# Ultra-Small-Angle X-ray Scattering Studies of Agglomerate Formation during Drying

A. Vertanessian,[1] M .J. Mayo,[1] A. J. Allen[2]

[1] *Deptartment of Materials Science & Engineering, Pennsylvania State University, University Park, PA, U.S.A.*

[2] *Materials Science & Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, U.S.A.*

## Introduction

The formation of agglomerates during ceramic powder processing is a pervasive problem that frequently prohibits the fabrication of fully dense ceramics. Though it is well known that drying of liquid-borne powders will create agglomerates, it is not known exactly how or why those agglomerates evolve. The problem of agglomeration is particularly acute in the nanosize regime, where it is argued that heightened powder dissolution[1] and diminished electrostatic repulsion[2] are strong driving forces for agglomerate formation in drying suspensions. The present study examines agglomerate shape and size development during drying of different nanocrystalline zirconia powder suspensions by ultra-small-angle x-ray scattering (USAXS) and field emission scanning electron microscopy (FESEM).

## Methods and materials

Yttria (8 mol%) stabilized zirconia (YSZ) nanocrystalline powders (8-nm crystallites) were produced by an aqueous chemical precipitation technique described elsewhere.[3] Aqueous (DDI water) suspensions of YSZ were prepared at pH 2 using $HNO_3$ as the pH-adjusting additive and at pH 9 using $NH_4OH$ as the pH-adjusting additive. The solids loading for SEM was approximately 5% mass fraction, and for USAXS it was 60% mass fraction (a nominal 10% volume fraction). After preparation, suspensions were agitated with an ultrasonic cleaner for 1 h. However, some settling out of larger particles prior to USAXS measurement was unavoidable.

FESEM was performed on both suspended and dried powders. Suspended powders were prepared by dipping a polished Al sample holder for 10 minutes into a 1% mass fraction solution of polyacrylamide, rinsing with water, then dipping into a pH 2 suspension of nanocrystalline YSZ powder, and finally air drying. In this procedure, the sample holder "captures" particles from the suspension, and particles are prevented from subsequently moving during drying. SEM of dried powders was performed by sprinkling powder over a wet colloidal Ag layer and allowing the Ag paint to dry. An Au coating was sputtered onto all specimens prior to viewing.

The Bonse-Hart USAXS facility at UNI-CAT[4,5] was used to examine the fine features of agglomerate structure during the drying of the suspensions. For each pH, samples were prepared in three forms: suspension, suspension air-dried to paste consistency, and suspension air-dried completely. The original (dry) powder was also studied. Suspensions and pastes were sealed in liquid cells incorporating a 1-mm x-ray flight path through the sample and polyamide film windows transparent to the incident and scattered x-ray beams. A scattering contrast between YSZ and water was assumed, and a water-filled cell was used as a buffer to subtract the background scattering and provide the incident beam normalization. The dry powders were sealed between layers of adhesive polyamide film and their thicknesses were measured individually by micrometer. A scattering contrast between YSZ and air was assumed and a double layer of adhesive polyamide film was used as a blank to subtract the background scattering and provide the incident beam normalization.

Absolute-calibrated USAXS cross section data, $d\Sigma/d\Omega$, were collected in the scattering vector, Q, range of 0.0001 $Å^{-1}$-0.25 $Å^{-1}$, were desmeared using the Lake desmearing algorithm,[6] and then analyzed using the entropy maximization routine MaxEnt[7] to extract basic particle size information. The scattering curves were also inspected for power laws in scattered intensity *versus* Q that might indicate either the presence of fractal aggregates and surfaces, or the formation of agglomerates in chains or sheets.

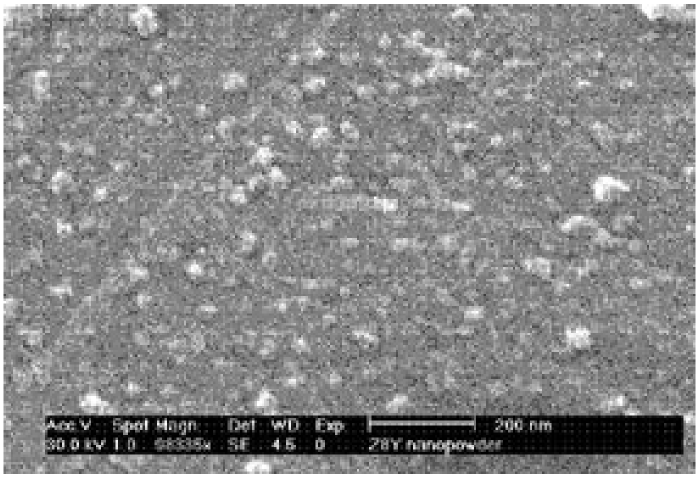

*FIG. 1. FESEM image of YSZ nanocrystalline powder dispersed in pH 2 suspension. Suspensions at pH 9 show nearly identical features.*

## Results

Initial powders were of nanocrystalline particle size, as shown in the FESEM micrograph presented in Fig. 1 of particles captured from a pH 2 suspension. Particles from a pH 9 suspension look the same with the bulk of the particle size distribution in the 100 Å-500 Å size range. In each case, the particles are composed of even smaller crystallites, as evidenced by XRD and BET measurements giving crystallite sizes for this powder of 81 Å and 93 Å, respectively.

These data are consistent with the MaxEnt particle size distribution shown in Fig. 2, derived from the USAXS measurement of a fresh pH 2 suspension, which shows a primary particle size of ≈80 Å and evidence of larger particles up to 500 Å in diameter and beyond. Thus, the starting powder is already agglomerated on a small scale, prior to drying of the suspension. MaxEnt size distributions determined for suspensions at other pH values are similar, as are those for the pastes and dried samples, but there are differences in the size distributions of coarser particles and in the relative volume fractions detected at sizes larger than 500 Å.

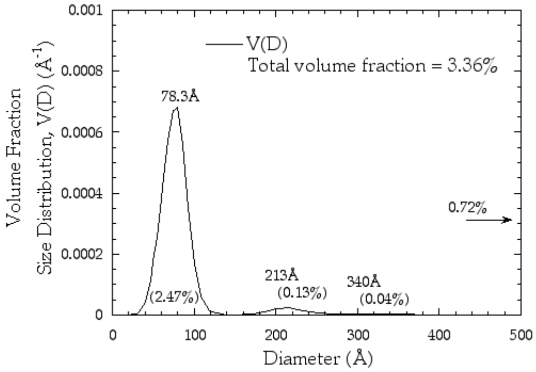

*FIG. 2. MaxEnt particle size distribution for YSZ nanocrystalline powder dispersed in pH 2 suspension. Suspensions at pH 9 show nearly identical features.*

However, some agglomerates are larger than the maximum ≈1 µm size detectable by USAXS.

While MaxEnt size distribution analysis is useful for deriving the primary particle size, it does not measure particles that have settled out of the suspension or are too large to be detectable by USAXS. Furthermore, inspection of the USAXS scattering curves themselves suggests that a more fundamental interpretation of the agglomerated morphology is possible than is obtainable by a size-distribution analysis alone. Figure 3 presents $d\Sigma/d\Omega$ *versus* Q for fresh suspensions with various pH values, together with the corresponding plots for the fully-dried powder residues.

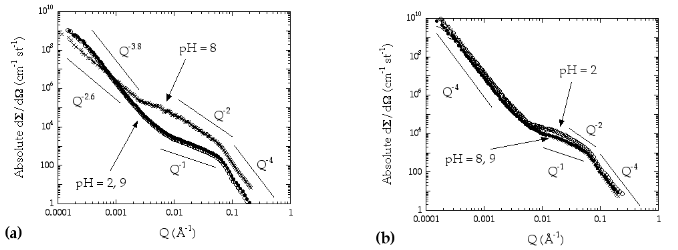

*FIG. 3. (a) USAXS absolute-calibrated desmeared $d\Sigma/d\Omega$* versus *Q for YSZ powder suspensions with pH values of 2, 8 and 9. (b) Corresponding data for fully-dried powder residues.*

Three distinct regions can be observed in the scattering. At high Q, slightly steeper than $Q^{-4}$ Porod scattering is observed, suggesting a diffuse interface at the surface of the primary particles. Transition to this final Porod regime occurs at the same Q for all powders, suspended or dried, consistent with a common fundamental particle size of ≈80 Å. In the next regime (moderate Q), data adhere to a power law dependence between $Q^{-1}$ and $Q^{-2}$, suggesting some organization of the primary particles into chains or sheets. The size range over which the chains or sheets exist would be from 80 Å up to ≈650 Å.

The third regime occurs at the lowest Q values, and corresponds to objects larger than 650 Å. For dried powders, a $Q^{-4}$ Porod law is observed, indicating large particles with smooth surfaces. In the case of both starting and suspended powders, *except* for the fresh suspension with pH 8, a surface-fractal power law between $Q^{-3}$ and $Q^{-4}$ is observed. Typically, the power law observed is between $Q^{-3.8}$ to $Q^{-3.5}$, suggesting a surface-fractal exponent, $D_s$, between 2.2 and 2.5. The transformation from a fractally-rough surface to a smooth surface is probably due to particles packing together at the agglomerate surface during the last stages of drying. For the suspension at pH 8, close to the isoelectric point for this system, a mass-fractal $Q^{-2.6}$ power law is observed, corresponding to a mass- or volume-fractal exponent, $D_v$, of 2.6. This suspension also shows the most sheet-like ($Q^{-2}$) structure in the intermediate Q regime. However, upon drying, the morphology, as measured by USAXS, becomes similar to those of the other dried suspensions.

## Discussion and Conclusions

Away from the isoelectric point, aggregation of the mutually repulsive primary particles into agglomerates is "reaction-limited" (i.e., there are many contacts before aggregation occurs). Formation of large, dense, fractally rough agglomerates is likely due to the entanglement of short chains of primary particles. At pH 8, where electrostatic repulsion is minimized, aggregation of the primary particles is "diffusion-limited," and large mass-fractal aggregates form.[8] Differences with pH in the µm-scale morphology of fully-dried suspensions, seen by SEM, are likely related to the nm-scale aggregation of primary particles, studied by USAXS. Indeed, at high pH, SEM shows large lamellae and coarse grains with lamellar substructure.

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