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Processing defects and their relevance to strength in alumina ceramics made by slip casting

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Abstract

Al_2O_3 made by slip casting inherently contained the elongated and the spherical shaped defects. The pores of elongated shape were formed through the liquid flow during the casting process, since they were found in all slip cast specimens and not found in the spontaneously dried specimen where no rigorous flow of water happened. The formation of these defects was insensitive to the slurry properties. The origin of spherical pores was likely due to the entrapped air bubbles during de-airing procedure. Their removal by de-airing was easy for a dispersed slurry having a low viscosity, but difficult for a flocculated slurry of high viscosity. The Weibull's plots for the flexural strengths are essentially the same in the region of high strengths. Specimens made from the flocculated slurry contain a higher concentration of the spherical pores, and some of the resultant specimens have low strength. The lower strength of those ceramics has been ascribed to more detrimental defects, i.e. the spherical ones.

Keywords: Al_2O_3; Microstructure-prefiring; Porosity; Slip casting; Strength

1. Introduction

Slip casting is an attractive forming method and is used widely in the commercial production of ceramics. One of the most favorable characteristics for the method is the high quality of products, which is often ascribed to their good microstructures realized with this particular processing.[1] However, this explanation appears inaccurate, since some important properties of ceramics, such as strength, are governed by few exceptionally detrimental defects, not by the prevailing microstructure.[2] These defects are minority members in the microstructure, and their characteristics are often only poorly known, especially in alumina ceramics.[3–15] A so-called "good microstructure" does not guarantee the absence of very detrimental defects, since they can not be found by normal characterization method of microstructure. Fractography is the most common method to examine them directly. In alumina ceramics, however, it is extremely difficult to identify defects with this method except in some special cases. To understand the properties of alumina ceramics made by slip casting, it is necessary to characterize detrimental defects in the material.

Detrimental defects in ceramics can be easily studied with optical microscopic tools developed recently.[7,10,16–25] In this method, specimens are thinned to tens of micrometers to make them transparent, and are examined with an optical microscope in the transmission mode. The volume of specimen under examination is a few cubic millimeters, which is large enough to contain some large processing defects. With conventional SEM observation, the volume of specimen examined is nearly zero, and only major microstructural features are identified. The present methods have been applied in the research of ceramics, and successfully clarified such difficult problems as the origins of sintering deformation,[21] seasonal variation of properties,[22] the detrimental effect of binder on microstructure development,[17] etc.

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This paper examines the microstructure of alumina ceramics made by slip casting with a particular focus on the large detrimental defects. The optical microscopic approach is applied again to examine the characteristics of these defects and their relevance to the flexural strength. The effects of slurry characteristics on these detrimental defects and their properties are also examined.

2. Experimental

2.1. Sample preparation procedure

Commercial low-soda alumina powder (AL-160SG-4, Showa Denko Co., Japan) was used as a raw material. Fig. 1 shows the procedure of sample preparation. The powders were dispersed with a commercial ammonium polycarboxylate dispersant (CELUNA D-305, Chukyo yushi Co.) in an ion exchanged water at the solid loading of 50vol%. The amounts of dispersant added to Al_2O_3 powder weight were varied from 0 to 2 mass%, with controlling pH values for the 0 mass% slurry. The slurries were ball-milled for 24 h in an alumina media and vacuum treated for 10 min for de-airing. A plaster mold was used for producing a compact (65×65×7 mm^3) by slip casting. An aluminum foil was also used for producing a compact (100×65×10 mm^3) by spontaneous drying. The compact detached from the plaster or foil was dried at 110°C for 24 h, and heated at 500°C for 5 h to remove the dispersant. The compacts were then sintered at 1600°C for 2 h in air.

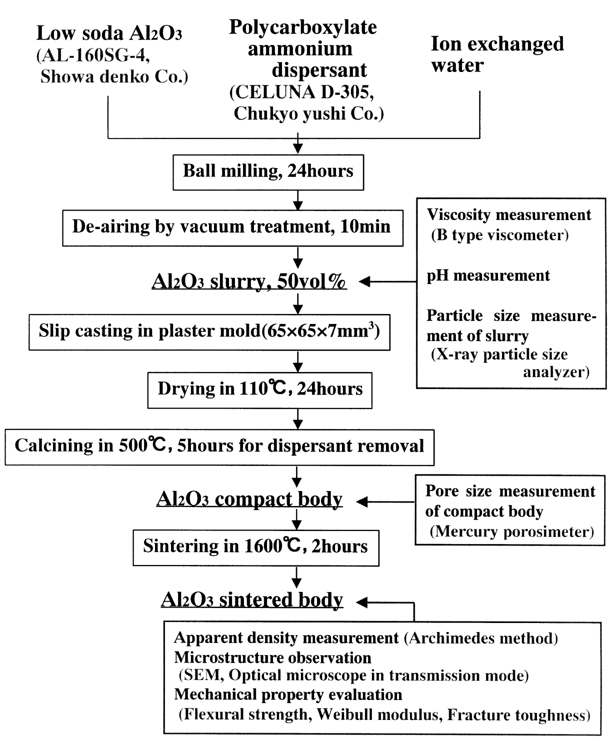

Fig. 1. Flow chart of Al_2O_3 slip casting process.

2.2. Evaluation

The apparent viscosity of the slurry was measured with a B type viscometer (Tokyo Keiki Co., Japan) at the shear rate 15 s^{-1}. The particle size distribution in the slurry was evaluated with an X-ray particle size analyzer (SediGraph 5100, Micrometrics Co.) for the slurry of solid content of 7 mass%. Particles were dispersed in a supernatant of centrifuged slurry. Archimedes method was used for determining the bulk density with ion exchanged water as the immersion liquid. The flexural strength of sintered bodies was determined with the method specified by JIS R1600 with a universal-testing machine. The specimen size was 3×4×40 mm^3. The outer and inner spans for four point bending mode were 30 and 10 mm, respectively, and the loading speed was 0.5 mm/min. The fracture toughness was measured with the single edge pre-cracked beam (SEPB) method specified by JIS R1607. The Weibull modulus was calculated with JIS R1625. The average particle size was determined by the intercept measurement on the polished and thermally etched surface of the sintered body. The surface of specimen was polished with diamond paste down to 0.5 mm. The internal structure of the sintered body was examined with optical microscopes (Model OPTIPHOT-POL and Model E600 POL-TP21, Nikon Co.) in transmission mode. The specimens were thinned, and both faces were polished with diamond paste (0.5 Mm) to the thickness or about 30 μm.

3. Results

Table 1 shows the change of apparent viscosity with the dispersant content. The minimum viscosity is found at the dispersant content about 0.2–0.4 mass% at room temperature. This minimum corresponds to the best dispersion of the slurry, i.e. a slurry system free from significant flocculation of raw powder.[11,14] In the following experiments, the slurries with the dispersant contents 0.2 and 2 mass% are selected to represent the dispersed and flocculated slurries, respectively.

Fig. 2 shows the particle size distributions for slurries with 0, 0.2 and 2 mass% of dispersant amounts. The slurry with 0.2 mass% dispersant is well dispersed and the other two are flocculated. These slurries have the same particle size distribution, with an average particle size around 0.7 μm. The distribution curve is typical for this type of powder, with a maximum around 10 μm and a minimum under 0.1 μm. Clearly, the slurry characteristics do not affect the particle size distribution. There is no indication of hard aggregates in these slurries also.

Fig. 3 shows the microstructures of ceramics prepared from the dispersed (dispersant 0.2 mass%) and the flocculated slurries (dispersant 2 mass%). They are basically the same and uniform, and are composed of

Table 1
Apparent viscosity of the Al_2O_3 slurries with various amounts of polycarboxylate ammonium dispersant inclusions

Dispersant amount mass%	0.2	0.4	1	2
Apparent viscosity mPa·s	360	360	1000	900

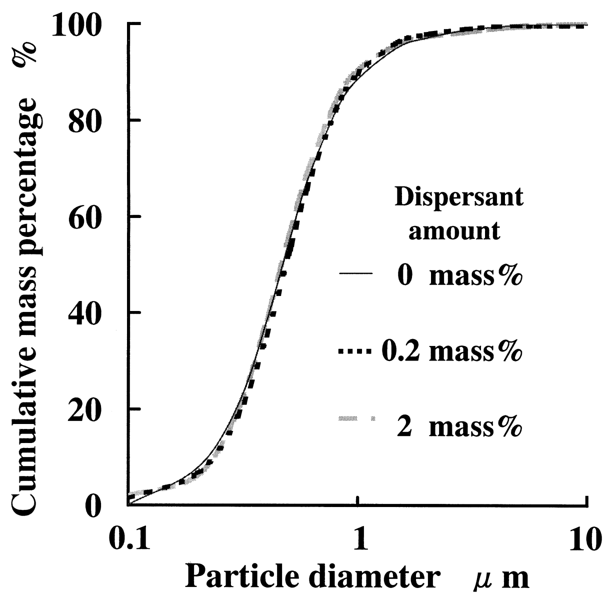

Fig. 2. Particle size distributions for the Al_2O_3 slurries with 0, 0.2 and 2 mass% of dispersants.

alumina grains of elongated shape. Mean grain sizes and the relative densities are 4.3 μm and 99.7%, and 4.2 μm and 98.7%, for the former and the latter specimens, respectively. Small pores of about 1 μm are found both in the grains and at grain boundaries. There is no indication of abnormal grain growth.

Fig. 4 shows the photomicrographs taken in transmission mode for sintered bodies prepared from the dispersed (dispersant 0.2 mass%) and the flocculated (dispersant 2 mass%) slurries. Black features of elongated shapes are found in both specimens. Their size is quite uniform and is about 10–15 μm long and a few micrometers wide. In addition to these pores of elongated shape, the specimen made from the flocculated slurry contains approximately round features also, as exemplified in Fig. 4(b). This type of large feature is rarely found in the specimen made from the dispersed slurry. Except for these round features, the microstructures shown by these micrographs are similar. A similar structure is also observed in specimens made from the slurry with no dispersant.

Fig. 5 shows the Weibull's plots for the flexural strengths of sintered bodies made from the dispersed (dispersant 0.2 mass%) and the flocculated (dispersant 2 mass%) slurries. Results are essentially the same in the region of high strength, but are significantly different in the region of low strength. The specimens made from the flocculated slurry contain a few test pieces of extremely

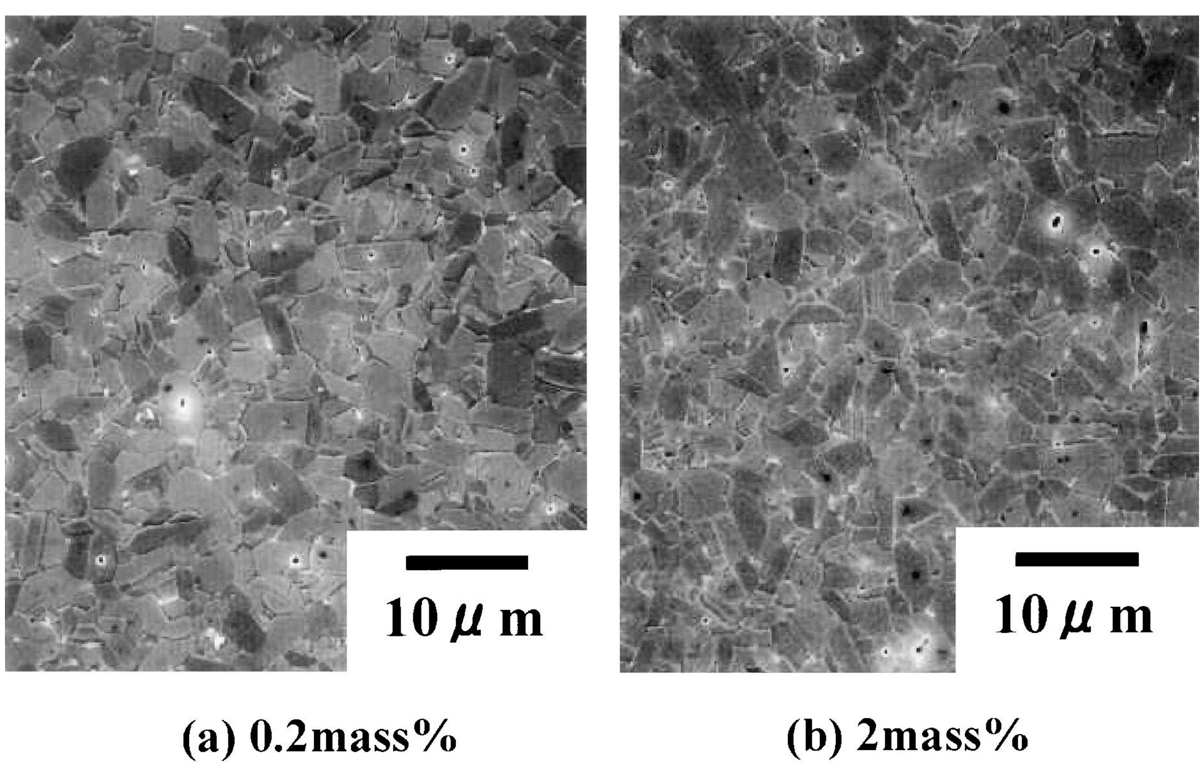

Fig. 3. Scanning electron micrographs of polished and thermally etched surfaces of Al_2O_3 sintered bodies prepared from the dispersed (dispersant 0.2 mass%) and the flocculated (dispersant 2 mass%) slurries.

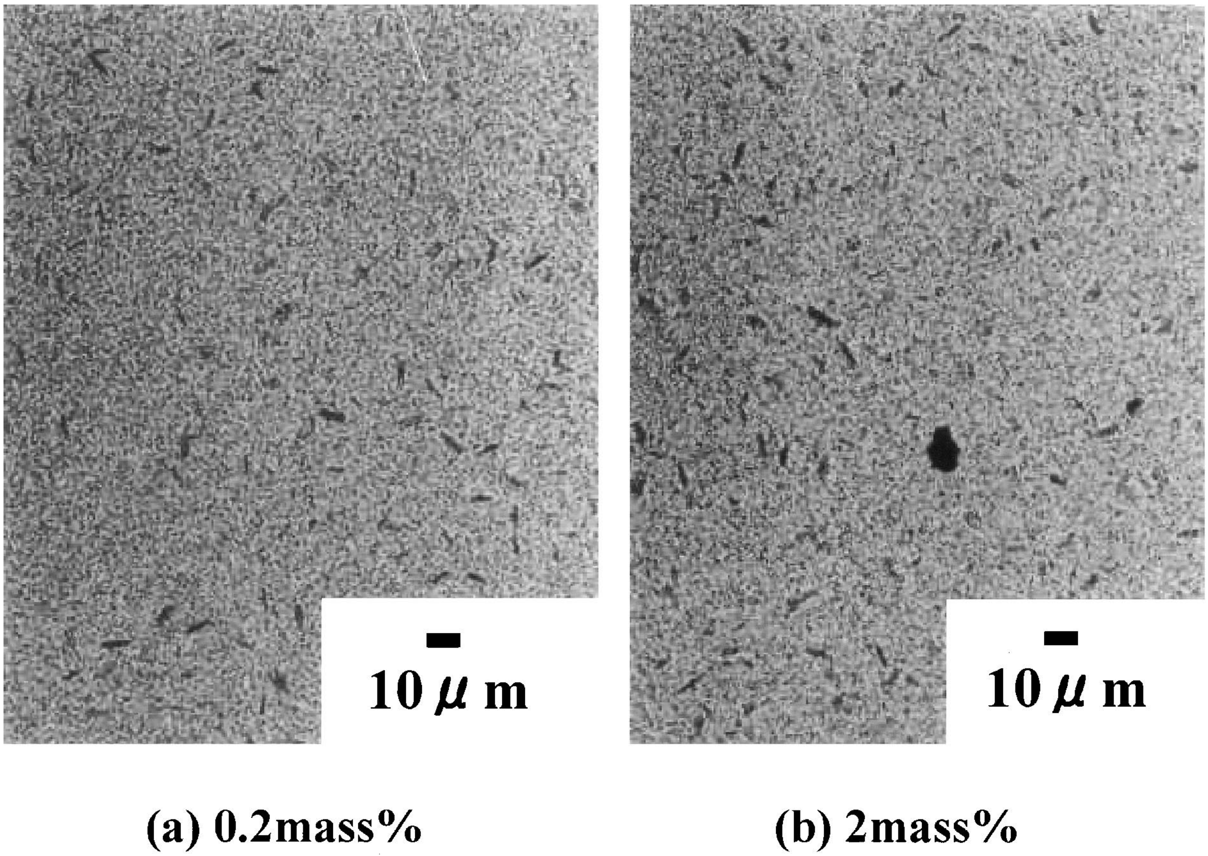

Fig. 4. Optical photomicrographs taken in the transmission mode of the Al_2O_3 sintered bodies prepared from the dispersed (dispersant 0.2 mass%) and the flocculated (dispersant 2 mass%) slurries.

low strength. The mean strengths are, however, approximately the same, and are 481 and 478 MPa for the former and the latter specimens, respectively. The fracture toughness values measured by the SEPB method are found to be the same for both materials, i.e. 4 $MPa{\cdot}m^{1/2}$.

Fig. 6 shows SEM micrographs of fractured surfaces. The typical features of fracture origins, such as mirrors, are indicated in the photos [especially Fig. 6 (b)]. Two types of pores are noted at the sites of fracture initiation. Specimens of low strength often show pores of round shape at the sites, which are indicated as "*P*" in Fig. 5. Those of rather high strength show pores of elongated shapes at the sites whenever one can be identified. The shape and size for the latter type of defect is similar to the dark features of the elongated shapes found in the above optical microscopy.

Fig. 7 shows an optical photomicrograph of a sintered body prepared by the spontaneous drying of the dispersed slurry without a plaster mold. This specimen has a much more uniform microstructure than those made by slip casting. It does not contain the large features of elongated shapes. Except for these large defects, essentially the same defect distributions are noted for the region of small defects under about 10 μm in specimens made by the slip casting and the spontaneous drying, by comparing the micrographs of Figs. 4 and 7

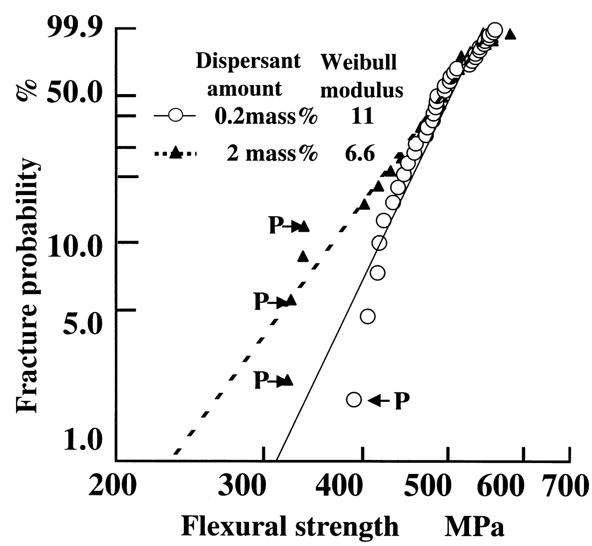

Fig. 5. Weibull's plots of the Al_2O_3 sintered bodies prepared from the dispersed (dispersant 0.2 mass%) and the flocculated (dispersant 2 mass%) slurries; "*P*" indicates the sample including the fracture surface which a spherical ball-like pore is present at the fracture origin in specimens.

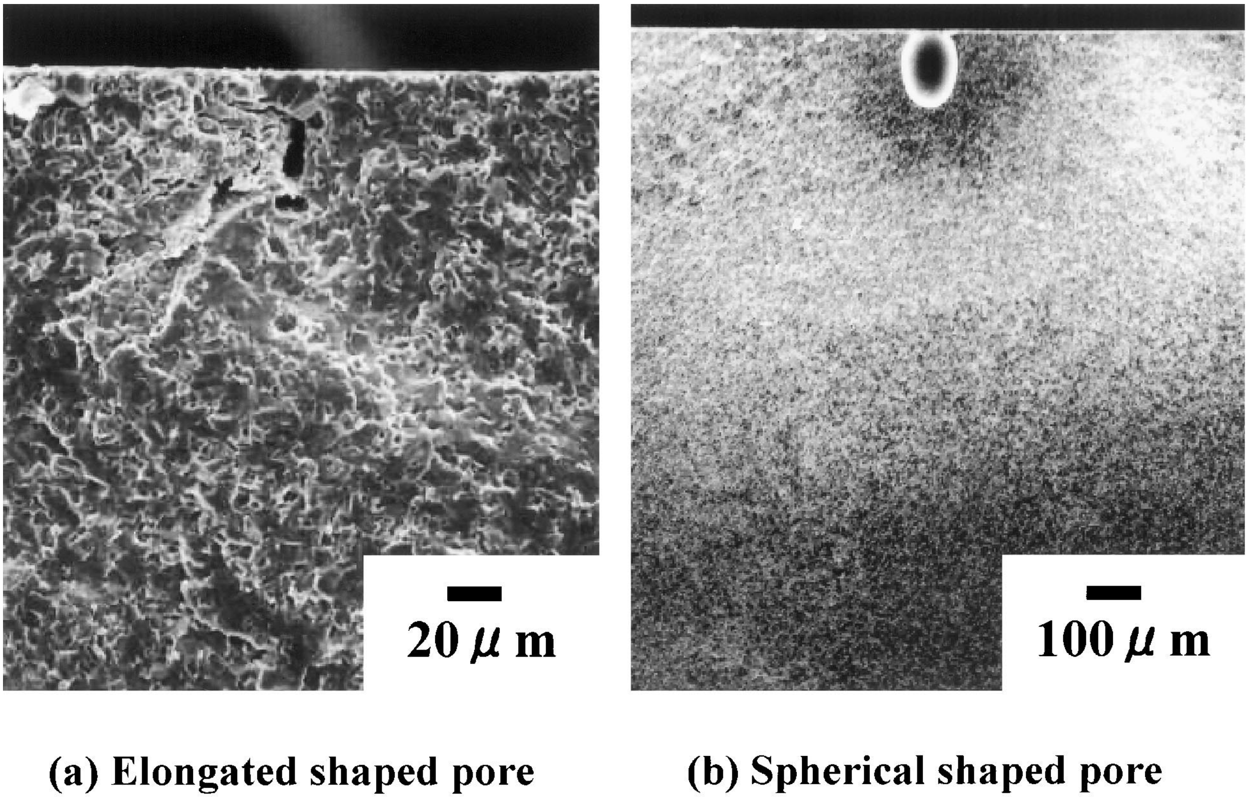

Fig. 6. Scanning electron micrographs of a fractured surface of the Al_2O_3 sintered body prepared from the flocculated (dispersant 2 mass%) slurry.

4. Discussion

The strength characteristics of the materials treated in this study can be explained by the microstructures, which are specific to the processing. Clearly, there are two types of defects in the ceramics made by the slip casting. One is of elongated shape and the other of a spherical shape. The former and the latter defects govern the fracture of ceramics in the regions of high strengths and low strengths, respectively. The characteristics of the latter defects are sensitive to the slurry properties, contrary to those of the former which appear not to be susceptible. Specimens made from the flocculated slurry contain a higher concentration of these spherical pores, and some of the resultant specimens have low strength.

Clearly, the pores of elongated shape are formed through the liquid flow during the casting process. They are found in all slip cast specimens in this study, and are not found in the specimen made by a spontaneous drying where no rigorous flow occurred or capillary suction of water to the mold is present. Their characteristics are rather insensitive to the slurry properties in the present system. This is interesting, since it was believed that they affected the structure and properties of ceramics at the start of the present study. Their strong effect on the pore size distribution has been well known for sintered bodies[18,20] made through the powder compaction method. The formation mechanism of pores of elongated shape is an important subject for a future study. The origin of large spherical pores is likely due to entrapped air bubbles. Their removal by de-airing is easy for a dispersed slurry

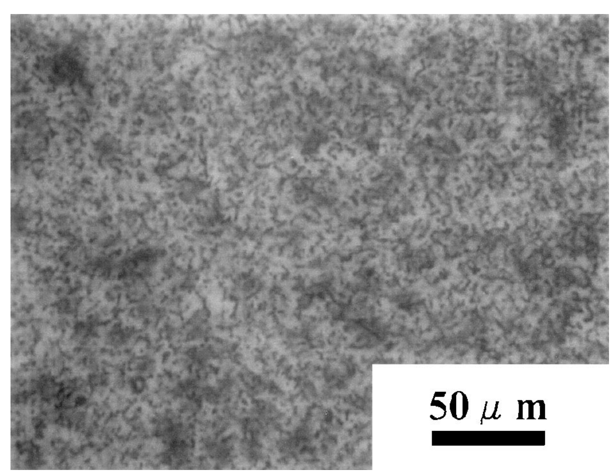

Fig. 7. Optical photomicrograph taken in the transmission mode of the Al_2O_3 sintered bodies prepared by the spontaneous drying process without plaster mold and the slip casting process of the dispersed (dispersant 0.2 mass%) slurry.

having a low viscosity, but difficult for a flocculated slurry of high viscosity.

It is interesting to compare the strength and microstructure found in this study to those made by the compaction process.[18,20–25] The ceramics made by slip casting have a higher flexural strength than those made by the powder compaction route from the same raw powder. A typical strength was approximately 350 MPa for the alumina ceramics made by the compaction process. The low strength of those ceramics has been ascribed to very detrimental defects in the microstructure. Pores in these materials have a rather widely distributed size. Although pores of size 40–50 μm are commonly noted in those specimens by microscopic examination in the transmission mode, the size distribution curve constructed suggested that pores of much larger size be present. A simulation study showed that the size of pores responsible for fracture is over 100 μm for these materials,[24] consistent with their low strength. The size of defects of elongated shape in the present slip cast specimen, however, is much smaller than this value, typically about 15×5 μm. The shape of defects is clearly less important than the marked size difference for the high strength of present specimens. Only when a slip cast specimen contains a large round pore as shown in Fig. 6 (b), the strength of the present specimen reduced to the value comparable to that of ceramics made through compaction process, as illustrated in Fig. 5.

The average size of the round pores in the slip cast specimen must be rather small. In the specimens made by the powder compaction process, the size distribution is extended to larger sizes, and a typical size of pore responsible for fracture was estimated to be over 150 μm, corresponding to the flexural strength of 350 MPa. In the slip cast specimen, the presence of these large pores must be rare, since the evacuating treatment of slurry must have removed large air bubbles, the origin of these round pores. Only small air bubbles should be able to survive in the slurry.

5. Conclusions

1. Al_2O_3 ceramics made by slip casting inherently contained elongated shaped defects and spherical shaped ones. The pores of elongated shape were formed through the liquid flow during the casting process, since they were found in all slip cast specimens and not found in the spontaneously dried specimen where no rigorous flow of water happened. These defects were insensitive to the slurry properties. The spherical pores were probably due to entrapped air bubbles during de-airing procedure. Their removal by de-airing was easy for a dispersed slurry having a low viscosity, but difficult for a flocculated slurry of high viscosity.
2. The elongated and spherical shaped defects governed the fractures of ceramics, respectively. The elongated shaped defects are found in both specimens prepared from the dispersed (dispersant 0.2 mass%) and the flocculated (dispersant 2 mass%) slurries. The Weibull's plots for the flexural strengths are essentially the same in the region of high strengths. Specimens made from the flocculated slurry contain higher concentration of the spherical pores, and some of the resultant specimens have low strength. The lower strength of those ceramics has been ascribed to more detrimental defects, i.e. the spherical ones.

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