
Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials

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PREPARATION OF STABLE NANO-SIZED Al_2O_3 SLURRIES USING WET-JET MILLING

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ABSTRACT

The agglomerated alumina powders with average particle size of 43 nm were pulverized by wet-jet milling process and the particle size distribution and stability of the obtained slurries were evaluated. The alumina slurries were prepared from alumina powder, distilled water and dispersant. The solid content of the slurry was 30 vol. %. The particle size distribution of the sample before wet-jet milling showed the broad peak at 10 μm corresponding to the agglomerations of the alumina powders. The viscosity of this slurry was 253 mPa·s and rapidly increased with time. The particle size distribution of the slurry after wet-jet milling at 50 MPa showed the 0.2 and 10 μm peaks. These sizes were larger than primary particle size and were originated from the agglomeration of the alumina powder. On the other hand, the powder after wet-jet milling at > 150 MPa was almost of dispersed particle size with a small amount of the agglomerations. These agglomerations were completely dispersed by > 5 passes of wet-jet milling. The viscosity of the obtained slurry was 16 times as low as that of the slurry before wet-jet milling and was stable for a long time.

INTRODUCTION

Nano-sized ceramic particles are widely used as polishing agents, fillers for sealant, films and paints, additives for conductive pastes and electronic components, photocatalysis and inorganic pigment. The nano particles should be mono-dispersed for these applications, however it is also known that the dispersion of nano-sized particles is difficult because of high agglutinability.

For break and pulverization of ceramic powders, ball milling and beads milling methods are available¹⁻⁴. Fadhel et al.¹ have investigated the dispersion of TiO_2 powder by the beads milling method. The average particle size after the beads milling was about 0.15 μm . Qiu et al.² have prepared the AlN slurry by the beads milling method with ZrO_2 media (diameter: 100 μm φ). The average particle size after beads milling was about 0.11 μm after 90 min of grinding. Tanaka et al.³ have carried out the ball milling and the beads milling for grinding alumina powder and the particle sizes of the obtained powders by both methods were > 0.1 μm . They reported that the particle size of the milled samples was reduced from the original before milling. The size reduction of ceramic particles during ball milling was calculated by particle element method (PEM)⁴. This result indicated that the size reduction rate depends on milling energy and these conventional milling methods were not adapted for nanoparticles.

Thus, these methods are preferable for submicron-sized particles however an appropriate method to pulverize agglomerations of nanoparticles is not yet available. Wet-jet milling method is a newer milling technique of the ceramic powders by collisions between the particles, and is preferable to homogeneously disperse the ceramic particles in the slurry. Monodispersion of the

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submicron-sized alumina particles by this method has been also reported⁵⁻⁷. The milling energy of the conventional methods was calculated from a container size, media size and amount and rotation speed. That of wet-jet milling method was, on the other hand, calculated from the pressure (velocity) of slurry in the collision region (jet milling pressure). Thus, this method is also available to the nano-sized particles by high jet milling pressure. In this study, the relationship between the jet milling pressure and flocculation size was evaluated and the stable nano-sized alumina slurries were prepared.

EXPERIMENTAL PROCEDURE

Nano-sized γ -alumina (Nano Tek®, C. I. Kasei, Japan) was mixed with 70 vol. % distilled water and 3.2 mass% poly (acrylic acid) (Aron A-6114, Toagosei, Japan) as a dispersant using a planetary homogenizer⁸ (AR-250, Thinky, Japan) for 10 min. The mixture was pulverized by a laboratory scale wet-jet milling system (PRE03-20-SP, Genus, Japan). The jet milling pressure was 50 – 200 MPa and the wet-jet milling was repeated 1 – 5 times. The viscosity and stability of the suspension were measured by Vibro-viscometer (SV-10, A&D, Japan) at 25°C. The particle size distribution of the alumina particles in the suspension was estimated by laser diffraction method (La-920, Horiba, Japan).

RESULTS AND DISCUSSION

Characterization of the slurry before wet- jet milling

Figure 1 shows the apparent viscosity of the slurry before wet-jet milling. The initial viscosity was 253 mPa·s and the viscosity increased with time. It is considered that the increase

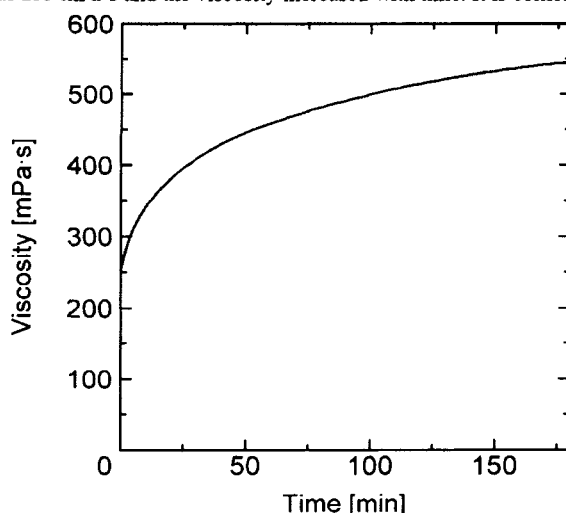


Fig. 1 Apparent viscosity of the slurry before wet-jet milling

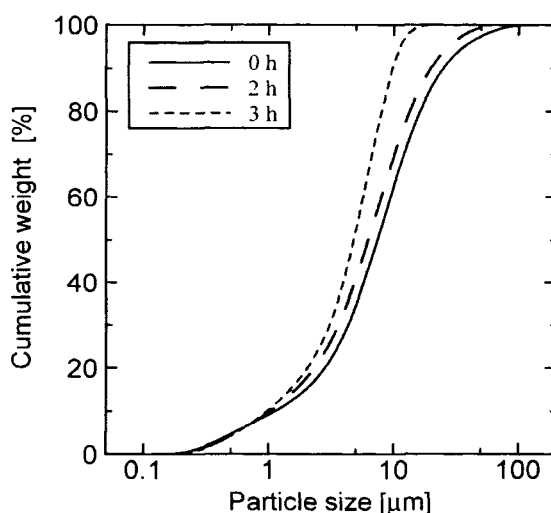


Fig. 2 Particle size distribution of the slurries before wet-jet milling

of the viscosity is due to re-flocculation of the alumina particles and the flocculated slurry shows thixotropic properties⁹. Figure 2 shows the particle size distribution of the slurry containing 30 vol. % alumina before wet-jet milling. To observe the re-flocculation of powders, those of the slurries after sitting for 2 and 3 h were also measured. The slurry before wet-jet milling shows with peak at 10 μm , which is larger than primary particle size (43 nm). And the particle size distribution of the slurries after sitting for 2 and 3 h shows decrease of the large particles ($> 5 \mu\text{m}$) and slight decrease of the small particles ($< 0.5 \mu\text{m}$). These decreases depend on setting time and indicate that the particles agglomerated and sedimented. This result shows a similar tendency to viscosity measurement.

Pulverization by wet-jet milling

Figure 3 shows the particle size distribution of the slurries after wet-jet milling at various milling pressure. The slurry treated with 50 MPa shows the 0.2 and 10 μm peaks, which were thought to be secondary and tertiary flocculation, respectively. The tertiary flocculation was pulverized at $> 100 \text{ MPa}$ of jet milling pressure. However, the particle size distribution of the slurries after wet-jet milling at $> 150 \text{ MPa}$ still showed a small amount of the agglomerations at about 1 μm . These agglomerations were completely crushed by repeating the wet-jet milling > 4 times. On the other hand, the secondary particle size decreased with increasing jet milling pressure. Figure 4 shows the relationship between jet milling pressure and mean size of the secondary flocculation. The secondary particle size decreased with increasing jet milling pressure but was satiated at 0.11 μm . This size is slightly larger than primary particle size. By contrast, the particle sizes of the slurries containing $< 10 \%$ powders were about 43 nm

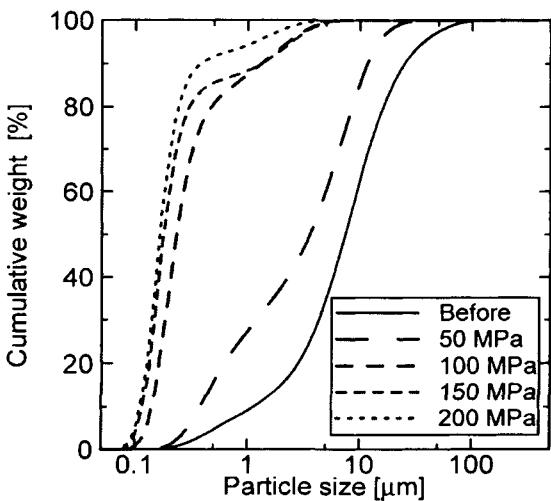


Fig. 3 Relationship between the jet milling pressure and particle size distribution of the slurries.

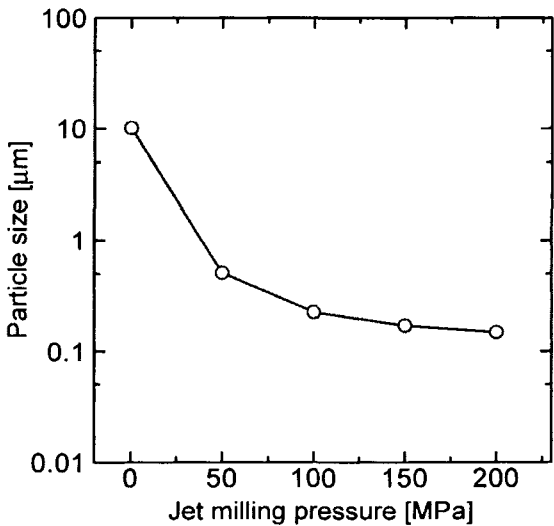


Fig. 4 Relationship between jet milling pressure and mean size of the obtained agglomerating powders.

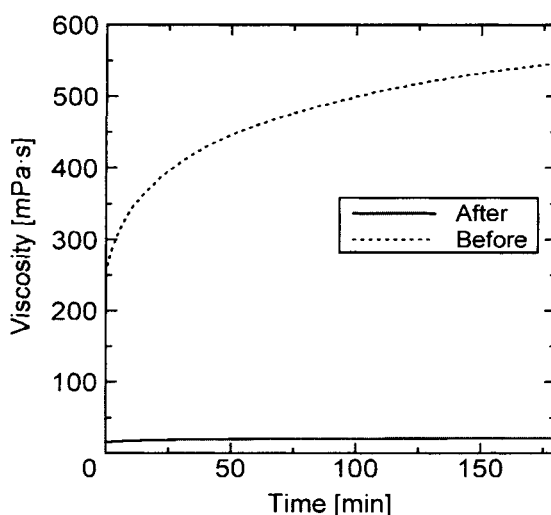


Fig. 5 Apparent viscosity of the slurry after wet-jet milling

corresponding to the primary particle size of the raw γ -alumina powder. Therefore, it is considered that this saturation may be due to a limitation of the dispersion of nano-sized particles in the concentrated slurries.

Stability of the obtained slurries

Figure 5 shows the viscosity of the slurry after wet-jet milling at 200 MPa. To comparison, that of the slurry before jet milling is shown in Fig. 5. The initial viscosity was 15.5 mPa·s, which was 16 times as low as that of the slurry before milling. The viscosity of the obtained slurry was stable for a long time. It is considered that thixotropic properties of the slurries significantly fell. In general, non-newtonian fluid, such as thixotropic and dilatant fluid, is not preferable from view point of the production efficiency. To address this problem, it is necessary to fall the thixotropic properties, however, an appropriate method for nanoparticles have not been reported. This wet-jet milling method may become one of the most suitable methods to lower the thixotropic properties.

Figure 6 shows the particle size distribution of the present slurries after standing for 0 – 24 h. The particle size distributions of the slurries after sitting were in excellent agreement with the original distribution (0 h), as expected. This result is indeed proof of the stability of the slurries.

SUMMARY

The agglomerated nano-sized alumina powders were pulverized by wet-jet milling method. The particle size distribution showed that the sample before wet-jet milling have a broad

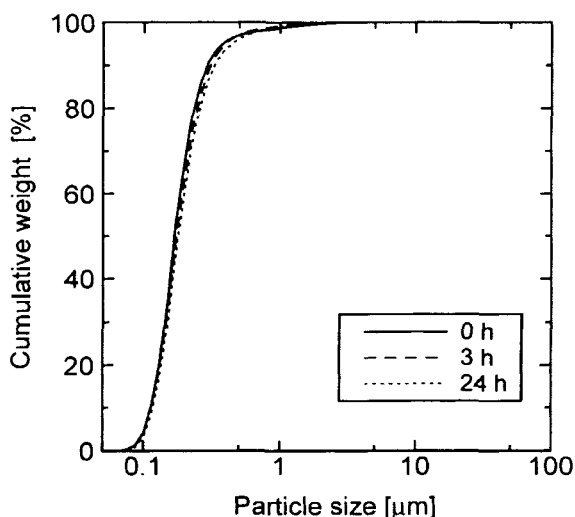


Fig. 6 Particle size distribution of the wet-jet milled slurries at (a) 200 MPa, repeating 5 times after 0 – 48 h

peak at 10 μm corresponding to the agglomerations. The viscosity of this slurry was 253 $\text{mPa}\cdot\text{s}$ and increased with time. The slurry showed thixotropic properties. On the other hand, the particle size distribution of the slurry after wet-jet milling at 50 MPa showed the 0.2 and 10 μm peaks. The secondary particle size decreased with increasing jet milling pressure, and the samples after wet-jet milling at 200 MPa showed peak at 0.1 μm with a small amount of the tertiary agglomeration. These agglomerations were completely dispersed by repeating the wet-jet milling > 4 times. The viscosity of the obtained slurry was 16 times as low as that of the slurry before wet-jet milling. These results suggested that the dispersion and stability of the nano-sized particles depended on the collision energy and collision frequency. And the wet-jet milled slurry was stable for a long time and its thixotropic properties significantly fell.

REFERENCES

- ¹H. Bel Fadhel, C. Frances, A. Mamourian, "Investigations on Ultra-fine Grinding of Titanium Dioxide in a Stirred Media Mill", *Powder Tech.*, **105**, 362-373 (1999).
- ²J.Y. Qiu, Yuji Hotta, Kimiyasu Sato and Koji Watari, "Fabrication of Fine AlN Particles by Pulverizing with Very Small ZrO_2 Beads", *J. Am. Ceram. Soc.*, **88**, 1676-1679 (2005)
- ³S. Tanaka, Z. Kato, N. Uchida, K. Uematsu, "Direct Observation of Aggregates and Agglomerates in Alumina Granules", *Powder Tech.*, **129**, 153-155 (2003).
- ⁴J. Kano, H. Mio, F. Saito and M. Tanjo, "Estimation of Size Reduction rate of Gibbsite in Tumbling Mills with Different Diameters by Computer Simulation", *J. Chem. Eng. Japan*, **32**, 747-751 (1999).

⁵N. Omura, Y. Hotta, K. Sato, Y. Kinemuchi, S. Kume and K. Watari, "Characterization of Al₂O₃ Slurries Prepared by Wet-jet Milling", *J. Ceram. Soc. Japan*, **113**, 491-494 (2005)

⁶N. Omura, Y. Hotta, K. Sato, Y. Kinemuchi, S. Kume and K. Watari, "Slip Casting of Al₂O₃ Slurries Prepared by Wet-jet Milling", *J. Ceram. Soc. Japan*, **113**, 495-497 (2005)

⁷N. Omura, Y. Hotta, K. Sato, Y. Kinemuchi, S. Kume, K. Watari, "Fabrication of Stable Al₂O₃ Slurries and Dense Green Bodies Using Wet-jet Milling", *J. Am. Ceram. Soc.*, **89**, 2738-2743 (2006)

⁸T. Isobe, Y. Kameshima, A. Nakajima and K. Okada, "Preparation and Properties of Porous Alumina Ceramics with Uni-directionally Oriented Pores by Extrusion Method Using a Plastic Substance as a Pore Former", *J. Eur. Ceram. Soc.*, **27**, 61-66 (2007)

⁹J.C. Chang, F.F. Lange and D.S. Pearson, "Viscosity and Yield Stress of Alumina Slurries Containing Large Concentrations of Electrolyte", *J. Am. Ceram. Soc.*, **77**, 19-26 (1994)