Influence of Dehydration Rate on the Degree of Particle Orientation in Alumina Green Body Made by Slip Casting

Satoshi TANAKA, Shinya WATANABE, Zenji KATO, Nozomu UCHIDA, Kozo YOKOTA,*  
Yoshihito KONDO* and Keizo UEMATSU

Department of Chemistry, Nagasaki University of Technology, 1603-1, Kamitomioka, Nagasaki-shi, Niigata 940–2188  
*Kagawa Industrial Technology Center, 587–1, Goto, Takamatsu-shi, Kagawa 761–8031

Orientation structure of particles was evaluated quantitatively by an optical method based on polarized light microscopy in an alumina green body prepared by slip casting method using porous alumina and plaster mold. The dehydration rate in the alumina mold was higher than that of the plaster mold. The alumina particles in the green body were always orientated parallel to the surface of the mold. The degree of oriented particles was affected by the dehydration rate during development of the cake. The degree of orientation in the alumina mold system was higher than in plaster mold system for rapid dehydration. The highest degree of particle orientation was obtained at regions near the mold, which was developed at the beginning stage of slip casting. The degree of orientation was explained by the dehydration rate in the mold system.

[Received August 6, 2004; Accepted October 26, 2004]

Key-words: Slip casting, Alumina, Polarized microscope, Green body, Orientation

1. Introduction

Relationship between the processing and the green body structure must be understood accurately in ceramics, since the latter directly governs the uniformities of shrinkage during sintering and also the characteristics of sintered bodies.1,2 Recent papers show that even a very weak particle orientation causes the anisotropic shrinkage and deformation during sintering in the green bodies made by extrusion molding,3 die-pressing,4,8 slip casting,9,10,11 and tape casting.12,13 However, the conclusions obtained through these studies remains qualitative. Because, this orientated structure was too weak to be detected by the X-ray diffraction analysis and other usual methods.12 Focused quantitative study is clearly needed to understand the effect of processing on the particle orientation.

Weakly orientated structure of particles can be evaluated using the optical microscopy in the alumina green bodies.9-13 In the optical method, a thin specimen cut from a green body is made transparent with an immersion liquid and is observed with a polarized light microscope in the transmission mode. The degree of orientation can be determined quantitatively through the measurement of birefringence at various places in the green body.13) The value obtained should be conveniently used to discuss the relation between the processing and the local structure within the compact. Past study showed that particles tend to align with their longitudinal directions parallel to the plaster surface in the slip cast alumina green body, and the orientation degree was slightly higher at the region near the plaster surface than the center region. This result suggests that the particle direction as well as the degree of orientation is governed by the processing conditions, particularly the dehydration rate during casting.

The objective of this study is to clarify the relationship between the degree of particle orientation and the dehydration rate in the slip casting bodies. The dehydration rates will be varied by using two types of mold. One is the porous alumina mold reported by Kondo et al, which minimizes the contamination of green body by impurity diffusion from the mold15 and is favorable for the processing of advanced ceramics. The developing rate of green body can be controlled by changing the pore diameter in the alumina molds.15) A plaster mold was used to represent the mold for conventional processing and to change the dehydration rate also.

2. Experimental procedure

A commercial grade low-soda alumina powder (AL–1605G4, Showa Denko K.K.) was used as a raw material. A commercial plaster and a porous alumina molds were used in order to change the dehydration rate. The porous alumina mold was made by uni-axial pressing at 60 MPa from alumina powder (AA05, Sumitomo Chemical Co., Ltd.), and calcined at 1000°C, which detail fabrication process was referred in Ref. 15. The pore radiuses are about 1.7 and 0.2 μm in the plaster and the porous alumina mold, respectively. The porosities are 48% and 41% of the plaster and the porous alumina molds, respectively.

The alumina powders, distilled water and poly acrylic acid 0.5 mass% (Ceruna D305, Chukyo-Yushi Co., Ltd.) as a dispersant were mixed to prepare slurry with solid loading 50 vol%. After ball milling for 20 h with alumina balls, the slurry was de-aired for 5 min in a vacuum. The slurry was cast in the mold and removed after solidified (Fig. 1). The cake obtained (10 mm × 50 mm × 50 mm) was dried for a week at the room temperature. The dried compacts were calcined at 1000°C to remove the dispersant in the compact.

The rheological characteristic of the slurry was examined with a concentric viscometer (VT550, HAAKE, and Switzerland). The viscosity was measured by increasing and then decreasing the shear rate for the range of 0 to 1000 s⁻¹ in 10
min. The temperature of the slurry was kept at 25°C during the measurement.

The dehydration rate \( Q \) was determined from the height of dehydrated layer \( L \) based on the Sobue’s analysis,\(^{16,17}\)

\[
Q = \frac{dL}{dt} \left( 1 - \frac{f_1}{f_2} \right)
\]

where \( f_1 \) is the solid volume in the slurry, and \( f_2 \) the solid volume in the cake. The \( dL/dt \) was calculated from the slope on the developing rate curve of dehydration layer.

The degree of particle orientation was determined using a polarized light microscope installed with a sensitive color plate (\( n = 530 \) nm) and a Berek compensator. Thin specimens (typically 0.2 mm thick) for measurement were prepared by cutting small pieces and grinding them with a sand paper. Diiodomethane was added to make them transparent. In the analysis, the longest axis \((a\)-axis\) in alumina particles is assumed to be orientated parallel to the face of mold.\(^{11}\)

During filtration, the shortest axis of particles is known to orientate perpendicular to the filter surface.\(^{16}\) The degree of particle orientation \( f \) is defined as the ratio of the apparent birefringence of the compact \( \Delta n_{\text{comp}} \) to that of alumina single crystal \( \Delta n_{\text{single-crystal}} = 0.0075 \)\(^{15}\) for the compact along the direction of the longest axis \((a\)-axis\) of hexagonal alumina, as follows,\(^{11}\)

\[
f = \frac{\Delta n_{\text{comp}}}{\Delta n_{\text{single-crystal}}} = \frac{\Delta n_{\text{comp}}}{0.0075}
\]

\[
\Delta n_{\text{comp}} = \frac{R_{\text{comp}}}{d \cdot \rho}
\]

where, \( R_{\text{comp}} \) is the retardation of the sample, \( d \) the thickness of the observation sample, and \( \rho \) the relative density. The apparent birefringence \( \Delta n_{\text{comp}} \) was calculated from the retardation \( R_{\text{comp}} \) for a compact, which was measured with the Berek compensator.\(^{11}\)

\[3. \text{ Result}\]

\textbf{Figure 2} shows the SEM micrograph of the alumina powder in this study. \textbf{Figure 3} shows their particle distributions measured by the X-ray sedimentation method. The particles have elongated shapes with sizes 0.2–1.0 \( \mu \text{m} \). The aspect ratio measured from the photograph is about 1.8.

\textbf{Figure 4} shows the rheological behavior of the slurry. The particles in the slurry are fairly well-dispersed. The shear-thinning behavior was noted, but the yield stress was almost zero in this slurry. No appreciable interaction is expected between particles in this slurry of high solid loading. Each particle should be able to move freely in the slurry in the casting process.

\textbf{Figure 5} shows the development of the dehydrated layer in casting. The development was much faster for the alumina mold than the plaster mold. Figure 5(b) shows the relationship between the square of the thickness of the dehydrated layer and the casting time. The square of the thickness increased linearly with the casting time.

\textbf{Figure 6} shows the dehydration rates calculated from the development rate of the dehydrated layer using Eq. (1) for the plaster and alumina mold. The dehydration rate has the highest at the beginning of the slip casting process, and decreases monotonously with time. The dehydration rate is approximately 3 times faster in alumina mold than the plaster mold.

\textbf{Figure 7} shows the SEM micrograph of the green body. The dehydration direction of water is a vertical direction in the photograph. The longest axes of particles are orientated in sideways slightly, that is perpendicular to the hydration direction. However, the orientation is too weak to be evaluated by XRD analysis.\(^{12}\)

\textbf{Figure 8} shows the crossed polarized light micrograph for
the specimen cut from a green compact near the center of the green body. The direction of dehydration is shown by the arrows. The brightness changed repeatedly from black to white and then to black with its rotation for every 45° as shown in the figure. The change suggests that the particles are
oriented in the green body. Observation at high magnification shows that large particles with elongated shapes clearly orientate with their longest axis parallel to the surface of the plaster and/or alumina mold. A narrow liner region of width approximately 10 μm is observed at the center of the compact. In that region, the direction of particle orientation is different from others. The particle orientation in the green body is schematically shown in Fig. 8(d).

**Figure 9** shows the distributions in the degree of particle orientation in the green bodies. The degree of particle orientation is high in the regions near the mold surface in both bodies. The alumina mold shows higher degree than the plaster mold for all regions. The highest value 0.17 was noted in the green body prepared with the alumina mold. It is interesting to note that the orientation degree is higher at the region near the mold and decrease towards the center of the compact. This result can be explained by the change of flow rate of water in the molding process. The symmetric values are noted in the degree of particle orientation with respect to the central line in the all samples.

**Figure 10** shows the effect of dehydration rate on the degree of particle orientation. The dehydration rate has a significant effect on the particle orientation. The degree of particle orientation in the green body increased monotonously with the dehydration rate and reached a certain value below 0.2 at high dehydration rate.

4. Discussions

4.1 Dehydration rate during slip casting

The dehydration rate could be controlled by changing the material for the mold. The liner relation in Fig. 5(b) agreed with the results of Adcock and Watanabe.\(^\text{15,17,20,21}\) This behavior shows that the flow through the cake governs development of the cake.\(^\text{17,22}\)

The effect of mold material on the dehydration rate can be discussed. The next relationship is known between the thickness of cake \(L\) and casting time \(t\), which is introduced by the Darcy’s law and the Kozeny–Carman equation.\(^\text{17}\)

\[
L^2 = \frac{2\Delta P g (1-f_s)^3}{9nS^2 f_s f_1 (f_s - 1) f_2} t
\]

where \(\Delta P\) is pressure drop within cake, \(g\) the gravity, \(\eta\) the viscosity of the slurry, \(S\) the specific surface area of the cake, \(f_s\) the volume fraction of particles in the slurry, \(f_s\) the volume fraction of particles in the cake, and \(f_s\) the volume fraction of the green body. The pressure drop is approximately equal to the capillary pressure \(\Delta P\) developed in the cylindrical pore in the mold in the slip casting process. The capillary pressure which develops a suction force of water is written as follows,

\[
\Delta P = \frac{2\gamma \cos \theta}{r}
\]

where \(\gamma\) is the surface energy of liquid, \(\theta\) the contact angle of water for the mold, and \(r\) the pore radius in the mold. The capillary pressure \(\Delta P\) is inversely proportional to the pore radius, since other parameters are almost the same among the molds used in this study. Therefore, the development rate of the cake is governed by the pore radius in the mold. The pore diameter is about 0.2 and 1.7 μm in the porous alumina and plaster mold, respectively. The suction force of alumina mold is about eight times of that of the plaster mold according to Eq.\(^\text{5}\). In the experiment, the development for the porous alumina mold is about three times of that of the plaster mold for all stage of casting. The pressure difference \(\Delta P\) in the plaster mold is about 0.057 MPa in Ref. 16. The result shows that the suction force saturates to a constant for small pore size in the porous alumina mold, because the maximum difference of pressure \(\Delta P\) attainable in an ambient condition is 0.1 MPa.

4.2 Particle orientation in slip cast green body

There is a clear correlation between the dehydration rate and the particle orientation. The longest axis, i.e., c-plane of alumina particles is orientated in parallel to the face of mold (Fig. 8). The degree of particles orientation increases with increasing the dehydration rate and reaches a high dehydration rate above 1 mm/min (Fig. 10).

At least two factors must be considered to discuss the results. One is the driving force for the particle orientation and the other is the kinetics for particle rotation. The driving force for the particle orientation should be the flow of water in the slurry when it dehydrates into the mold. High driving force should favor the orientation, since the flow of water at the developed cake/slurry boundary drives the direction of particles orientation. Kinetically, the particles must be rotated and
settled in the most stable position on the growing surface of the cake during the development of the cake. The high dehydration rate gives high driving force for orientation, but short time for particle orientation. There may be an optimum or saturation in the degree of particle orientation with the driving force. Excessively high driving force and/or dehydration rate may not contribute to high particle orientation and leads to a saturation.

The distribution of particle orientation within the cake is understandable. The dehydration rate is fast at the beginning stage in the slip casting. The particles received high driving forces for rotation by the water flow. The driving force decreases continuously with the casting process, and the degree of orientation decreases towards the center of the cake.

A different structure is observed at the center region of the cake. Particles are oriented in the central line also but in different direction. Particles in this region are oriented to the direction almost perpendicular to those in the cakes of both sides. The structure in this region was developed at the last moment of the casing between the two cake/slurry fronts. The particles in this region receive forces from both sides, and may align perpendicular relative to the particles of both sides. The line is similar to the weld line. The crack during drying sometimes occurs at this center line.

5. Conclusions

Orientation structure of particles was examined quantitatively by an optical method based on polarized light microscopy in the alumina green body prepared by slip casting method using the porous alumina and the plaster mold. The dehydration rate in the alumina mold is higher than that of the plaster mold for pore diameter and porosity. The longitudinal axes of particles in the green body were always orientated parallel to surface of the mold. The degree of orientated particles was affected by the dehydration rate during development of the cake. The degree of orientation in the alumina mold system was higher than plaster mold system for rapid dehydration. The highest degree of orientated particles was obtained at the regions near the mold, which was developed at the beginning stage in slip casting. The degree of orientation was explained by the dehydration rate in the molds system.

Acknowledgment This research was partly supported by Grant-in-Aid of the COE program in Nagaoka University of Technology for Scientific Research from the Japan Ministry of Education, Culture, Sports, Science and Technology.

References