



ACOUSTICS AND ELECTROACOUSTICS FOR CERAMICS

Determination of both the particle size distribution and the zeta potential of ceramic slurries is of key importance in optimizing performance. The particle size of the slip is closely related to inhomogeneities, which in turn relate to fracture origins as well as shape distortion/cracking during drying, pyrolysis and sintering. The zeta potential of the slurry particulates can be used as a tool for optimizing chemical dosage to achieve the desired colloid stability and size distribution.

Introduction

Traditional measurements of particle size and zeta potential usually involve light scattering or sedimentation techniques and require extreme dilution of the ceramic slip. This dilution step can possibly change both the size distribution and the zeta potential of the sample, thereby distorting the very information being sought. Characterizing the concentrated sample directly would allow us to realistically judge the true agglomeration status of the slip and to optimize the dosage of various chemical additives in situ. In contrast, measurements of the diluted samples with traditional methods may reveal only the primary size of the raw materials since the usual sample preparation steps of dilution, chemical modification, stirring and perhaps even sonication have destroyed much of the useful information about the original slurry. Two complementary ultrasonic techniques have now been developed which allow such direct measurement of ceramic slurries, as is, without any sample preparation or dilution (1,9).

Acoustic spectroscopy measures the attenuation and sound speed of ultrasound pulses as they pass through concentrated slurries. The measurements are made over a wide range of frequencies and the resulting spectra are used to calculate the particle size distribution over a range from 10 nm to more than 10 μm .

Electroacoustic spectroscopy measures the interaction of electric and acoustic fields from which the zeta potential can be determined.

Both spectrometers are now commercially available, either separately, or combined in a single instrument such as the Dispersion Technology DT1200, see Figure 1. These methods provide accuracy and precision of a few percent on samples as small as 30 to 100 ml, and in just a few minutes time. A unique feature is the ability to determine separate particle size distributions for mixed systems such as alumina/zirconia slurries. Automated titration equipment invokes changes in agglomeration as a function of pH or dispersant dosage, which allows the ceramic processor to optimize performance at minimum chemical cost and operate the process under the best conditions.



Figure1: The DT-1200 system.

Although much of the experimental method is new, the overall approach is based on a well-established scientific background (2,3,4,5,6). In both methods the interaction of sound with the dispersed particles provides useful information. However, the driving force and measured parameters are different in each case.



General Use

Acoustic spectroscopy can provide accurate particle size data even in concentrated slurries. Figure 2 A shows the measured particle size distribution for four different alumina slurries. Figure 2B shows the experimental attenuation for these samples along with the best-fit theoretical curve for the measured size distribution.

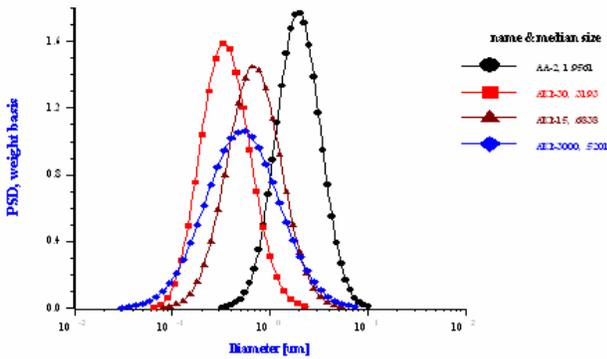


Figure 2A: Particle size distributions

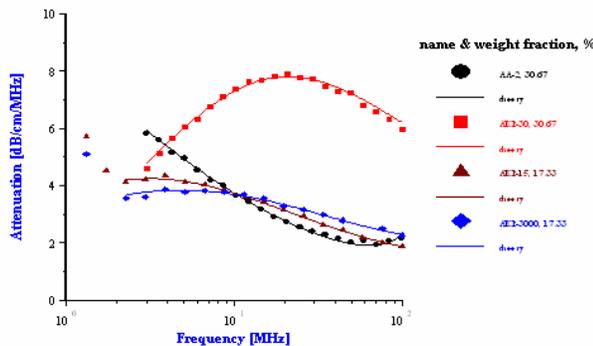


Figure 2B: Acoustic attenuation spectra

Acoustic spectroscopy is applicable to virtually all ceramic materials. Figure 3 shows typical particle size distributions for a variety of commonly used ceramic materials.

For many applications it is important to recognize particle size sub-populations in the final slurry. Such bimodal distributions might result from agglomeration of primary particles caused by non-optimum dispersant addition, or in the following example, from

an intentional addition of a second size fraction.

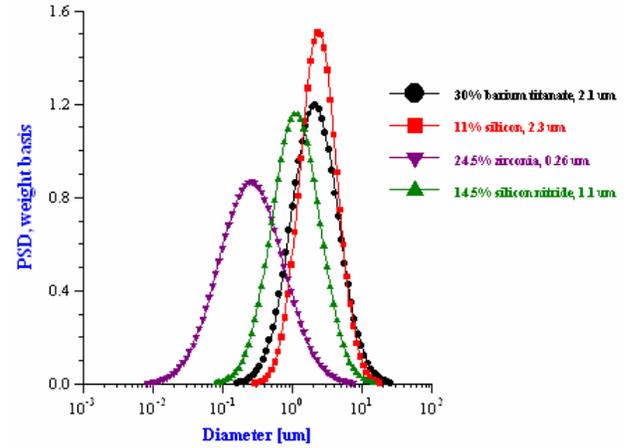


Figure 3: PSD's for ceramic materials

Figure 4A shows the acoustic attenuation spectra for three 10 volume % alumina slurries: a 0.36 micrometer sample, a 2 micrometer sample, and a 1:1 mix of the two. The theoretical spectra fit quite precisely the experimental data giving high confidence in the results. Figure 4B shows the resulting size distributions for the two single component slurries (blue and black curves) as well as the bimodal distribution for the mixed slurry (red curve).

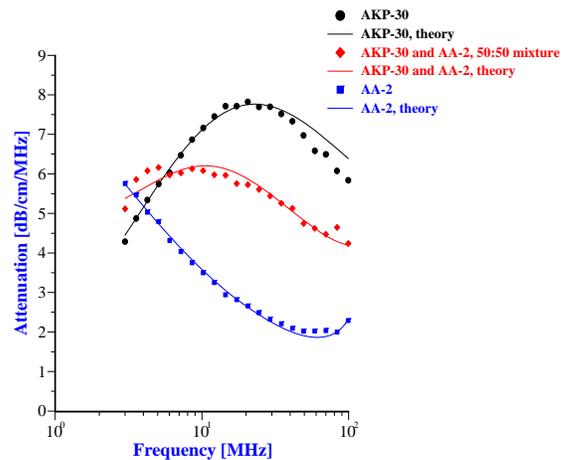


Figure 4A: Attenuation spectra of alumina

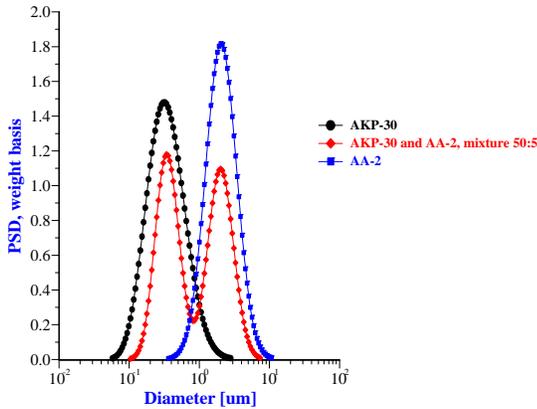


Figure 4B: PSD's for alumina

CMP Slurries

In other applications it is important to be able to detect a very small sub-population of a few large aggregate particles mixed with a large number of much smaller particles. For example, chemical mechanical polishing (CMP) slurries are used in the semiconductor industry to planarize silicon wafers at various steps in the production of computer chips. One large aggregate particle can cause a major scratch and destroy circuit performance. Figure 5 shows the ability of acoustic spectroscopy to detect one relatively large 1 micron particle per million smaller 300 nm particles.

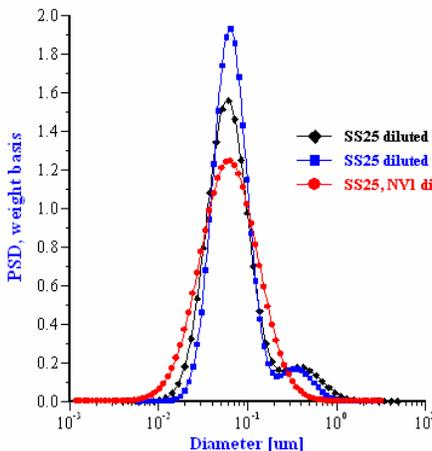


Figure 5: CMP slurries

Mixtures of Components

In many ceramic applications the ceramic slip is actually a mixture of more than one solid component. Traditional optical or sedimentation techniques can find providing correct interpretation of such mixtures challenging and typically assume that all particles have a common set of physical properties. In contrast, commercially available software for acoustic spectroscopy has evolved to the point that allows the specification of at least two classes of dispersed particles. For example, Figure 6 shows an example of a mixed system of alumina and zirconia particles. Figure 6A shows the attenuation spectra for three 5 volume % slurries: a 2 micrometer single component alumina, a 0.3 micrometer single component zirconia, and a 1:1 mix of the two ingredients. Again, the theoretical spectra fit the experimental data quite precisely giving high confidence in the results. Figure 6B shows the resulting single mode particle size distribution for each oxide measured separately, as well as two separate single mode distributions measured for each component in the mixed slurry system.

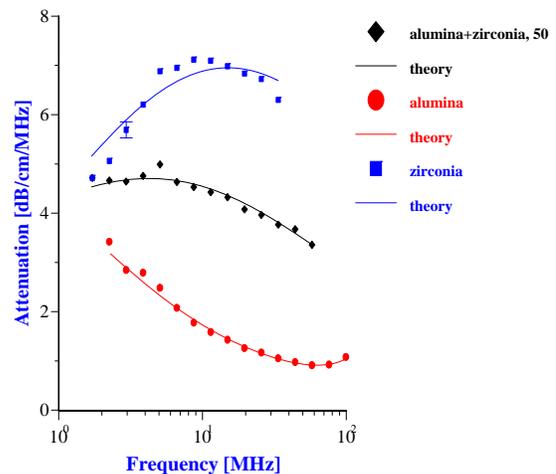


Figure 6A: Attenuation spectra

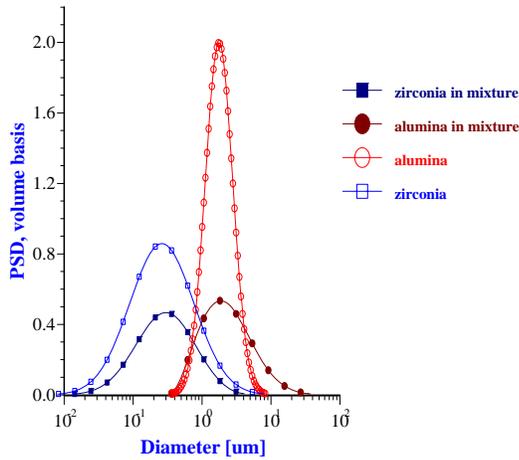


Figure 6B: PSD results

Including Zeta Potential

It is not always appreciated that the particle size distribution of a slurry is not simply a function of the primary size of the constituent ingredients, but instead is a result of many complex chemical and mechanical operations on the system. The zeta potential of the system is one parameter that can be used to investigate this complex relationship. Figure 7 compares zeta potential data for a typical rutile and alumina sample using electroacoustic data. The pH at which the zeta potential goes to zero is referred to as the isoelectric pH. Different materials may have quite different isoelectric points as is evident from this figure. If we desire good stability, then we need to operate far enough from the isoelectric point to achieve a zeta potential in excess of say 20-30 mV, either plus or minus. For the alumina shown this would suggest that to obtain optimum stability for this alumina, one should adjust the pH to avoid the pH range between 8 and 11 where the zeta potential is less than 20 mV. This complex relationship between zeta potential and particle size distribution can be easily understood using acoustic spectroscopy. Figure 7A shows the size distribution for this same alumina at a pH of 4.0. In contrast

Figure 7B shows the size distribution for the same sample where the pH was adjusted to 9.0, very close to the isoelectric point.

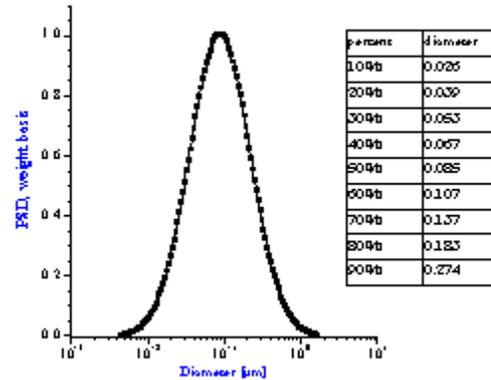


Figure 7A: Alumina slurry at pH 4 with zeta potential of +40 mV. Unimodal distribution.

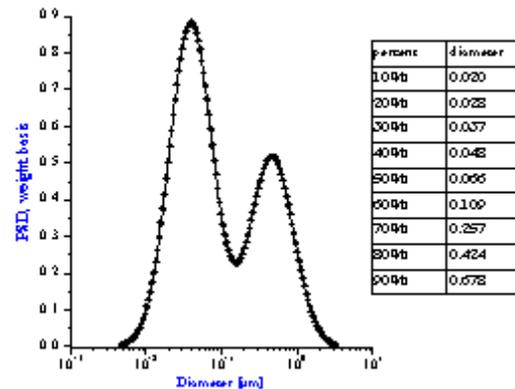


Figure 7B: alumina slurry at pH 9 having zeta potential of only +5 mV. Bimodal distribution.

In the real world, the situation is sometimes even more complex. The particle size and zeta potential is not just a function of the final chemical state of the system, but may depend also on the history of how the system reached this state. In other words, the complete history of the sample may be important as is illustrated in Figure 8, a case



history of a plant manufacturing silicon nitride.

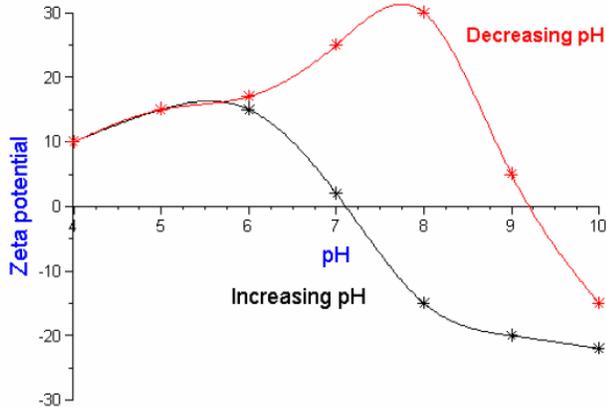


Figure 8: pH vs. zeta potential titration of silicon nitride.

The red curve shows the zeta potential as the pH is decreased to an acid condition. From just this data alone one would think that a pH of 7- 8 would provide adequate zeta potential for stability. However, operating experience in the plant indicated otherwise. A clue to the problem was found by reversing the titration towards more alkaline conditions. The reverse titration, shown by the blue curve, revealed that the isoelectric point decreased by 2 pH units after the slurry was exposed to this acid condition. Investigation of plant operations showed that the slurry processing normally included such an acid wash. In order to obtain adequate stability following this acid condition, the data suggests that the process pH must be readjusted to a point either significantly below or above this new isoelectric point. But how can we explain this dramatic shift in the isoelectric point? The explanation is actually quite simple. The initial slurry had a very small level of contamination, which was insignificant in terms of the overall stability of the system. However, under acid conditions this minor component dissolved. Upon subsequent change to more alkaline conditions, this dissolved material re-precipitated on the surface of the major silicon nitride component. Now this minor component,

although present only in seemingly insignificant quantity, nevertheless dominated the surface chemistry of the silicon nitride material. By realizing that the final state is dependent on the history of the sample the process could be modified to accommodate this change.

Conclusion

In summary, acoustic and electroacoustic spectroscopy provide not only a useful method for characterizing the final aggregative state of a ceramic slip, but also an important tool to help us understand, optimize, and control this state. These acoustic techniques will become more widely adopted as process engineers and researchers realize the benefits of supplementing dilute measurement of raw materials with actual measurements of the final concentrated product.

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