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Dispersed/flocculated size characterization of alumina particles in highly concentrated slurries by ultrasonic attenuation spectroscopy

Shin-ichi Takeda [a,*], Philip J. Goetz [b]

[a] *Department of Applied Chemistry, Faculty of Engineering, Okayama University, 3-1-1 Tsushima-naka, Okayama, 700, Japan*

[b] *Pen Kem, Inc., 5 Hillside Av., Mt. Kisco, NY 10549, USA*

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Abstract

In recent years, several advances have been made in ultrasonic attenuation spectroscopy for monitoring particle size distributions of highly concentrated slurries. This paper presents experimental proof that ultrasonic attenuation spectroscopy is capable of characterizing dispersed or flocculated particle size in highly concentrated slurries. Well-characterized alumina was used for testing the theory. The instrument for measuring ultrasonic attenuation spectra covers a wide frequency range from 1 to 100 MHz and converts them into particle size distributions. It is shown that the particle size distribution obtained before sonication indicates a bimodal distribution, but that after ultrasonication the distribution is reduced to a log normal for which the median size agrees quite well with a priori known particle size. Hence we confirmed that this technique can differentiate well-dispersed and flocculated particle size in slurries without dilution.

Keywords: Alumina particles; Ultrasonic attenuation spectroscopy; Slurries; Dispersed/flocculated size

1. Introduction

Inhomogeneities that originate in the particle-packing structures during shape forming of ceramic powders are important to control, because they can produce fracture origins in sintered materials or they can lead to shape distortion and cracking during drying, pyrolysis, and sintering [1–4]. Such inhomogeneities are closely related to the particle size distribution in the prepared slurries. In general, slurries used in actual ceramic processing contain multiple components such as sintering aids, dispersants and binders which interact in complex ways, and as a result, proper control of the particle-packing structure is a difficult problem [5]. These components can alter the interfacial chemistry during processing [6]. In addition, the mixing process itself, where these components react with the powder surface in aqueous solutions, may change the charged state at the powder/solution interface. Wide variations in particle size distribution and surface chemical properties of powders thus occur between manufacturers and even between batches from the same source.

Properties of the green body such as density and porosity have been measured in order to judge whether an employed condition of processing is proper or not. This indirect information has been applied to compensate for property fluctuations during or after sintering. Once one can estimate the particle size distribution during processing or prior to sintering, such information will facilitate

* Corresponding author.

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analysis and easily avoid problems prior to casting and firing.

Ultrasonic attenuation spectroscopy is developing rapidly as an alternative to light scattering methods for the determination of particle size distributions [7–9]. Many publications related to ultrasonic attenuation spectroscopy have appeared since 1991 when McClement's review of this technique was published [10,11]. The development of a commercial instrument for automatic measurement using acoustic or electroacoustic spectroscopy has also been completed and the instruments are now on the market. The greatest advantage of acoustic spectroscopy compared with other techniques, such as light scattering, is the capability to characterize intact concentrated dispersed systems. That is, we do not have to dilute the slurries when we estimate the well-dispersed/flocculated particle size distribution in slurries. In this sense, we will use the term "highly" to describe the concentration of slurries much higher than that appropriate for the light scattering technique.

In the present paper, we confirm the capability to differentiate the well-dispersed and flocculated states in highly concentrated slurries using ultrasonic attenuation spectroscopy.

2. Materials and experimental procedure

2.1. Powders and prepared suspensions

Commercial-grade high purity powder of Al_2O_3 (AKP-30, Sumitomo Chemical Co., Ltd., Tokyo, Japan) was used. The median particle size reported by the manufacturer was 0.32 μm, which is the size measured by the laser diffraction method in a well-dispersed diluted suspension. The particle size distribution of this dry powder in air (about 50% relative humidity) as measured by the API Aerosizer (Amherst Process Instruments, Inc., Hadley, MA USA) is shown in Fig. 1. This result shows that the particle was flocculated before mixing with aqueous solution and then broken up in the solution.

Slurries with 10 vol.% solids were prepared by dispersing dry powder in distilled water, and then the pH of the suspension was adjusted to 4.0 ± 0.2 with 1 M HNO_3. Two kinds of mixing procedures were employed to confirm the capability of distinguishing the dispersed and flocculated size of particles in the highly concentrated slurries; one slurry was stirred for 5 min using a magnetic stirrer and the other was ultrasonicated for 1 min using a high intensity ultrasonic probe (100 W) after pH adjustment. Readjustment was performed for each slurry when its pH was changed by stirring or sonication.

2.2. Measurement technique

A precise and detailed background of the theory for ultrasonic attenuation spectroscopy has been described elsewhere [9]. The attenuation spectra of the sample slurries were measured using an Acoustophor PK-8000 (Pen Kem, Inc., Mt. Kisco, NY, USA). The attenuation was measured over a frequency range from 1 to 100 MHz. The variable gap technique makes it possible to exclude calibration procedures. There is no restriction on the volume fraction, but the sample must be fluid in order for the peristatic pump to pump the sample through the measuring chamber.

Analysis software converts attenuation spectra into the particle size distribution minimizing the difference between theoretical and measured attenuation spectra. The absolute error of the theoretical fit is the measure of this difference. In the case of the log–normal distribution, the absolute error is minimized by adjusting the median size and standard deviation of the log–normal distribution. In the case of the bimodal distribution, the absolute error is also minimized by adjusting the median size and standard deviation of each size mode.

3. Results and discussion

Fig. 2 shows the measured attenuation spectra in decibels per centimeter per MHz ($dB\,cm^{-1}\,MHz^{-1}$). Experimental points at low frequencies (<3 MHz) are excluded because of the large errors (those frequencies lay too close to the transducer piezo crystal harmonics). It is clearly seen that there is a distinct difference in the measured attenuation spectra between stirred and ultrasonicated slurries, which suggests the presence

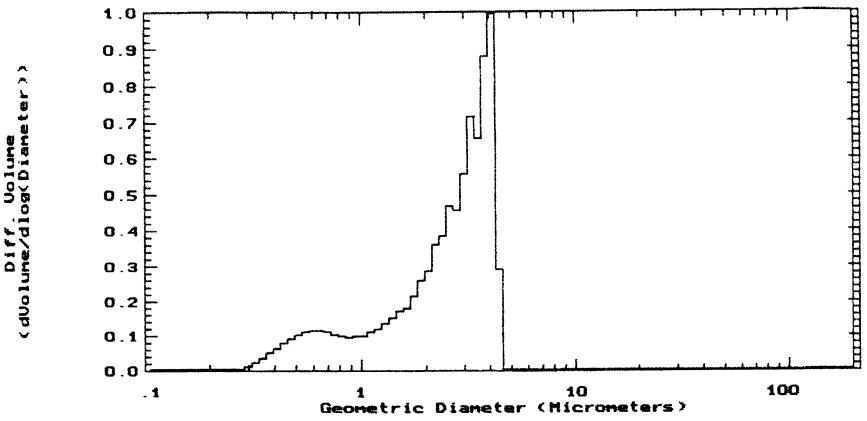

Fig. 1. Particle size distributions for dry Al_2O_3 powder in air measured by the API Aerosizer (Amherst Process Instruments, Inc., Hadley, MA, USA).

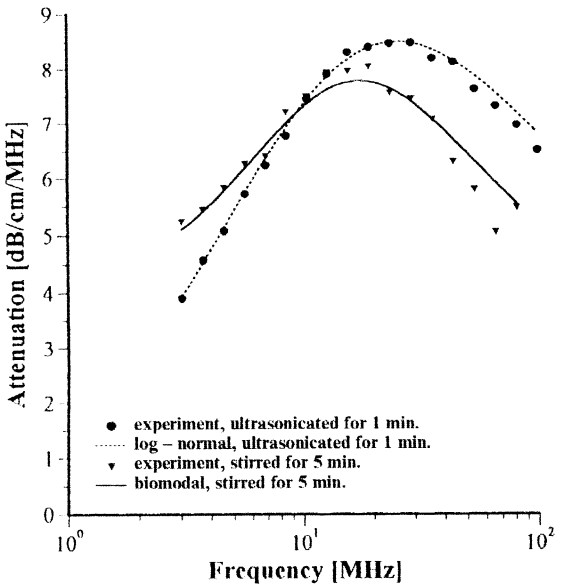

Fig. 2. Experimental and best-fit theoretical attenuation spectra for ultrasonicated and stirred Al_2O_3 slurries, 10% by volume at pH4.

of different particle size distributions in these two slurries.

The spectrum obtained from the stirred slurry is adequately approximated by the bimodal distribution. In contrast, the log–normal distribution provides the best fit to the measured attenuation spectrum of the ultrasonicated slurry. Corresponding particle size distributions are shown in Fig. 3. A particle size distribution curve measured in the stirred slurry has two peaks. The median size of the low size peak was 0.29 μm and that of the higher size peak was 1.1 μm.

Because the low size peak corresponds to the primary size of the alumina particle (0.32 μm) as reported by the manufacturer, then the higher size peak must correspond to the flocculated size. The appearance of a higher size peak in the particle size distribution curve suggests that the flocculated particles still remain in the slurry even after stirring.

In contrast, the peak corresponding to the flocculated size disappeared in the particle size distri-

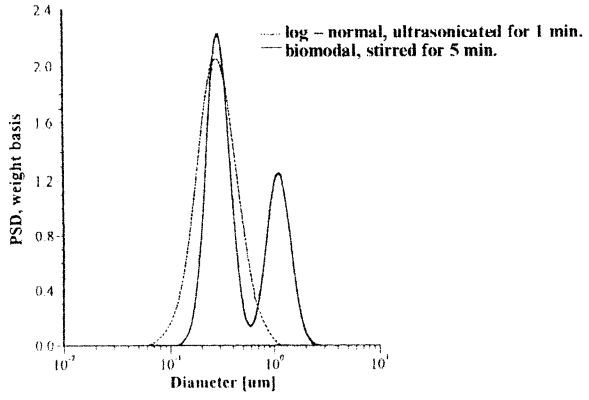

Fig. 3. Particle size distributions for ultrasonicated and stirred Al_2O_3 slurries, corresponding to attenuation spectra shown in Fig. 2.

bution curve obtained from the ultrasonicated slurry. The particle size distribution curve then shows the log-normal distribution, of which the median size was the same as the primary size reported by the manufacturer. When the ultrasonicated slurries were prepared, ultrasonication was applied to the stirred-only slurry. The disappearance of the higher size peak demonstrates that the sonication process breaks up the flocculated particles.

In order to test the capability of this technique to estimate the particle size distribution in a mixed system where two kinds of particles with different sizes are dispersed, a series of model systems were prepared and the particle size distribution was measured. The mixed systems for the test consisted of 10 vol.% of Al_2O_3 powders with a size of 0.32 μm (AKP-30) and 2.0 μm (AA-2, Sumitomo Chemical Co., Ltd., Tokyo, Japan). Fig. 4 shows the particle size distributions which were calculated by assuming that the two different sizes of Al_2O_3 powders are in a well-dispersed state with different ratios: (a) 70:30, (b) 50:50 and (c) 30:70% by volume in the slurries. Attenuation curves measured are shown in Fig. 5 where the points are measured one at each frequency, and the curves

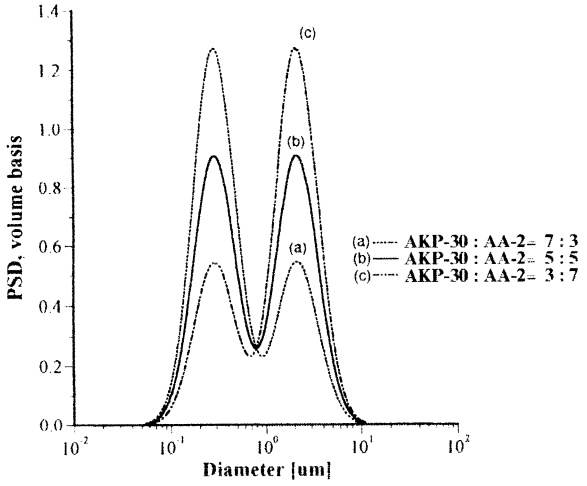

Fig. 4. Particle size distributions for well-dispersed 10 vol.% of Al_2O_3 slurries consisting of 0.32 μm (AKP-30) and 2.0 μm (AA-2) particles with ratios of (a) 70:30, (b) 50:50 and (c) 30:70 in vol.%. The aqueous solution used for this system contains 0.2 mass% of solium hexametaphosphate.

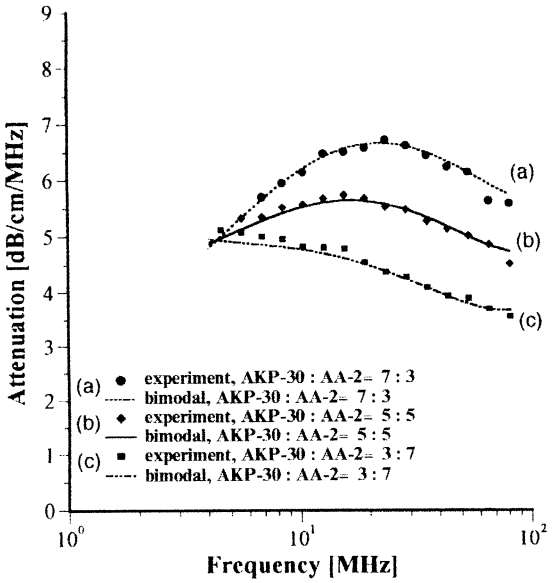

Fig. 5. Experimental and theoretically calculated attenuation spectra, corresponding to the particle size distributions shown in Fig. 4.

are drawn by the calculation based on the particle size distribution as shown in Fig. 4. It is seen that every bimodal distribution provides a good fit to the measured attenuation points, which demonstrates the capability of characterizing the mixed system. When the fraction of 2.0 μm Al_2O_3 powders increases, the attenuation spectrum obtained appears to be shifted to the lower left. The same tendency is seen in Fig. 2 by comparison of the spectra for stirred and ultrasonicated slurries, suggesting the presence of the higher size peak in the particle size distribution in stirred slurries.

These results demonstrate the capability of the ultrasonic technique to monitor the presence of flocculated particles in highly concentrated slurries and to distinguish the primary size from the flocculated size.

4. Conclusion

The capability of estimating the primary and flocculated size distribution using ultrasonic attenuation spectroscopy before firing was investigated. The results obtained demonstrate the capability to

monitor the presence of flocculated particles in a highly concentrated slurry and to distinguish the primary size from the flocculated size.

References

[1] F.F. Lange, Processing-related fracture origins: I, observations in sintered and isostatically hot-pressed Al_2O_3/ZrO_2 composites, J. Am. Ceram. Soc. 66 (1983) 396–398.

[2] F.F. Lange, M. Metcalf, Processing-related fracture origins: II, agglomerate motion and cracklike internal surfaces caused by differential sintering, J. Am. Ceram. Soc. 66 (1983) 398–406.

[3] F.F. Lange, B.I. Davis, I.A. Aksay, Processing-related fracture origins: III, differential sintering of ZrO_2 agglomerates in Al_2O_3/ZrO_2 composite, J. Am. Ceram. Soc. 66 (1983) 407–408.

[4] I.A. Aksay, F.F. Lange, B.I. Davis, Uniformity of Al_2O_3/ZrO_2 composites by colloidal filtration, J. Am. Ceram. Soc. 66 (1983) C190–C192.

[5] V.A. Hackley and S.G. Malghan, Investigation of parameters and secondary components affecting the electroacoustic analysis of silicon nitride powders, in: S.G. Malghan (Ed.), Electroacoustics for Characterization of Particulates and Suspensions, National Institute of Standards and Technology Special Publication 856, US Department of Commerce, 1993, pp. 161–179.

[6] CesaranoJ., III, I.A. Aksay, A. Bleier, Stability of aqueous α-Al_2O_3 suspensions with poly (methacrylic acid) polyelectrolyte, J. Am. Ceram. Soc. 71 (1988) 250–255.

[7] T.A. Strout, Attenuation of sound in high-concentration suspension: development and application of an oscillatory cell model, Thesis, The University of Maine, 1991.

[8] A.K. Holmes, R.E. Challis, D.J. Wedlock, A wide-bandwidth ultrasonic study of suspensions: The variation of velocity and attenuation with particle size, J. Colloid Interface Sci. 168 (1994) 339–348.

[9] A.S. Dukhin, P.J. Goetz, Acoustic spectroscopy for concentrated polydisperse colloids with high density contrast, Langmuir 12 (1996) 4987–4997.

[10] J.D. McClements, Ultrasonic characterization of emulsions and suspensions, Adv. Colloid Interface Sci. 37 (1991) 33–72.

[11] J.D. McClements, Ultrasonic determination of depletion flocculation in oil-in-water emulsions containing non-ionic surfactant, Colloids Surf. 90 (1994) 25–35.