Observation of sintering behavior and grain growth in gel-cast method for near net shape

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The sintering shrinkage behavior of gel-cast body was studied to be clarify what has influence to the green property, and causes the deformation in sintering, beside the slurry property in gel-casting method. The alumina sintered body was fabricated by gel-cast method. The two type mold, Flat-mold and Vertical-mold, were used for investigating the difference between the outside, central, upper and bottom of the sintered body. The measurement of sintering shrinkage shows that sintering shrinkage occurred toward the center. And, from the observation of cross-section SEM in sintered body, there were long grains along the mold wall in Flat-mold, and the grain size was larger in bottom of the body in Vertical-mold. It is suggested that the effect of interaction from the mold-wall, and effect of sedimentation causes the deformation of sintered body.

Key-words : Gel-casting method, Sintering shrinkage, Near net shape, Particle packing state, Grain growth

The gel-casting method is well known as obtaining homogeneous green density and drying shrinkage.1,2,4 In this process, the ceramics slurry including organic monomer and cross linker are casted into the mold and solidified by polymerization of monomer.1,2,3 The particles in slurry were fixed with polymerization. And, the green body having homogeneous density can be obtained using the slurry which has fine dispersion state.3,4 M. A. Janney et al. fabricated the silicon nitride rotor with gel-casting method,1,3 the average of green density was 53.77% and its variation in green density was extremely low, within 0.2 wt %.1,4 And more, there are some reports about fabricating the alumina body by gel-casting method. Those sintering shrinkage were 15–17% from high solid loading slurry over the 55 vol %.1,3,4 In these reports, with optimizing the slurry condition, the homogeneous green density and smaller sintering shrinkage were obtained, and possibility to achieve the near net shape was suggested.

However, it is necessary for achieving the near net shape to clarify what has influence to the green property, and causes the deformation, beside the slurry property in gel-casting method. For example, the sedimentation during polymerization of the organic monomer causes density difference between upper and bottom of the green body.3,4 In this study, the factor affecting on density uniformity of green body and, particle packing state in gel-casting process were investigated, from the results of measurement and observation.

The alumina sintered body was fabricated by gel-casting method. Alumina powder [AL-1605G4 (median diameter: 0.55 μm), Showa Denko (Ltd.)], deionized water, dispersant: Ammonium carboxylate [Sera D-305, Chukyo-Yushi (Ltd.)], monomer: methacrylamine (MAM) and cross-linker: N,N'-methylene-bis-acrylamide (MBAM) were mixed with pot-milling for 48 h, the solid loading of alumina slurry, 53 vol % (81.8 wt %), 54 vol % (82.4 wt %), and 55 vol % (83.0 wt %), was adjusted, respectively. Monomer and cross-linker amount ratio was adjusted for alumina powder, 9.0 wt % and 0.45 wt % (ratio of monomer/cross-linker = 20/1). The radical generator as reaction initiator: Ammonium persulfate and the catalyst: N,N,N',N'-tetramethylenediamine were added in deforming/mixing process. And, the ceramics slurry was casted into mold and solidified by polymerization for 30 minute. After solidified, wet green body was demolded. The green body was dried in vacuum, 80°C, 0.1 Pa, after drying in room temperature at atmospheric pressure for six days.

To observe the shrinkage behavior during firing, the mold sized X: 70 mm, Y: 70 mm, Z: 20 mm, was used in casting, as shown in Fig. 1. The gel-casted body was separated to 9 parts (divided into three, in each of vertical and horizontal direction), and the size difference before and after sintering were measured. In this paper, the separated parts were called in alphabet and number. The alphabet means the type of mold, F as Flat-mold and V as Vertical-mold. The number means position of the part in casted body, showed in Fig. 1. For example, the separated parts which fabricated by Flat-mold and position “1” was called “F-1”. And, fabricated by Vertical-mold and position “1” was called “V-1”.

The Flat-mold was used for investigating the difference between central part and mold wall side of the casted body. And the Vertical-mold was used for investigating the difference between the upper and bottom side of the casted body. The acrylic resin was selected as a material of mold. The size difference before and after the firing of each direction, X (horizontal), Y (vertical) and Z (thickness), was measured to obtain the shrinkage ratio.

The binder burned out at 700°C, and fired in condition at 1600°C. Cross-section of the each part was polished. And grain boundary removal by thermal etching at 1500°C, 5 min. The observation of grain growth state was performed by field emission scanning electron microscope (JSM-7600F, JOEL) in each separated parts.

It is important to to reduce the sintering shrinkage, in order to achieve the near net shape. With the lesser sintering shrinkage, the dimensional errors will be prevented. The effect of increasing solid loading in gel-casting slurry on reducing the sintering
shrinkage was investigated. Figure 2 shows the average of sintering shrinkage of the body fabricated from 53, 54 and 55 vol% slurry with the Flat-mold. In sintering shrinkage, with increasing the solid loading to 55 vol% from 53 vol%, it was reduced to 14.8% from 15.6%. Even 1%, it has great meaning in case of fabricating the large sized body, or being required for high dimensional accuracy.

The sintering shrinkage of each direction, X, Y and Z, were compared, for consideration of the shrinkage behavior. The 53 vol% solid loading slurry was chosen to fabricate the sintered body for investigation, because of largest shrinkage (in Fig. 2) to clarify the difference. Figure 3 shows sintering shrinkage in each separated parts, (a) in direction of X (horizontal), Y (vertical), and Z (thickness), (b) average of each directions. The number means the position of the separated parts as shown in Fig. 1. The sintering shrinkage was lowered to about 14%, with “F-2” and “F-8” in X-direction, “F-4” and “F-6” in Y-direction. And, the shrinkage was increased to about 16%, with “F-4” and “F-6” in X-direction, and “F-2” and “F-8” with Y-direction. In the parts between the corner parts, the shrinkage increased in one direction (X or Y) and decreased in another direction (X or Y). Moreover, in the square parts, “F-1”, “F-3”, “F-7” and “F-9”, shrinkage of X-direction and Y-direction were almost same as 15.5%. With Z-direction the highest shrinkage was observed in the central part “F-5” and it was 16.7%. These results show the shrinkage occurred towards the center of the casted body. In Fig. 3(b), the shrinkage of average of X, Y, and Z, was constant, around 15.6%. It means the green density were not so different in each parts. Even having the good uniformity, the shrinkage direction will not necessarily be isotropic, was suggested.

The state of grain growth in sintered body was observed to discuss how sintering shrinkage dimensions were determined. Figure 4 show the cross-section SEM photograph, with (a) near the outside of “F-1” and (b) center of “F-5”. These parts were separated from the sintered body, shaped by Flat-mold, “F-1” from outside and “F-5” from center of the sintered body. In

![Fig. 1. Green body with the Flat-mold and the Vertical-mold were separated to 9 parts for measuring sintering shrinkage and observation.](image)

![Fig. 2. The average of sintering shrinkage of each with different slurry solid loading. The sintering shrinkage was reduced to 14.6% in 55 vol% solid loading.](image)

![Fig. 3.](image)

![Fig. 4.](image)
The sintering shrinkage (%) of (a) each directions, and (b) average of each directions in each parts (showed in Fig. 1), shaped by the Flat-mold green body. The shrinkage occurred toward center of the sintered body, although average of each direction were almost constant.

Fig. 4(a), there were long grains, which were arraying along the outside of the sintered body. The long grains decreased as distance from the outside. In Fig. 4(b), the almost all of the grains have isotropic shape. In general, the grain growth occurs by fusing the contacted powder particles. And, the grain grows to the direction in which more contact points of powder particles exist. However, during solidifying, outside of sintered body has been at the wall side of the casted body. The particle packing state is predicted as shown in Fig. 5. It is estimated that the particles are aligned tightly along the wall by some interaction force between slurry and mold-wall, during solidification of the gel-casting slurry. There are more particle contact points near the mold-wall side than inside. And, the long grain was observed along the wall at sintered body.

Moreover, the upper side of sintered body was deformed like concave meniscus and the upper side of casted slurry formed concave meniscus in the mold. The gel-casting slurry is estimated to solidify under the influence of surface tension between the slurry and the mold wall, and powder particles arranged tightly in wall side.

Figure 6 shows the cross-section SEM photograph, with (a) “V-1” and (b) “V-9”. These were separated parts from the sintered body, shaped by the Vertical-mold, “V-1” from upper and “V-9” from bottom of the sintered body. Mostly, particle size in Fig. 6(a) are 2–4 µm, and in Fig. 6(b) are over 4 µm. The large grain tends to grow for easier sintering, increased particle contact point. The particle contact points are increased by higher green density or containing small raw particles in green body. From SEM observation in Fig. 6, it is considered that the density of bottom parts were increased or there were small particles increased at bottom side of green body. And, in gel-casting method, it is considered that the difference of sintering shrinkage between upper side and bottom side occurred by sedimentation.

In summary, the sintering shrinkage is not isotropic, and it occurred towards the center of the sintered body. However, the average of sintering shrinkage of each direction were almost
same in each position parts. From the cross-section observation with SEM, there are long grains along the outside of the sintered body which has been mold wall side when casted. And, larger grains exist in bottom of the casted body.

From these fact, it is considered that the effect of interaction from the mold wall, and effect of sedimentation causes the deformation of the sintered body. For achieving the near net shape, they must be considered, beside the condition, dispersion state and solid loading.

References