **9**(5), 1208-13 (1994).
19. K. Uematsu, J. -Y. Kim, M. Miyashita, N. Uchida and K. Saito, "Direct Observation of Internal Structure in Spray-dried Alumina Granules," *J. Am. Ceram. Soc.*, **73**(8), 2555-57 (1990).
20. N. Shinohara, M. Okumiya, T. Hotta, K. Nakahira, M. Naito and K. Uematsu, "Seasonal Variation of Microstructure and Sintered Strength of Dry-pressed Alumina," *J. Am. Ceram. Soc.*, **82**(12), 3441-46 (1999).
21. N. Shinohara, M. Okumiya, T. Hotta, K. Nakahira, M. Naito and K. Uematsu, "Formation Mechanisms of Processing Defects and Their Relevance to the Strength in Alumina Ceramics Made by Powder Compaction Process," *J. Mater. Sci.*, **34**, 4271-77 (1999).