

Preparation of Zirconia-Alumina Ceramics From Narrow-Sized Powders

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Alumina-zirconia composites were prepared from concentrated slurries of narrow-sized zirconia and alumina powders. Composite samples fired at 1500°C had room-temperature bending strengths approaching 700 MPa. In contrast, alumina samples, which were processed and mechanically tested under similar conditions for comparison with the composite samples, had room-temperature bending strengths approaching 500 MPa.

There is currently great interest in designing transformation-toughened ceramics such as zirconia-toughened alumina. Several different preparative routes including mechanical mixing of powders, attrition milling of zirconia grinding media, sol-gel synthesis, reactive sintering, and evaporative decomposition of slurries have been used to control the chemistry and the microstructure of sintered zirconia-alumina ceramics and thereby their mechanical properties.^{1,2} Specifically, toughening resulting from stress-induced transformation or microcrack nucleation may be optimized by minimizing zirconia particle size and size distribution. Also, maintenance of tetragonal zirconia is essential for stress-induced transformation toughening, whereas maintenance of a uniform zirconia-particle distribution is important for optimizing microcrack nucleation-induced toughening.

The present report describes the preparation of zirconia-alumina composites by mixing submicrometer zirconia and alumina powders of narrow size distribution. By controlling the starting zirconia powder-size distribution and homogeneously distributing it in the alumina matrix, control of the final sintered zirconia grain size and size distribution might be attained. This approach has potential advantages over those techniques that do not control the initial particle size and size distribution of the zirconia.

Experimental Procedure

Starting Materials

Two types of narrow-sized zirconia powders were used in the preparation of the composites. The first powder was a monodispersed zirconia, nominally 250 nm in diameter, prepared from the controlled hydrolysis of zirconium *n*-propoxide.^{3*} The second powder was a commercially available zirconia[†] of narrow size distribution, nominally 150 nm in diameter. Commercial undoped and doped (nominally 0.2 wt% MgO) alumina powders[‡] were separated into narrow size classifications via a semicontinuous centrifugation process that follows the Svedberg-Nichols modification of Stokes' law of settling.⁴ Five narrow-sized cuts were produced in five separate centrifugation steps. Size cuts of 200 to 300 nm undoped and 200 to 300 nm doped alumina were used to prepare composite and alumina samples, respectively. Scanning electron micrographs of representative samples of the alkoxide-derived zirconia and the size-classified alumina powders, and the corresponding particle-size distributions determined by photon correlation spectroscopy, are displayed in Fig. 1.

Procedure

Figure 2 illustrates schematically the processing steps to go from the starting powders to the final sintered ceramics. The zirconia powders used to prepare those samples for which mechanical properties were measured were first hydrothermally treated. The treatment involved heating dilute pH-stabilized aqueous dispersions of zirconia in a closed vessel at 250°C for 2.5 hours. The hydrothermal treatment resulted in a reduction in powder weight loss (as determined by thermogravimetric analysis) from 25% to <10% for the alkoxide-derived powder and from 18% to <10% for the commercial powder. The hydrothermal treatment caused the alkoxide powder to transform from amorphous to tetragonal, while the commercial zirconia powder remained monoclinic. Particle-size analysis[§] performed after the hydrothermal treatment revealed no statistically significant change in particle size or size distribution. Scanning electron microscopy verified that the zirconia particles retained their spheroidal morphology.

Composite green bodies were formed by ultrasonically dispersing the zirconia (hydrothermally treated or untreated) and the sized alumina in deionized water at pH 10 or 3.0. The solids content of the dispersion was increased by centrifugation at 3000 rpm for 1.0 to 3.0 hours (the longer centrifugation times were needed for the smaller particle-sized commercial zirconia powder) and decantation of the supernatant followed by redispersion of the sediment with the addition of a small amount of deionized water; the resulting high solids concentrations prevented segregation of the zirconia and alumina powders during the forming process. The efficient mixing of the two powders was verified by backscattered electron imaging and energy dispersive spectroscopy on a scanning electron microscope of the final sintered ceramics. The dispersion was concentrated from nominally 30% solids by weight to $\geq 65\%$ solids by weight. Alumina slurries prepared for comparison with the composite samples were processed in the same manner.

Composite green bodies with a nominal zirconia content of 20 wt% were prepared from the concentrated slurries. The slurries were consolidated in a

*Alfa Products, Danvers, MA.

†Nyacol Products, Ashland, MA.

‡RC-172DBM with and without MgO, Reynolds Metals Co., Bauxite, AK.

§Model N4D, Coulter Electronics, Inc., Hiialeah, FL.

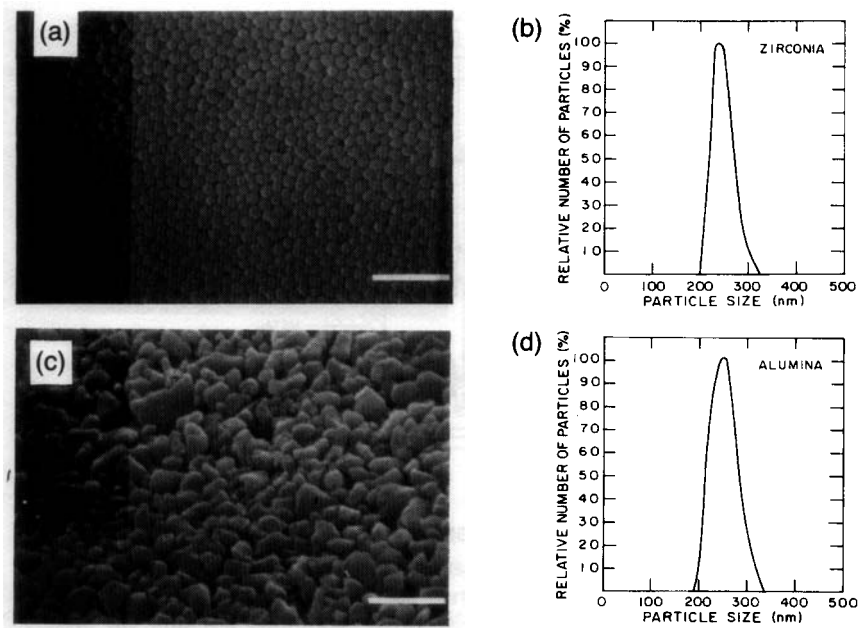


Fig. 1. Scanning electron micrographs of alkoxide-derived zirconia and size-classified alumina (200 to 300 nm) are pictured in (a) and (c), respectively. (Bar = 1000 nm.) Particle-size distributions for both the alkoxide-derived zirconia and the size-classified alumina are given in (b) and (d), respectively.

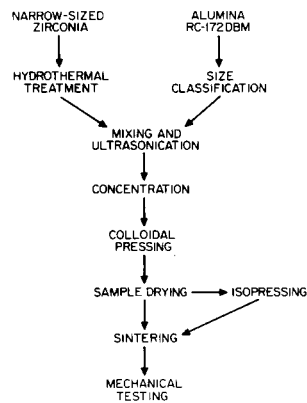


Fig. 2. Processing flow diagram.

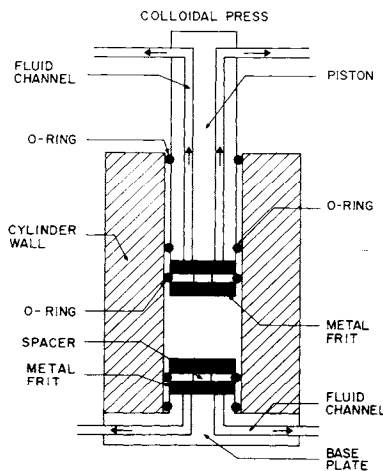


Fig. 3. Schematic of colloidal press.

colloidal press that consists of a sleeve, a fixed base plate, and a piston (see Fig. 3). Both the piston and base plate are fitted with channels that allow the passage of fluid. The solids are trapped between sheets of 200 nm filter membranes[†] supported on porous metal frits placed on the faces of the piston and base plate. Samples were pressed at loads of 39 MPa with hold times at pressure of 30 minutes. Green bodies measuring 38 mm in diameter by at least 12.7 mm in height were obtained for the composite material, while green bodies measuring 38 by 25 mm were obtained for the alumina samples.

The green bodies were dried at room temperature for several days prior to placement in a drying oven. Once in the drying oven, the green bodies were heated to 100°C in air. After oven drying, several samples were isopressed at 275 MPa. Sintering was done in air with a 2°C/min ramp to 600°C with a one-hour soak at temperature. Samples were heated at 10°C/min to their final sintering temperature. The composite samples were fired at 1500°C for one or two hours, while the alumina samples were fired at 1400° or 1500°C for two hours. Samples were cooled at approximately 10°C/min to 800°C. Further cooling to room temperature was uncontrolled.

The sintered samples were machined** into bars measuring 25 by 1.5 by 2.0 mm. Mechanical testing was performed using a four-point test jig with inner and outer span lengths of 10 and 20 mm, respectively. Samples were stressed at a crosshead rate of 0.025 mm/min, corresponding to a stress rate of 50 MPa/s.^{††} Vicker's indentation was performed on the polished surfaces of both composite and alumina samples. The indentation testing was done at a load of 10 kg using a crosshead rate of 0.005 mm/min to full load.

[†]Cat. No. FGLP-02500, Millipore Corp., Bedford, MA.

**Bomas Machine Specialties, Somerville, MA.

^{††}Instron Engineering Corp., Canton, MA.

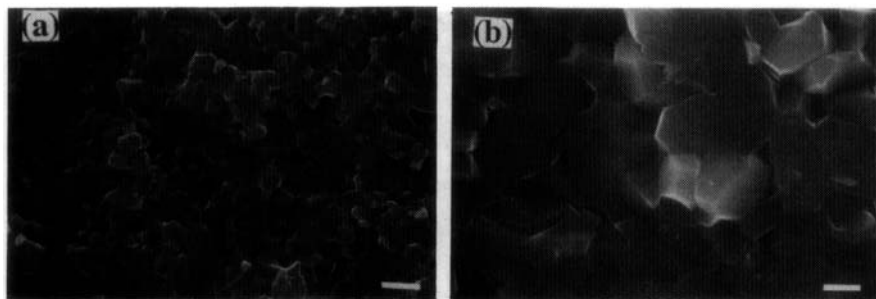


Fig. 4. Scanning electron micrographs of fracture surfaces of (a) composite and (b) alumina samples, both sintered at 1500°C for 2 h. (Bar = 1000 nm.)

Characterization Techniques

Scanning electron microscopy^{††} using both secondary and backscattered imaging was used to characterize the particle size of starting materials and grain sizes in the sintered ceramics. X-ray diffraction^{§§} was conducted using CuK α radiation at an accelerating voltage of 25 kV. Both thermogravimetric and differential thermal analysis^{¶¶} (at a heating rate of 10°C/min, with alumina used as the reference material) were also used to characterize starting materials. Energy dispersive spectroscopy^{***} using a 150 eV EDAX Si(Li) detector on the SEM using ZAF standardless analysis was used to check the chemical homogeneity of the sintered ceramics. Densities of green bodies were determined by a geometric method, that is, by weighing the samples and determining their volume from measurements of both the height and diameter measured with a micrometer.

Results and Discussion

Composite slurries prepared with hydrothermally untreated alkoxide-derived zirconia powders yielded green bodies with densities 50 to 55% of theoretical; the higher green densities were obtained from slurries dispersed at pH 3. Extensive cracking during drying prevented whole samples from being fired; thus all further discussion will be concerned with composites prepared using the hydrothermally treated zirconia powders. Composites formed from both the alkoxide-derived and Nyalcol zirconia powders yielded green bodies with densities greater than 60% of theoretical. Alumina samples processed at pH 3 also gave green bodies with densities greater than 60% of theoretical.

The sintered composite material, which was fired at 1500°C for either one or two hours, had densities of 91 to 93% of theoretical, while the alumina samples fired for similar times at 1400° and 1500°C had densities \geq 95% of theoretical. The microstructures of the composite and the alumina ceramics (fired at 1500°C for two hours) are illustrated in Fig. 4. A comparison of the two micrographs, which are representative of the two materials, shows that the presence of the zirconia

^{††}Hitachi Model 530-S, Lakeville, CT.

^{§§}Model 11CK3, General Electric, Milwaukee, WI.

^{¶¶}STA 429, Netzsch Inc., Exton, PA.

^{***}System 5000 version 1.059, EG&G Ortec, Oak Ridge, TN.

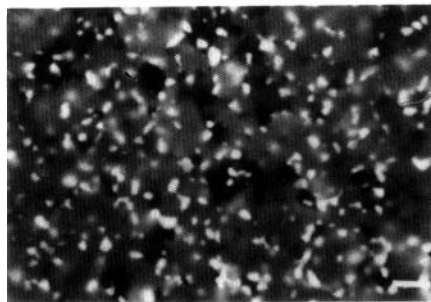


Fig. 5. Backscattered scanning electron micrograph of a sintered and polished composite sample. (Bar = 1000 nm.)

inhibits grain growth of the alumina. Polished sections of the composite material were thermally etched (1500°C, 30 minutes) to determine grain sizes. Visual inspection of the SEM micrographs gave alumina and zirconia grain sizes of 2500 and 400 nm, respectively, in the composite material, and alumina grain sizes of 5000 nm in the alumina ceramics.

Several polished sections of the composite material were chemically analyzed by energy dispersive spectroscopy and examined by backscattered electron imaging (BSE). Figure 5, which is a BSE micrograph of a typical composite fired at 1500°C for two hours, shows that the small (nominally 400 nm) zirconia grains are distributed homogeneously throughout the alumina matrix. This homogeneous distribution was verified by BSE imaging at length scales up to the sample size. The placement of several zirconia grains extending into the black voids also suggests that some of the observed porosity is due to pullouts during the diamond polishing. Representative EDS analysis showed mean zirconia contents of 17.0 wt% with standard deviations of ± 0.21 wt% across the polished section.

Preliminary mechanical test results at room temperature are tabulated in Table I. Both the mean bending strength and the Weibull modulus are given.⁵ The data presented in Table I illustrate several interesting observations. Comparison of the two composite samples 104-1 and 104-2 shows no measurable increase in strength with isopressing, while an increase is observed for the two alumina samples 106 and 107. This different behavior might indicate larger defects in the alumina that were healed by isopressing. Table I also shows that alumina bars cut parallel to the direction of pressing show substantial increases in both the bend strength and Weibull modulus relative to bars cut perpendicular to the direction of pressing. This might indicate some anisotropy inherent to colloidal pressing.

Figure 6 is a plot of the probability of failure (P_f/P_f) versus the stress at failure (S_f) for samples 104-1 and 104-2. Figure 6 shows strengths approaching 700 MPa; however, as indicated by the low Weibull modulus values, there is a large amount of scatter of the strength values. The fracture surfaces of samples that broke under low stress displayed a substantial amount of a glassy phase. EDS analysis of this phase showed the presence of large amounts of SiO₂ (62 wt%) and MgO (38 wt%). Since all processing was done in plastic except for the hydrothermal treatment, where a glass liner was used, replacement of the glass liner with one made of stainless steel may eliminate the SiO₂ and MgO. In contrast, fracture surfaces of the samples that failed at higher stress levels were

Table I. Mechanical Properties of Zirconia-Alumina Composites and MgO-Doped Alumina

Sample No.	ZrO ₂ Powder	Dispersion pH	Mean Strength (MPa)	Weibull Modulus	Sintering Time (h)	Sintering Schedule T (°C)
ZrO ₂ -Al ₂ O ₃ composites*						
77	A [†]	10	463	14.6	1.0	1500
5	A	10	604		2.0	1500
104-1	N [‡]	3	516	6.0	2.0	1500
104-2 [§]	N	3	538	7.0	2.0	1500
MgO-doped Al ₂ O ₃						
100		3	301	2.6	2.0	1500
102 [§]	(perpendicular)	3	401	6.0	2.0	1400
102 [§]	(parallel)	3	496	12.5	2.0	1400
106 [§]		10	401	3.0	2.0	1400
107		10	255	2.0	2.0	1400

*20 wt% zirconia nominal composition.

[†]Alkoxide-derived zirconia.

[‡]Commercial zirconia.

[§]Samples were isopressed 276 MPa (40 000 psi).

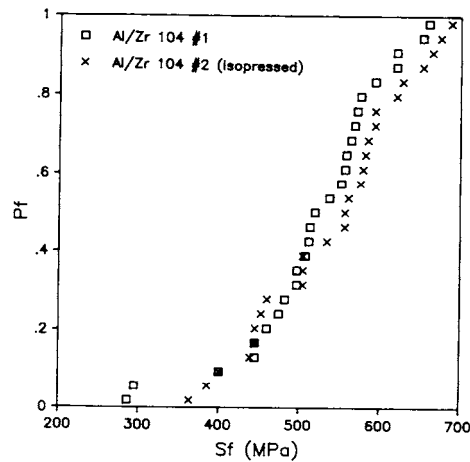


Fig. 6. Plot of probability of failure (P_f) vs stress at failure (S_f) for composite samples 104-1 and 104-2.

observed to contain agglomerates of zirconia or alumina. The introduction of a settling step prior to the forming step may remove such agglomerates along with any dust (also a possible source of SiO₂ contamination).

The toughness values (K_{Ic}) calculated⁶ for indentations performed on composite samples were between 3.5 and 4.0 MPa · m^{1/2}. Indents on both composite and alumina samples fired at 1400°C had equivalent indent dimensions.

Summary

Green bodies of composite and pure alumina samples were prepared from concentrated slurries. Sintered composite samples, while slightly lower in density

than pure alumina samples, exhibited higher room-temperature bending strengths, with strengths approaching 700 MPa. Strength-limiting defects present in the composite appear to be agglomerates of both powders and a glass phase (SiO_2 and MgO).

Acknowledgments

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