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DISCLAIMER

FABRICATION AND CHARACTERIZATION OF OXIDE FIBROUS MONOLITHS PRODUCED BY COEXTRUSION

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ABSTRACT

Unidirectional fibrous monoliths (FMs) based on dense, strong $ZrSiO_4$ cells that were surrounded by a porous, weaker $ZrSiO_4$ cell-boundary phase were fabricated. A duplex filament was coextruded, sectioned, bundled, and the resulting bundle was extruded to form a new filament. This filament was cut and packed into plate and bar dies to produce FM test specimens. Four-point flexural tests were conducted on the cell material, cell-boundary material, and FMs. After testing, fracture surfaces and cross sections were examined by scanning electron microscopy. The FMs exhibited graceful failure in flexural testing, and the fracture surfaces exhibited clear evidence of crack deflection and delamination.

INTRODUCTION

A fibrous monolith (FM) is a composite ceramic that contains a strong cellular phase surrounded by a phase that is designed to dissipate energy during fracture. FMs, which are produced from powders, retain some load after the peak load and thus fail gracefully. They constitute a low-cost alternative to conventional continuous-fiber ceramic composites [1-5].

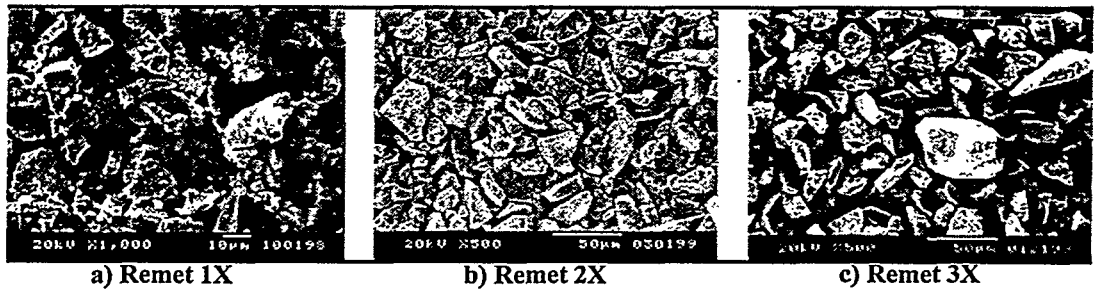
FM structures can be produced from many materials systems. Commercial products available from Advanced Ceramics Research (Tucson, AZ) include Si_3N_4/BN, SiC/graphite, various carbides and borides, and cermets [6]. To produce an FM structure, hot pressing is generally used to densify the materials [3-5]. The current focus is on oxide FMs that can be sintered at atmospheric pressure; use of sintering reduces costs substantially and allows greater freedom in design.

Cell materials of interest are Al_2O_3, mullite, yttrium aluminum garnet, and $ZrSiO_4$. Each of these materials exhibits good high-temperature properties. Through doping and control of powder particle size, these materials can be processed over a range of densities and strengths [7]. The FMs that are being produced contain a porous

boundary phase that surrounds strong, dense cells[8]. $ZrSiO_4$ was chosen for the first set of FMs because $ZrSiO_4$ powders are readily available and require little secondary processing. The initial goal was to produce $ZrSiO_4$ samples over a range of densities and strengths and then to fabricate duplex structures with matched shrinkages during sintering and thermal contraction during cooling. Once suitable powders and firing schedules had been identified, $ZrSiO_4/ZrSiO_4$ FMs were fabricated and their microstructures and mechanical properties were characterized.

EXPERIMENTAL PROCEDURES

$ZrSiO_4$ powders were obtained from Alfa Aesar (Ward Hill, MA) and Remet Corporation (Utica, NY). The Alfa Aesar powder was used for the dense cells, and the Remet powder was used for the porous cell boundary. The as-received Alfa powder had an average particle size of 1.0 μm. After ball-milling for 72 h in isopropyl alcohol, the powder had an average particle size of ≈0.5 μm. Remet flour-grade powder was first processed by a sedimentation technique to remove the finest particles. Three Remet powders were classified by sedimentation once, twice, or thrice; the resultant powders are designated 1X, 2X, and 3X. Representative scanning electron photomicrographs of these powders are shown in Fig. 1. The average particle sizes for these powder were ≈13.5, 22, and 29 μm; the principal difference between the three powders is the fraction of fines that remained after settling.



a) Remet 1X b) Remet 2X c) Remet 3X

Fig. 1. $ZrSiO_4$ powders after classification by settling.

The first FMs that were produced consisted of Alfa zircon as the cell and Remet 1X as the cell boundary. Each powder was mixed with organics and vibratory-milled for 24 h; formulation details are provided in Ref. 7. The mixtures were de-aired and tape cast to a thickness of ≈0.6 mm and dried for 24 h. Dried tapes were stripped, compacted, and placed in containers. The resultant plastic masses were mixed in a Brabender high-shear mixer (South Hackensack, NJ) to ensure homogeneity. After the Alfa $ZrSiO_4$ and Remet 1X $ZrSiO_4$ masses were mixed, they were coextruded. Each plastic mass was fed into a separate extruder hopper and forced into a coextrusion die to produce an initial duplex filament (Fig. 2).

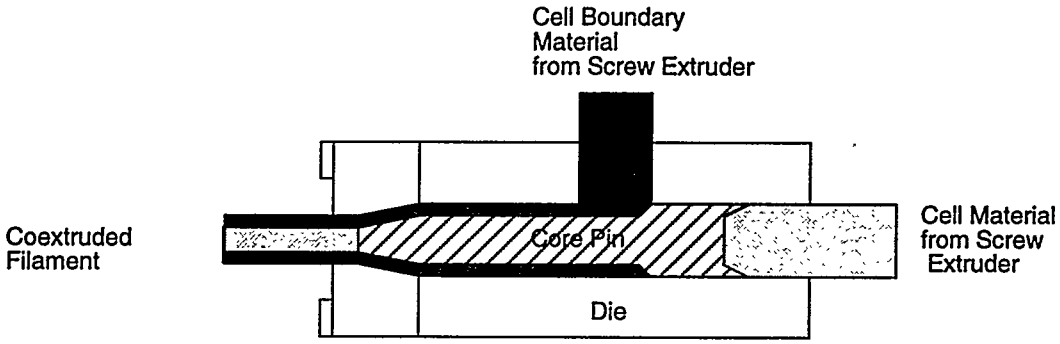


Fig. 2. Schematic diagram of coextrusion process.

The initial filaments were dried for several days then cut into 10-cm-long sections and bundled. The filament bundles were placed in a ram extrusion die and extruded to a final diameter of 4.8 mm (Fig. 3).

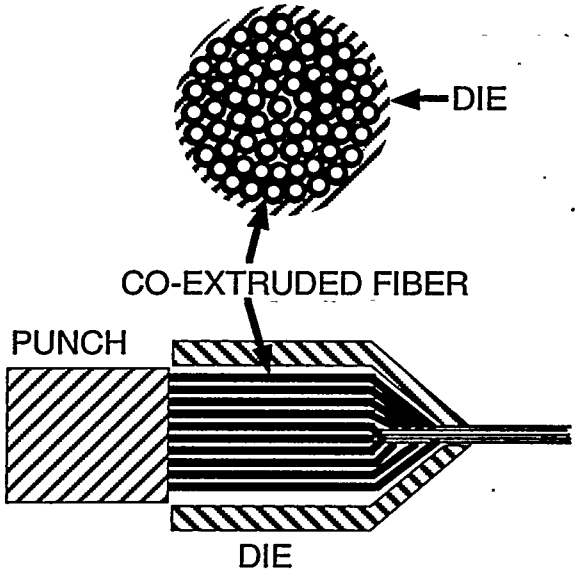


Fig. 3. Schematic diagram showing bundle of coextruded filaments and subsequent ram extrusion to form filaments for FM fabrication.

The resultant multifilaments were cut into 5-cm-long sections and pressed in a bar die at a pressure of ≈100 MPa. Organics were removed by heating in flowing N_2. Each bar was heated to 140°C at 50°C/h and held for 0.1 h. After the hold, each bar was heated to 500°C at 5°C/h, held for 6 h, and then cooled to room temperature at 50°C/h. After binder burnout, the bars were sintered in air at 1550°C for 3 h.

The fired FMs were cut to dimensions of ≈ 45 x 5 x 3 mm for four-point flexural testing. Monolithic bars of Alfa and 1X Remet were fabricated for comparison; all monolithic bars were sintered at 1550°C for 3 h. [7]. The Alfa bars were ≈95% dense and the 1X Remet bars were ≈70% dense. The tensile surface of each bar was ground and polished to a 1-μm finish. The testing fixture had an inner span of 15 mm and an outer span of 40 mm. The samples were loaded in an Instron Model 4505 tester (Canton, MA). A computer connected to the Instron unit recorded load and displacement data.

Scanning electron microscopy (SEM) was conducted on several fracture surfaces and polished cross sections.

RESULTS AND DISCUSSION

The FM bars experienced ≈23 vol.% shrinkage between initial pressing and the fired state. Representative SEM photomicrographs of a fired FM bar are shown in Fig. 4.

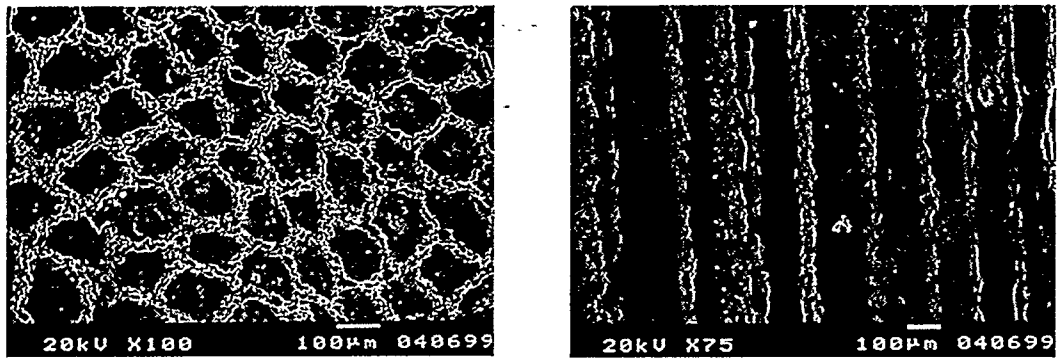


Fig. 4. SEM photomicrographs of transverse and longitudinal cross sections of $ZrSiO_4/ZrSiO_4$ FM bars.

The FM bars were ≈80 vol.% cell and 20 vol.% cell boundary. This is slightly higher than the ratio of 85 vol.% cell and 15 vol.% cell boundary that is generally observed for Si_3N_4/BN FMs [5]. The average cell size of the $ZrSiO_4/ZrSiO_4$ FMs was ≈150 μm.

The longitudinal cross section in Fig. 4 revealed good alignment of the individual filaments and relatively smooth interfaces. Shear instabilities during extrusion appear to have been minimal.

Four-point-flexure data for Alfa, Remet 1X, and FM bars are shown in Figs. 5 and 6. The Alfa $ZrSiO_4$ bars exhibited fast fracture at maximum stresses of ≈200 MPa. The 1X Remet $ZrSiO_4$ bars also exhibited fast fracture, but the maximum stresses were only ≈30 MPa. Unlike the Alfa and Remet 1X $ZrSiO_4$ bars, the FM bars exhibited graceful failure (Fig. 6). Nonlinearity was observed before the maximum load was reached, and some load-bearing capability was retained to large displacements. The average maximum stress was ≈100 MPa. Although the FM bars were weaker than the Alfa bars, their strains to failure were much higher. Tests on notched specimens are in progress.

SEM indicated that the unloading steps that were observed in the FM stress-vs.-displacement curves were probably caused by energy-dissipating events, such as crack delamination, crack deflection, and possibly limited cell pullout (Figs. 7 and 8). Figure 7 is a side-view photomicrograph of a fractured FM sample. The primary crack follows a tortuous path though the FM, making several 90° deviations through the cell-boundary phase before continuing through the FM. In the fracture surface shown in Fig. 8, delamination along the cell-boundary phase and crack deflection are evident.

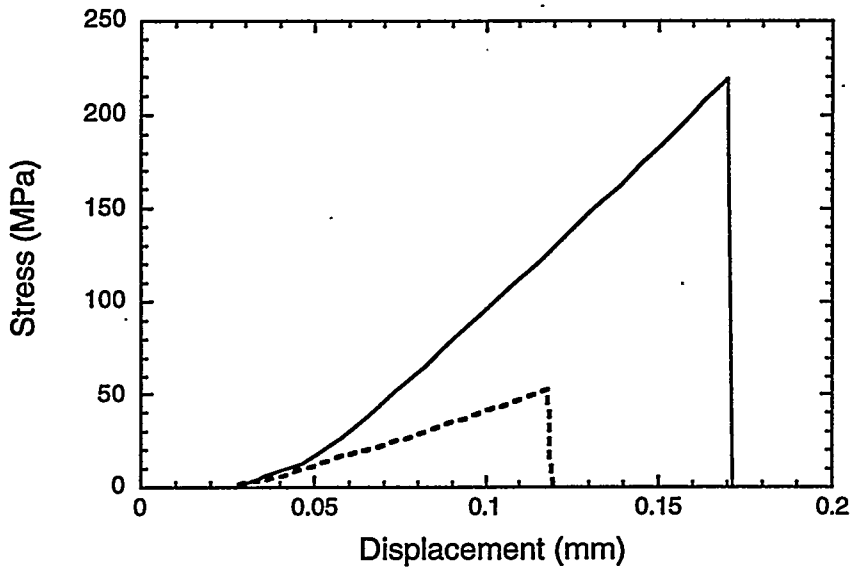


Fig. 5. Stress-vs.-displacement curves for representative Alfa $ZrSiO_4$ bars (solid line) and 1X Remet bars (dashed line).

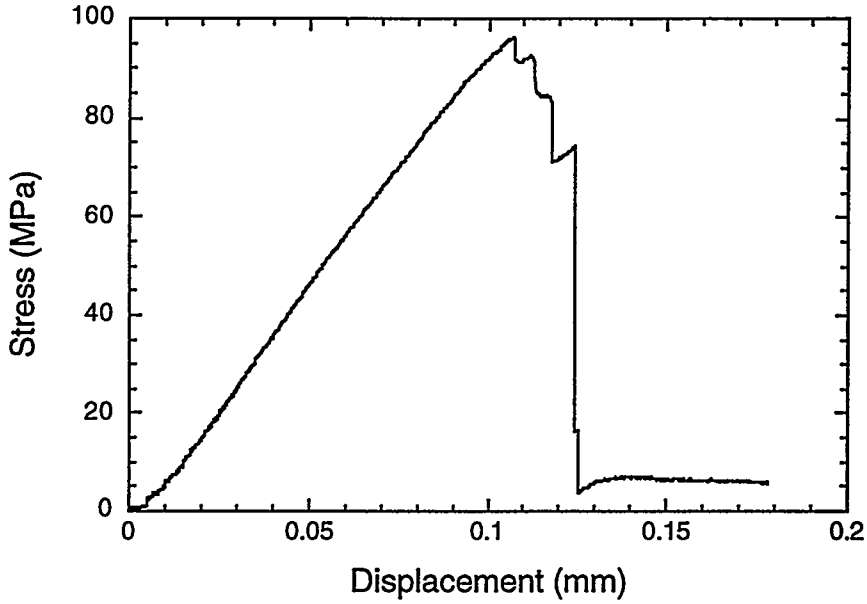


Fig. 6. Stress-vs.-displacement curves for representative FM bar.

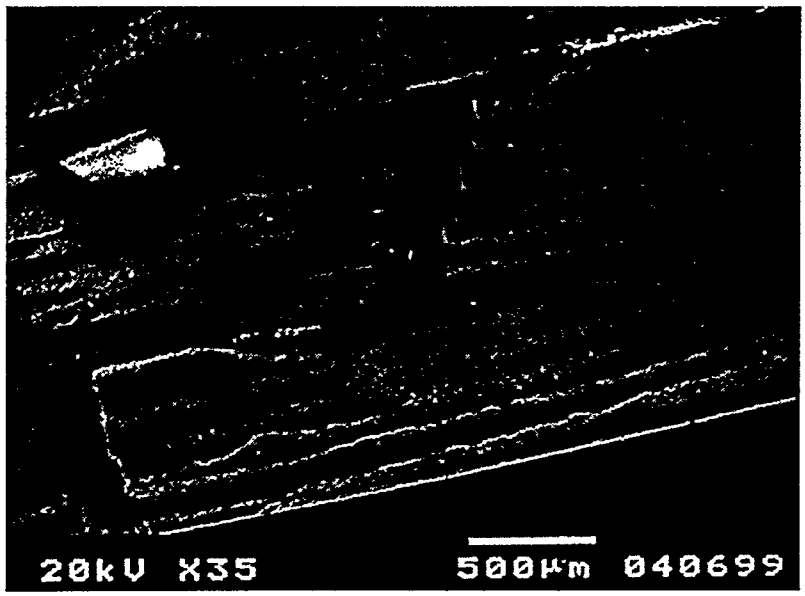


Fig. 7. SEM photomicrograph of crack through FM bar.

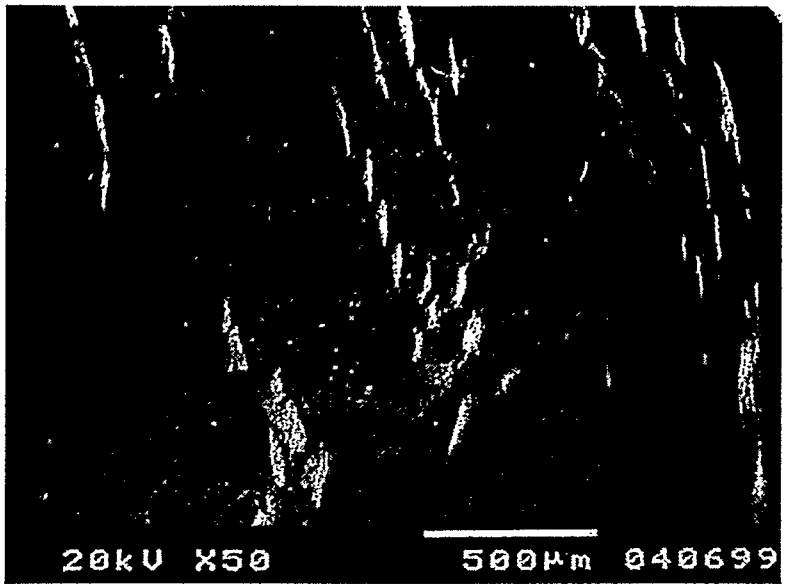


Fig. 8. SEM photomicrograph of FM fracture surface.

Current fabrication efforts are focused on strengthening the $ZrSiO_4$ cells and promoting more crack deflection through use of Remet powders 2X and 3X. Reduction in the concentration of fine $ZrSiO_4$ powder in the cell boundaries should further weaken the cell/boundary interfaces and promote additional delamination and deflection. Bars with controlled flaws for testing notch sensitivity are now being fabricated, and the extent of cell pullout is being quantified by SEM.

SUMMARY

$ZrSiO_4$-based fibrous monoliths (FMs) containing porous cell boundaries and dense cells were fabricated by extrusion and sintering. Bars of this material exhibited significant energy dissipation during fracture and retained some load to large displacements, but also exhibited ≈50% of the strength of monolithic dense $ZrSiO_4$ bars. The FM bars exhibited clear evidence of crack deflection and delamination.

The $ZrSiO_4$ FMs have served as prototypes for refining processing and characterization methods. Once optimal structures and properties have been obtained for the $ZrSiO_4$ FMs, work will shift to oxides that exhibit better promise for practical structural applications, such as mullite and Al_2O_3.

ACKNOWLEDGMENTS

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