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Fabrication of stable Al_2O_3 slurries and dense green bodies using soft-energy milling process

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Abstract

Wet-jet milling and planetary homogenizing processes as soft-energy milling methods were employed as a novel method to prepare stable Al_2O_3 slurries. The viscosity of slurries prepared from the soft-energy milling was constant and stable for long time, as compared to ball-milled slurries. Though Al_2O_3 particles surface after ball milling yielded more hydroxyl groups, Al_2O_3 particles surface after the soft-energy milling was similar state to raw particles surface. Relative density of the green bodies prepared from the wet-milled slurries was about 67% and was independent on the slurry solid content. On the other hand, the relative density of the green bodies prepared from the ball-milled slurries increased with increasing solid content. Linear shrinkage of the sintered bodies prepared from the soft-energy milled slurries was independent of the slurry solid content, whereas that of the sintered bodies prepared from the ball-milled slurries increased with decreasing solid content.

Keywords: Milling; Suspensions; Slip casting; Al_2O_3

1. Introduction

Stable dispersion of ceramic powders in a liquid medium is required in colloidal processing methods such as slip casting and tape casting to fabricate ceramic products.[1–5] It is known that a good dispersion of ceramic particles in an aqueous medium is very important to form homogeneous structure of green bodies. In general, ball milling and planetary ball milling are used to prepare ceramic slurries. However, ceramic particles after these milling processes have tendency to re-flocculate. Hence, the re-flocculated slurries do not cause inhomogeneous structure of green bodies but high shrinkage after sintering.

The ceramic slurries must satisfy the following conditions to produce high dense green bodies by slip casting: (1) high solid content and (2) good dispersion.[6,7] A good dispersion of ceramic particles in the slurry is achieved by ensuring strong electrostatic and steric repulsion compared to the interparticle van der Waals forces. However, because the active sites such as lattice defect and radicals are induced on the surface of particles by the excess collision energy with ball,[8] ceramic particles after ball milling have tendency to re-flocculate.[9]

The re-flocculation of particles causes a viscosity increase and thixotropic property.[10] The flocculated particles result in inhomogeneous and loose structured green bodies, i.e. broad pore size distribution and low relative density.[1]

Recently, in chemical engineering, food technology, medical and biological fields, the wet-jet milling and the planetary homogenizing has been developed as a new method of mixing and dispersion.[11] In this wet-jet milling process, the particles in the suspension or solution collide mutually at high pressure and high speed. In the planetary homogenizing, the mixing and dispersion are performed by the collision with mesh. Using these effects, the grain refinement, emulsifying and homogenization are achieved within a short period of time.

In this work, wet-jet milling and planetary homogenizing processes as soft-energy milling methods were employed as a novel method to prepare stable Al_2O_3 slurries. The effects of the solid content of slurry on the wet-jet milling and the planetary homogenizing were investigated. Furthermore, the differences of the characteristics between soft-energy milled and ball-milled slurries were analyzed and discussed.

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2. Experimental procedure

2.1. Slurry preparation

A commercially available high purity α-Al_2O_3 (AKP-20; Sumitomo Chemical, Japan) with an average particle size (D_{50}) of 570 nm was used in this work. A commercially available NH_4^+ salt of poly(acrylic acid; PAA, Aron A-6114; Toagosei, Japan) was used as the dispersant. The aqueous suspensions containing 10, 30 and 50 vol.% of Al_2O_3 powder were prepared in 0.12 wt% dispersant solution. Diagrams of the wet-jet mill (PRE03-20-SP; Genus, Japan) and the planetary homogenizer (Planet H; Gokin Planetaring, Japan) system employed in this study are shown in Fig. 1. In the case of the wet-jet milling, slurry was pumped into the collision unit at 300 m/s of collision speed where the mutual collision of the particles took place. In the case of planetary homogenizing, slurry was put into the centrifuge tube with mesh. Centrifuge tube was revolved while rotating for 1 min. The revolution and rotation speed are 1000 rpm and 4375 rpm, respectively. For the purposes of comparison, the Al_2O_3 slurries (10, 30 and 50 vol.%) were also prepared by ball milling. The ball milling was performed for 24 h at 60 rpm using high-grade Al_2O_3 balls with a diameter of 10 mm. The slurry to ball ratio is 1:2 in volume relation.

2.2. Characterization

The rheological characteristics of the slurries were measured using Sine-wave vibro viscometer (SV-10; A&D, Japan) at 20 °C. The viscosity of slurry was calculated from the current to move transducers placed in the slurry (a frequency of 30 Hz and an amplitude of 0.2 mm). Acoustic Spectrometer (DT-1200; Dispersion Technology, USA) was employed for particle size distribution analysis. IR measurements of the Al_2O_3 powders following milling were carried out by Fourier transformed infrared spectroscopic analysis (Spectrum GX; PerkinElmer, USA), whose sample chamber could be purged with nitrogen gas to diminish the influence of water vapor and carbon dioxide in the atmosphere. Particle surface after milling were observed by a transmission electron microscopy (TEM, JEOL, JEM-2010, Japan).

2.3. Slip casting and sintering

Slip casting was carried out with a gypsum mold to form green bodies of 20 mm in diameter, which were dried at room temperature. For sample characterization, five pellets were prepared. Relative density of the green bodies was estimated using Archimedes' method after calcination at 800 °C. The green bodies were sintered at 1600 °C for 2 h in air at the same heating and cooling rates of 100 °C/h. Relative density of the sintered bodies was also determined by Archimedes' method.

3. Results

Fig. 2 shows apparent viscosity of the slurries at different solid content prepared by soft-energy milling (wet-jet milling and planetary-homogenizing) and ball milling. The viscosity of the wet-jet milled and the planetary-homogenized slurries is almost constant for long times except for the planetary-homogenized 50 vol.% slurry. On the other hand, the viscosity of ball-milled slurries increases rapidly with time, indicating re-flocculation of Al_2O_3 particles after ball milling. Moreover, after 150 min of measurement, the viscosities of the ball-milled 10 and 30 vol.% slurries are higher than that of 50 vol.% one. This behavior is so that the solid content around viscometer-sensor placed in the slurry was increased by sedimentation of re-flocculated particles. Owing to this constancy, the wet-jet milled and planetary-homogenized slurries are more stable and have much lower viscosity than that the ball-milled slurries at prolonged times.

Fig. 3 shows particle size distribution of Al_2O_3 particles after wet-jet milling, planetary-homogenizing and ball milling. After 24 h ball milling, the mean particle size is about 570 nm as well as the primary particle size of raw materials. This result suggests that ball milling requires long time to pulverize the materials to the primary particle size. The particle size distribution of the wet-jet milled and the planetary-homogenized Al_2O_3 is identical with that of 24 h ball-milled Al_2O_3. This indicates that it is pos-

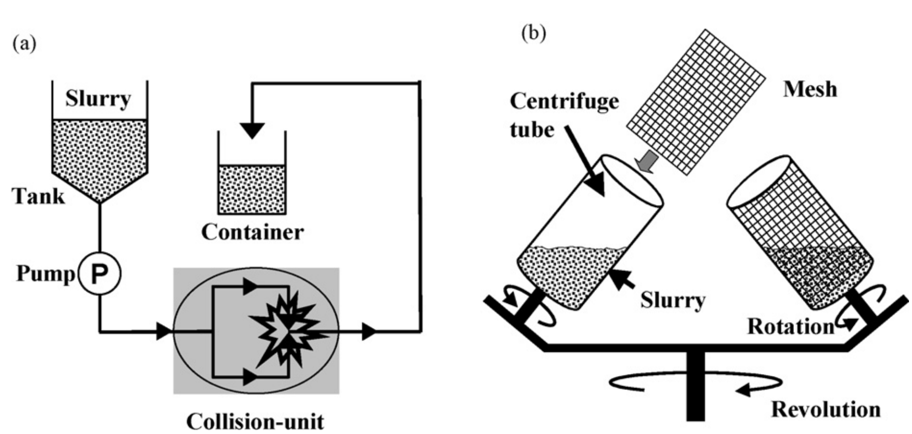

Fig. 1. Diagrams of (a) wet-jet mill and (b) planetary homogenizer system.

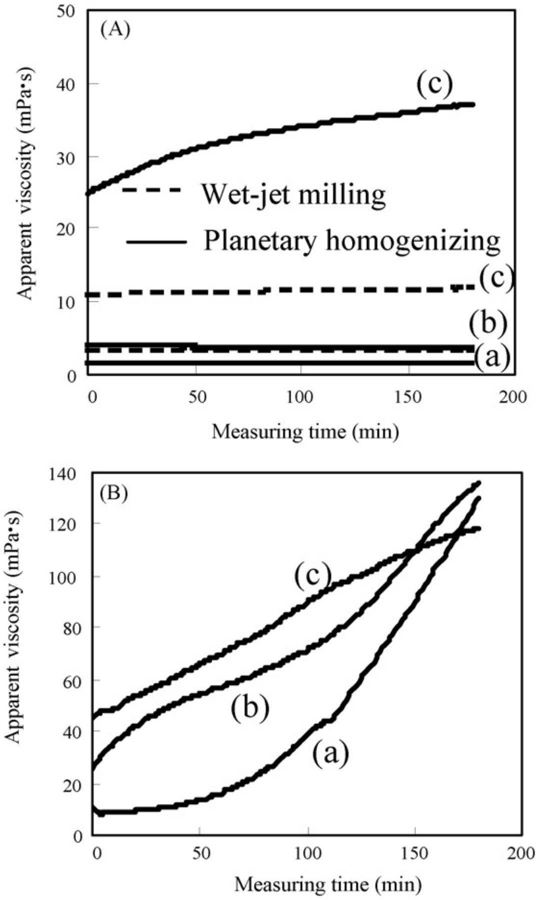

Fig. 2. Apparent viscosity of slurries prepared from (A) wet-jet milling and planetary homogenizing and (B) ball milling. Solid content is (a) 10 vol.% (b) 30 vol.% and (c) 50 vol.%.

sible to pulverize raw materials to the primary particle size in a very short-time by the wet-jet milling.

Fig. 4 presents FT-IR diffuse reflection spectra of raw Al_2O_3 and Al_2O_3 particles before and after milling at 30 vol.% of solid content. All spectra possess several sharp bands at around 3652, 3548 and 3480 cm^{-1}. These peaks are assigned to hydroxyl (OH) stretching vibrations (ν_{OH}) of a bayerite-type species

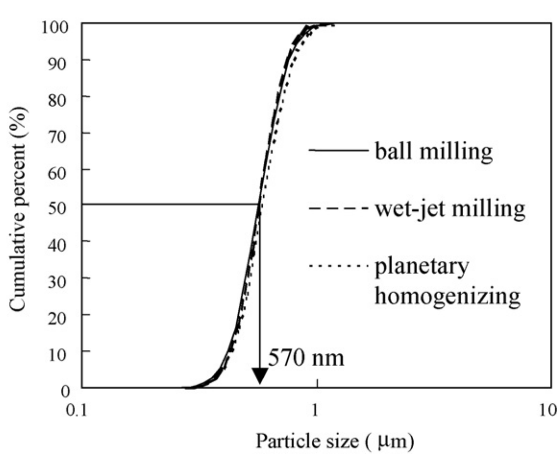

Fig. 3. Particle size distribution of Al_2O_3 particles after wet-jet milling, planetary-homogenizing and ball milling.

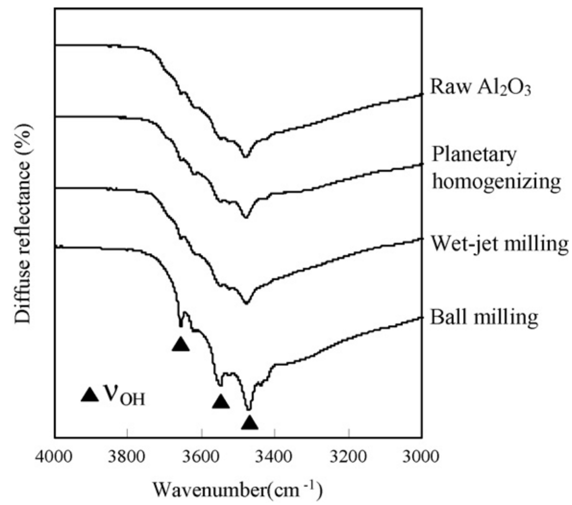

Fig. 4. FT-IR diffuse reflection spectra of raw Al_2O_3 and Al_2O_3 particles before and after milling at 30 vol.% of solid content.

(α-$Al(OH)_3$).[12] Spectra of the wet jet-milled and the planetary-homogenized Al_2O_3 powders are identical with those of the raw Al_2O_3 powders. On the other hand, the intensities of the peaks associated with ν_{OH} of α-$Al(OH)_3$ increase and the peak at 3480 cm^{-1} shifts to 3469 cm^{-1} in the case of ball milling. Furthermore, in the spectra of the ball-milled Al_2O_3, some other new peaks appear at around 3621 and 3529 cm^{-1}. These peaks are assigned to ν_{OH} of a gibbsite-type species (γ-$Al(OH)_3$).[12]

Fig. 5 shows TEM photographs of raw, wet-jet milled, planetary-homogenized, and ball-milled Al_2O_3 particle. After ball milling, the amorphous Al_2O_3 is adsorbed on the Al_2O_3 particle surface. Moreover, the crystal lattice cannot be seen on the Al_2O_3 surface. In the case of the we-jet milled and the planetary-homogenized particles, the surface is very clear and the crystal lattice is observed on the particle surface as well as the raw Al_2O_3 particle. Therefore, the wet-jet milling and the planetary-homogenizing processes do not give damages to Al_2O_3 particles during milling.

Fig. 6 shows relative density of green bodies measured by Archimedes' method as a function of solid content. The relative densities of the green bodies fabricated by wet-jet milled and planetary-homogenized slurries are significantly higher than those of the green bodies prepared from ball-milled slurries. Green bodies from the wet-jet milled and the planetary-homogenized slurries have a constant relative density without depending on solid content. In the case of the wet-jet milled slurry, the relative density was about 65% or more. On the other hand, relative density of green bodies from the ball-milled slurry is strongly dependent on and increases linearly with solid content. It note that the relative density of the green body prepared from planetary-homogenized slurry with low solid content (10 vol.%) is the same as that of the green body prepared from the ball-milled slurry with a much higher solid content (50 vol.%).

Fig. 7 shows linear shrinkage along the diameter and relative density of the sintered bodies as a function of solid content. Linear shrinkage of the sintered bodies fabricated from the ball-

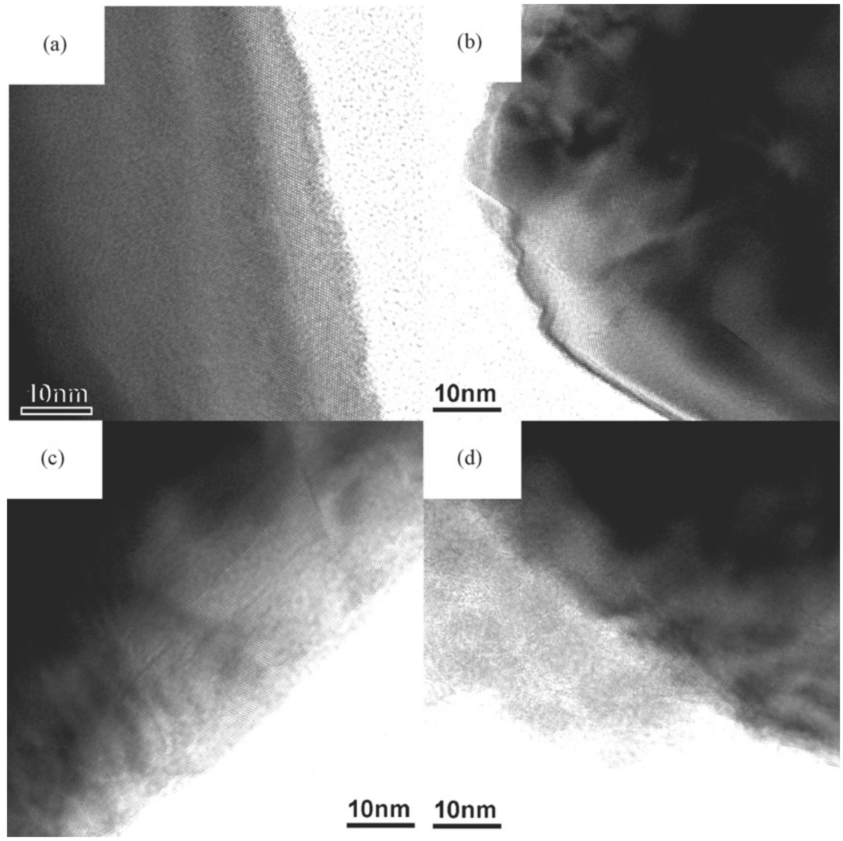

Fig. 5. TEM photographs of (a) raw, (b) wet-jet milled, (c) planetary-homogenized, and (d) ball-milled Al_2O_3 particle.

milled slurries decreases with increase in the solid content. On the other hand, linear shrinkage of the sintered bodies prepared from the wet jet-milled and the planetary-homogenized slurries is very low and independent of the solid content. Linear shrinkage of the sintered body fabricated from the wet jet-milled slurry with low solid content (10 vol.%) is almost equal to that of the body fabricated from the ball-milled slurry with high solid content (50 vol.%). All the sintered bodies have similar high relative density of 96% or more.

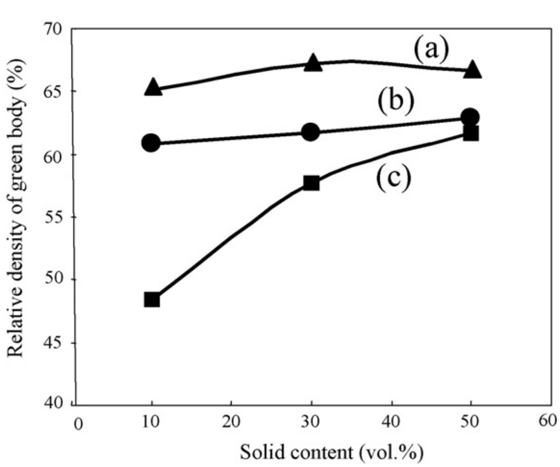

Fig. 6. Relative density of the green body prepared from (a) wet-jet milled, (b) planetary-homogenized, and (c) ball-milled slurries as a function of the solid content.

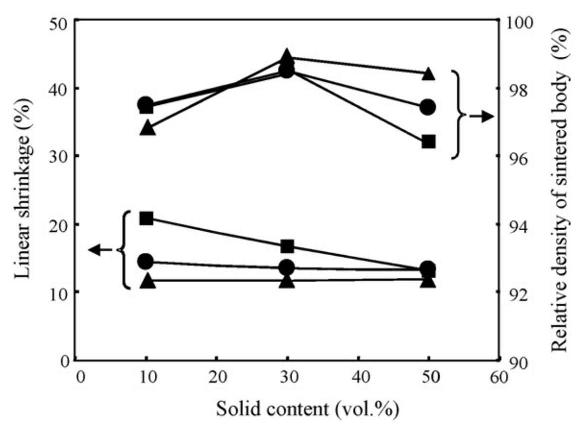

Fig. 7. Linear shrinkage and relative density of the sintered bodies prepared from (triangle) wet-jet milled, (circle) planetary-homogenized, and (square) ball-milled slurries as a function of the solid content.

Fig. 8 shows appearance of the sintered compacts prepared from the wet-jet milled and the ball-milled slurries. The circles drawn in broken line express the size of green compact before sintering. It is clearly seen that the shrinkage of sintered body from the wet-jet milling is smaller than that from the ball milling.

4. Discussion

The viscosity of wet-jet milled and planetary-homogenized slurries is very low and stable for long times. Furthermore, green bodies prepared from the wet-jet milled and the planetary-

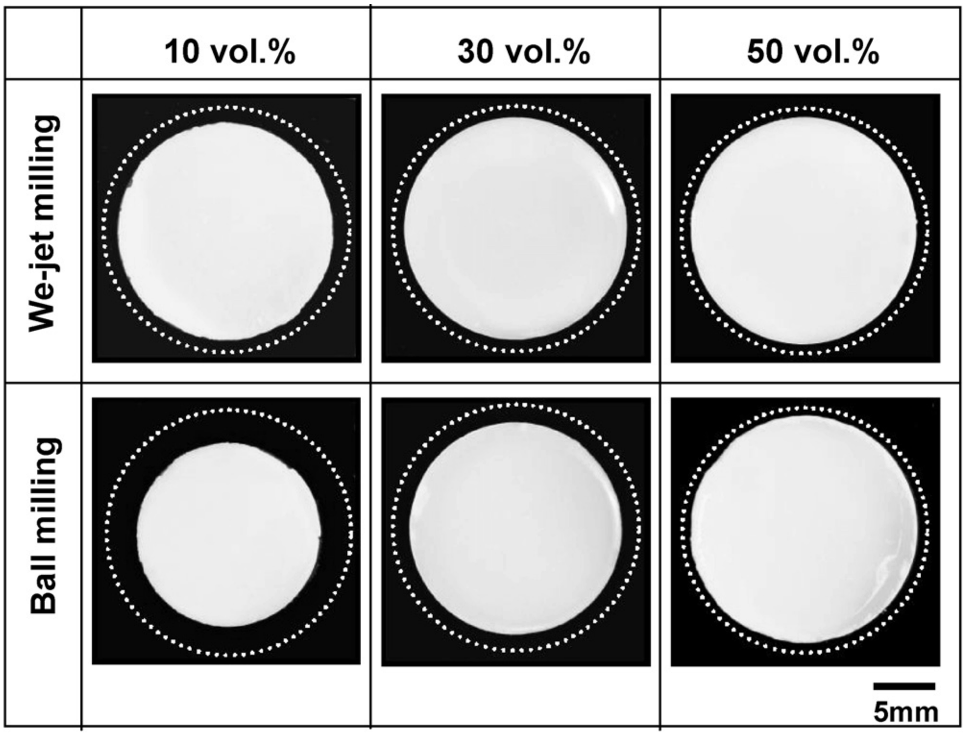

Fig. 8. Appearance of the sintered compacts prepared from wet-jet milled and ball-milled slurries.

homogenized slurries have a high relative density of about 65% and 60% or more, respectively. After sintering at 1600 °C, the green bodies prepared from the wet-jet milled and the planetary-homogenized slurries have low linear shrinkage less than 12% and 14%, respectively. On the other hand, the viscosity of the ball-milled slurries is increases rapidly with time. When the ball-milled slurries are used for slip casting, the green bodies with low packing density are obtained.

It should be of interest to discuss the maximum collision energy given to the particles by collision among particles, mesh or ball media for the explanation of the differences observed between wet-jet milled, planetary-homogenized and ball-milled slurries. When assuming that potential energy of Al_2O_3 ball is converted to collision energy, the maximum collision energy of ball milling is calculated from ball size (ϕ 10 mm) and drop distance of the ball media (5 mm), the collision energy is about 1×10^{-4} J. On the other hand, the maximum collision energy of wet-jet milling is calculated from collision speed and mass of Al_2O_3 particle and is about 1.9×10^{-10} J. The collision energy of planetary homogenizing calculated from mass of mesh and collision speed (= rotation speed) is about 7.8×10^{-8} J. The collision energy of wet-jet milling and planetary-homogenizing is significantly small than that of ball milling, and Al_2O_3 powder is pulverized well by soft-energy. Therefore, the surface of Al_2O_3 particles maintains initial condition after wet-jet milling and planetary-homogenizing as shown in FT-IR spectra (Fig. 4) and TEM observation (Fig. 5). Furthermore, as shown in Fig. 4, many OH groups are induced on the surface of Al_2O_3 particles after ball milling. This increase of OH groups after ball milling is believed that it is caused by the activation of particle surface. It is known[8] that the active sites such as lattice defects and radicals are induced on the surface of particles and the surface becomes activated by the excess collision energy of ball milling. These active sites induce an increase of the attractive force between particles and enhance the re-flocculation of particles. Hence, the viscosity of ball-milled slurries increase with time rapidly, and Al_2O_3 particles in the ball-milled slurries packed loosely. On the other hand, the collision energy of wet-jet milling and planetary homogenizing is remarkably low compared to the collision energy of ball milling. Therefore, Al_2O_3 particles keep initial surface condition and strong repulsion force after wet-jet milling and planetary homogenizing. This strong repulsion force leads good dispersed and stable slurry. Thus, the wet-jet milled and planetary-homogenized slurries show very low viscosity and high packing density of green bodies. We believe that since the surface of Al_2O_3 particles after soft-energy milling as wet-jet milling and planetary homogenizing maintains the initial condition, the relative density of green body and the linear shrinkage of sintered body are independent of the solid content.

5. Conclusion

Soft-energy milling slurries prepared from wet-jet milling and planetary-homogenizing were stable for long times. The green bodies prepared from the soft-energy milled slurries by slip casting had high relative densities and the density was independent of the slurry solid content. Since the relative density of green bodies prepared from wet-jet milled and planetary-homogenized slurries was almost the same without depending on the solid contents of slurry, the linear shrinkage during sintering at 1600 °C for 2 h was also remained constant at about 12–13%. On the other hand, the viscosity of slurries from ball milling was higher than that of the soft-energy milled slurries and increased rapidly with time. The relative density of green bodies from the ball-milled slurries was lower than those prepared from the soft-energy milled slurries and was strongly dependent on the solid content. Therefore, linear shrinkage during sintering was also dependent on the solid content and increased with decrease in the solid content of the slurry.

Soft-energy milling process can prepare the more stable slurries within a short time. This process will greatly contribute to reduce the processing time of ceramic manufacturing and to improve the properties of ceramic products.

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