Uniformity of Al_2O_3-ZrO_2 Composites by Colloidal Filtration

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Dispersion states of aqueous composite Al_2O_3/ZrO_2 colloidal suspensions were studied by measuring particle size distribution as a function of pH. Mutual dispersion was achieved at pH values of 2.0 to 3.5. Consolidated composites formed by colloidal filtration reflected the uniformity of the colloidal state. The mean flexural strength (896 MPa) of the sintered compacts was 1.6 times that of bodies consolidated by isostatic pressing.

INTRODUCTION

PREVIOUS work has shown that agglomerates in a consolidated powder system shrink away from their surrounding powder matrix during sintering to produce crack-like voids responsible for fracture.[1,2] Since agglomerates are inherent to dry-powder consolidation routes (submicrometer powders spontaneously agglomerate due to van der Waals forces), it was obvious that other consolidation routes capable of avoiding agglomeration must be sought.

Colloidal systems have this potential; spontaneous agglomeration can be avoided by producing repulsive forces between particles either electrostatically or sterically.[3] Particles in a well-dispersed colloidal suspension can be consolidated by filtration, gravitation or centrifugal settling, evaporation, and electrophoresis. It was reasoned that if agglomeration could be avoided, the uniformity of the consolidated state would reflect the uniformity of the colloidal state. Work was therefore initiated to examine this premise. The Al_2O_3/ZrO_2 composite powder system was chosen for comparison with previous results obtained by dry-powder consolidation routes.[4,5] An electrostatic route[3] was chosen to obtain dispersion in the colloidal state. Filtration was chosen as the consolidation method since it was suspected to minimize particle-size/phase-density segregation effects. As will be illustrated, the colloidal filtration* route to consolidation did significantly help reduce the agglomerate size relative to a dry-powder route.

EXPERIMENTAL PROCEDURES AND RESULTS

The composition chosen for this study included 30 vol% ZrO_2 with 2.5 mol% Y_2O_3 since previous work[4] has demonstrated that, at this composition, tetragonal ZrO_2 could be fully retained to achieve significant toughening and strengthening.

Powders and Dispersion Studies

Commercial-grade powders of Al_2O_3† and ZrO_2 (2.5 mol% Y_2O_3)‡ were used. X-ray diffraction analysis of the Al_2O_3 indicated only α-Al_2O_3; similarly, the ZrO_2 was determined to be tetragonal in form.

Dispersion studies in deionized water were performed with the as-received powders using particle/agglomerate size analysis§ to evaluate the degree of dispersion. Oxide surfaces in an aqueous medium are generally charged positively under acidic and negatively under basic conditions.[6] The pH value where a neutral surface is achieved is referred to as the isoelectric point. The magnitude of the surface charge increases as the pH value of the suspension deviates from the isoelectric point. It was therefore anticipated that both Al_2O_3 and ZrO_2 would be best dispersed under acidic and basic conditions. The pH adjustments, with the addition of reagent-grade HCl or NH_4OH, were made until suspensions of either Al_2O_3 or ZrO_2 (containing ≈2 vol% solids) displayed maximum dispersion (Figs. 1 and 2). The Al_2O_3 suspensions displayed best dispersion in the pH ranges 2.0 to 3.5 and 10.2 to 12.0. Similarly, tetragonal ZrO_2 could be best dispersed under both acidic (pH 1.5 to 3.5) and basic (pH 9.0 to 9.5) conditions (Fig. 2). Comparison of these dispersion regions clearly indicates that a mutual dispersion of α-Al_2O_3 and tetragonal ZrO_2 used in this study could only be achieved under acidic conditions in the pH range 2.0 to 3.5 where the two dispersion ranges overlap.

Scanning electron and transmission electron microscopy (SEM and TEM) analyses of the as-received powders revealed extensive agglomeration; ball-milling was therefore necessary to break up the agglomerates. Milling in water at a pH value of 2.0 to 2.5 was conducted with alumina balls in an alumina jar.¶ The effect of milling on dispersion was monitored by measuring particle/agglomerate size distributions.

In the case of α-Al_2O_3, agglomerates were weak, and ≈80% of the system could be reduced to the submicrometer size range with an average particle size of ≈0.5 μm within 1 h of milling. This average particle size corresponded closely to the average individual crystallite size determined by TEM, indicating that the agglomerates were weak and could be broken into individual particles during milling. The weak nature of the α-Al_2O_3 agglomerates was also apparent in the significant changes that

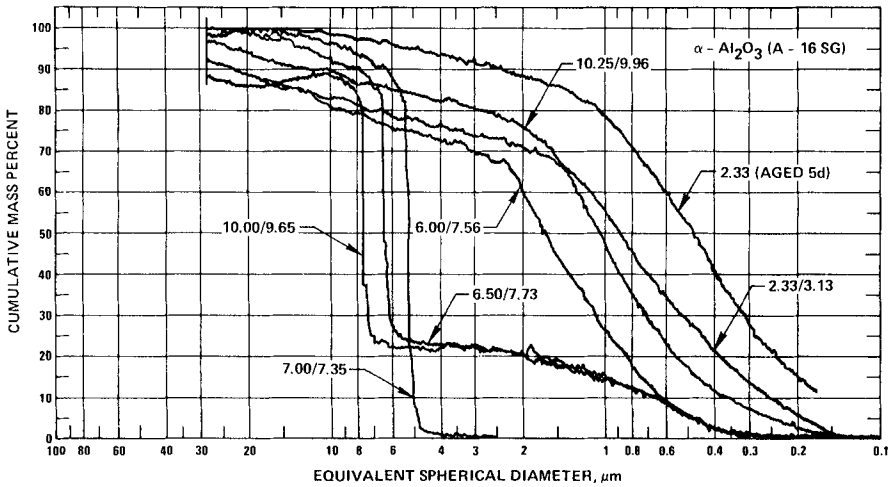

Fig. 1. Particle/agglomerate size distribution of α-Al_2O_3 in aqueous suspensions at pH levels indicated; numbers separated by slash correspond to pH at beginning and end of experiment, respectively.

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*This technique is more popularly known as slip casting and is purposely avoided in the present report since "slip" does not adequately describe the colloidal nature of a particulate-fluid system.

†A-16SG, Aluminum Company of America, Pittsburgh, PA. Major impurities: 0.05 to 0.09% Na_2O, 0.02 to 0.04% SiO_2, and 0.01 to 0.02% Fe_2O_3.

‡Zircar Products, Florida, NY. Major impurities: 1.5% HfO_2, 0.2% Al_2O_3, 0.1% CaO, 0.01% MgO, 0.01% Fe_2O_3, and 0.3% Cl.

§Sedigraph 5000D, Micromeritics Instrument Co., Norcross, GA.

¶Norton Co., Akron, OH: 85% Al_2O_3, 11% SiO_2, 1.2% CaO, 2.0% MgO.

were observed in the particle size distribution of the suspensions on aging. A comparison of the particle size distribution of the as-received material at a pH value of 2.33 with that of a suspension aged at the same pH for 5 days illustrates this change (Fig. 1). In fact, nearly identical size distributions could be obtained by aging and ball-milling.

On the other hand, when the as-received ZrO_2 powders were aged in acidic or basic suspensions, the change in the size distribution indicated that agglomerates larger than 2 μm did not break up significantly (Fig. 2(*B*)). Unlike the Al_2O_3 system, ZrO_2 powders could not be completely deagglomerated in short milling (<20 h). The TEM observations indicated an average crystallite size of ≈0.05 μm; the average agglomerate size after 16 h of milling was 0.5 to 1.0 μm, and ≈99% of the system could be reduced to a particle/agglomerate size of <3 μm. Longer milling was not attempted to avoid the high degree of contamination from the milling media.

The composite Al_2O_3-ZrO_2 suspensions (30 vol% ZrO_2 (+2.5 mol% Y_2O_3)) were prepared with a 25 vol% solid content dispersed at a 2.5 pH value and were then milled for 16 h primarily to reduce the size of the ZrO_2 agglomerates. For this condition the average particle/agglomerate size of the composite suspension was ≈0.6 μm (Fig. 3), indicating that a mutual dispersion was achieved.

Consolidation

Gypsum molds (prepared by mixing gypsum powder with water at a weight ratio of 100:75) were used as the filtering medium. The green density of the Al_2O_3+ZrO_2 composite powder was between 50 and 55% of the theoretical density.

Sintering and Microstructures

Consolidated, composite specimens were sintered at 1600°C in air for 2 h.[4] Sintered densities measured by the Archimedes technique were >98.5% of the theoretical. The SEM micrograph of the sintered structure shown in Fig. 4 illustrates the two-phase microstructure and indicates that the uniformity achieved in the suspension stage through mutual dispersion (Fig. 3) was retained in the consolidated state. This micrograph also shows many uniformly distributed crack-like voids (<10 μm) which were produced by differential sintering of large ZrO_2 hard agglomerates that had not been completely broken apart during milling.

Mechanical Measurement

Flexural strength measurements were obtained on the material corresponding to Fig. 4 by four-point bending (inner span 1.27 cm, outer span 2.54 cm) with diamond-cut specimens (≈0.32 by 0.32 cm in cross section) finished with a 220-grit diamond grinding wheel. The average strength of five specimens was 896 MPa (827 to 965 MPa range).

An apparent amorphous impurity phase was identified at the fracture origins (Fig. 5). Energy dispersive X-ray analysis of the fracture origins revealed Si, Mg, Ca, Cl, and S as major impurities. The Si, Mg, and Ca relate to the milling media. The major source of the Cl impurity is the ZrO_2 powder. A possible source of S would be the gypsum molds used in filtration. Thus, it was concluded that the fracture origins were related to milling media acquired during attrition of hard agglomerates.

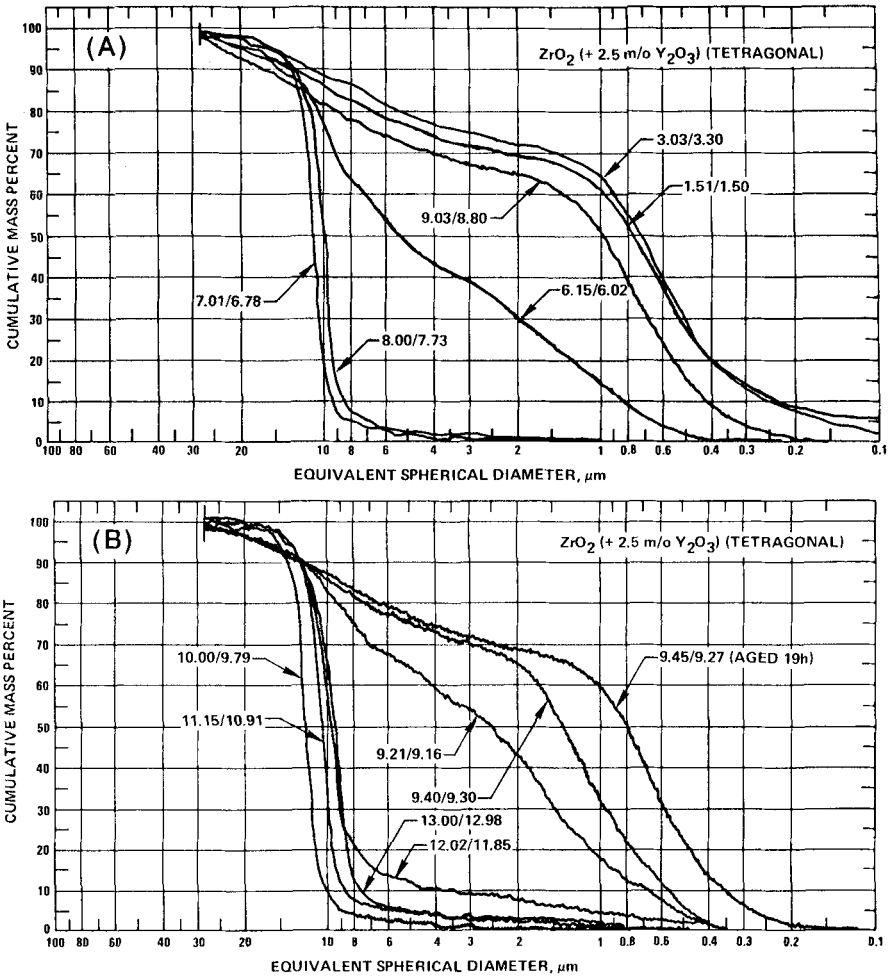

Fig. 2. Particle/agglomerate size distribution of tetragonal ZrO_2 (+2.5 mol% Y_2O_3) in aqueous suspensions in pH range of (*A*) 1.51 to 9.03 and (*B*) 9.21 to 13.00.

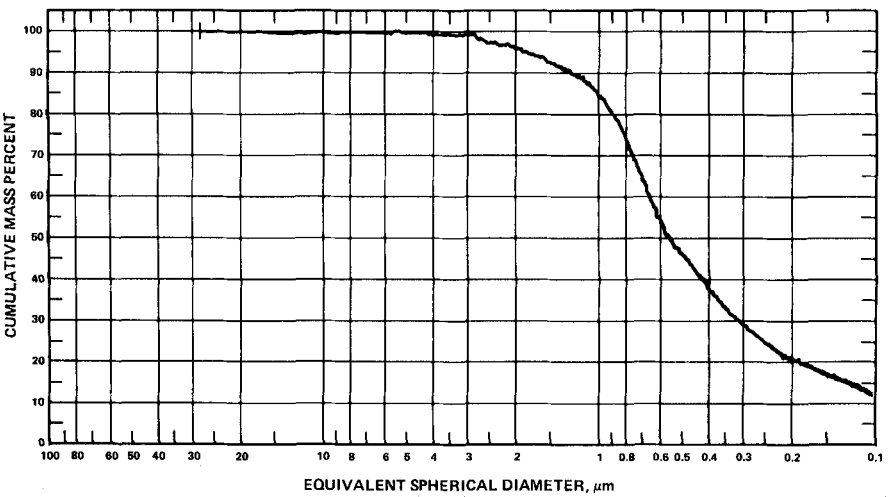

Fig. 3. Particle/agglomerate size distribution of Al_2O_3+30 vol% ZrO_2 (+2.5 mol% Y_2O_3) composite system at pH 2.0 after 16 h of milling at pH 2.5.

Discussion and Conclusions

The major result of this work shows that the colloidal filtration route to powder consolidation has the potential of reducing

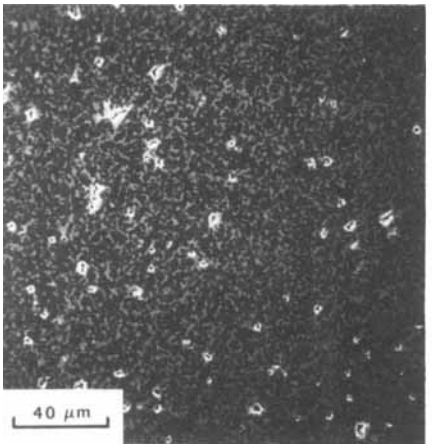

Fig. 4. Scanning electron micrograph of Al_2O_3+30 vol% ZrO_2 (+2.5 mol% Y_2O_3) composite which was filtered from suspensions corresponding to Fig. 3 and sintered at 1600°C for 2 h. Light gray regions are ZrO_2 and dark regions Al_2O_3.

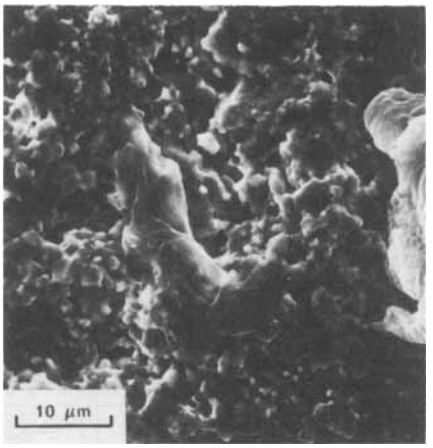

Fig. 5. Amorphous impurities at fracture origin of composite corresponding to Fig. 4.

the size of agglomerates found in dry powders because of van der Waals attractive forces. Large crack-like voids produced by the differential sintering of agglomerates were not observed at the fracture origins despite the fact that smaller (<10 μm) crack-like voids were left by unmilled hard agglomerates. The average strength of the composite material prepared by the colloidal filtration route was 896 MPa vs 550 MPa for the same composite consolidated with a dry-powder route, i.e. an increase of ≈63% obtained by changing the powder dispersion and the consolidation route to decrease the agglomerate size.

As illustrated in Fig. 5, the fracture origins in the material consolidated by the colloidal filtration route were related to the milling procedure which appeared necessary to reduce the size of hard agglomerates.

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Photochemical Reaction in a Reduced Soda-Lime-Silica Glass Containing Ce^{3+} and As^{3+}

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The photochemical reaction between Ce^{3+} and As^{3+} in a reduced $16Na_2O \cdot 11CaO \cdot 73SiO_2$ glass (mol%) was examined by exposing it to an Xe or Hg arc. In addition to Ce^{4+}, a paramagnetic $As(II)O_2^{2-}$ center having C_{2v} symmetry and a trapped electron center were identified by ESR. The $As(II)O_2^{2-}$ defect is the origin of the unidentified ESR signal which correlates with the discoloration of a borosilicate glass developed for solar energy application.

DISCOLORATION in glass induced by solar irradiation has been known as solarization since Faraday discovered the deepening purple color in manganese-containing glass.[1] Although suppression of solarization in glass for optical use is an important problem in glass technology,[2] the phenomenon itself is not well understood at present.[3] Clarification of the valence and coordination structure of solarizable constituents[4] before and after electron transfer induced by solar rays and determination of new photochemical reactions in glass are necessary for a complete understanding of solarization.

In this communication, the photochemical redox reaction of Ce^{3+} and As^{3+} (not As^{5+}) in a reduced soda-lime-silica glass is reported. As far as we know, there has been no report concerning this reaction, whereas the photochemical reaction of Ce^{3+} with As^{5+} has received considerable attention.[5,6]

Sample glasses of nominal composition (in mol%) $16Na_2O \cdot 11CaO \cdot 73SiO_2 \cdot 0.75As_2O_x \cdot 0.015CeO_2$ were prepared from reagent-grade chemicals under reducing conditions. To create a reducing atmosphere, half of the total amounts of Na_2O and CaO in the batch was supplied as the oxalates (which evolve CO gas on decomposition at high temperatures) and the remainder as the carbonates. Cerium and arsenic were added to the batch as aqueous solutions of $Ce(NO_3)_3 \cdot 6H_2O$ and As_2O_5. The batch was melted in an alumina crucible with an alumina cover to preserve the reducing action during melting. Glass rods (3 mm in diameter and 300 mm long) were obtained by mechanically pulling the melt with a fused quartz tube. The rods were subjected to uv irradiation from a 500-W Xe lamp or 100-W ultrahigh-pressure Hg lamp at room temperature.

Figure 1 shows the electron spin resonance (ESR) spectra for uv-irradiated glasses. The complex curves between 0.30 and 0.36 T can be regarded as superpositions of two independent signals. The first signal, appearing in the central region (g=2), is almost identical to that reported by Stroud,[7] who observed such a signal even in arsenic-free glass containing Ce^{3+} on uv exposure and assigned it to a trapped electron center.

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