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ABSTRACT

Most work on ceramic fibrous monoliths (FMs) has focused on the Si_3N_4/BN system. In an effort to develop oxidation-resistant FMs, several oxide systems have recently been examined. Zirconia-toughened alumina and alumina/mullite appear to be good candidates for the cell phase of FMs. These composites offer higher strength and toughness than pure alumina and good high-temperature stability. By combining these oxides, possibly with a weaker high-temperature oxide as the cell-boundary phase, it should be possible to produce a strong, resilient FM that exhibits graceful failure. Several material combinations have been examined. Results on FM fabrication and microstructural development are presented.

INTRODUCTION

The best commercially available ceramic fibrous monoliths (FMs) are based on Si_3N_4/BN [1-3]. These materials take advantage of the high strength and toughness of Si_3N_4, while the weak BN provides a path for crack deflection [3-7]. To achieve high density, these materials require hot pressing at temperatures of $\approx 1700°C$ in an inert atmosphere. Although Si_3N_4/BN FMs exhibit good mechanical properties, they suffer from oxidation problems. To avoid the problem of oxidation, use of oxide materials in FMs has been proposed [8]. As an added advantage, these materials would possibly be sinterable in air, thus avoiding the hot-pressing process. The main limitation of oxides is that their strength, especially at elevated temperatures, is generally significantly less than that of Si_3N_4.

In recent studies, large residual compressive stresses have been shown to increase the strength of oxide-based laminates [9,10]. The residual stresses are caused by differences between the coefficients of thermal expansion (CTEs) of the various layers. Green et al. [9] made use of a compressive layer just below the surface to arrest crack growth in glass. Rao et al. [10] demonstrated that a system of Al_2O_3 layers plus mullite/15 vol.% Al_2O_3 layers, with a thickness ratio of

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≈16:1, exhibits a threshold strength that is based on cracks being arrested at each compressive layer. These results depend on very large, ≈1 GPa, residual stresses.

Residual stresses in the layers can be estimated by solving the following equations, wherein ε is the strain that is the result of the differences in CTE.

$$\sigma_1 = \varepsilon * \frac{E_1}{1-v_1} * \left[1 + \frac{t_1}{t_2} * \frac{E_1/1-v_1}{E_2/1-v_2} \right]^{-1}$$

$$\sigma_2 = -\sigma_1 * \frac{t_1}{t_2}$$

$$\varepsilon = (\alpha_1 - \alpha_2) * \Delta T$$

In these equations, σ is stress, E is Young's modulus, v is Poisson's ratio, t is the layer thickness, α is the thermal expansion coefficient, T is temperature, and the subscripts refer to the two respective constituents in the laminate [10].

Based on these equations, the two keys to generating high residual compressive stress are the thicknesses and differences in CTE. Thick layers of the higher-CTE material minimize the residual tensile stress, and thin layers of the lower-CTE material maximize the residual compressive stress.

Two basic approaches can be used in applying residual-stress techniques to FMs. The first is to use a material with a higher CTE for the cell-boundary phase and a material with a lower CTE for the cell phase. This approach would produce a cell phase that is in compression, which would increase its strength, and a cell-boundary phase that is in tension, which could increase its ability to deflect cracks from the load-bearing cell phase. The second approach involves a three-phase system, which consists of a weak cell boundary and a duplex cell. The cell would consist of a core of a higher-CTE material and a sheath of a lower-CTE material. The cell boundary would be porous, and thus promote crack deflection [11-13].

Our work examines the properties of alumina-based materials for the development of oxide/oxide FMs. These FMs have been fabricated by the coextrusion methods that were used to produce zircon-based FMs [13]. We focused initially on producing a three-phase FM: porous cell boundary plus a duplex cell that features an outer layer in compression.

EXPERIMENTAL PROCEDURES

Alumina-based composites were selected because have been thoroughly studied and offer a good combination of properties [14]. We decided to use ZrO_2 and mullite to tailor CTEs. High-purity Al_2O_3 with 0.05 wt.% MgO (Malakoff Industries Inc., powder RC-HP DBM), 3-mol%-Y_2O_3 stabilized ZrO_2 (Tosoh

Corp., powder TZ3Y), and nominally stoichiometric mullite (Kyoritsu Ceramic Materials Co. Ltd., powder KM101) were used. Composite powders were prepared by ball-milling various compositions for 24 h in isopropanol. The powders were then dried and screened through a 325-mesh sieve.

To evaluate sintering response, 1 g pellets were pressed uniaxially and sintered in air for various times at various temperatures. Larger bars were also prepared for CTE measurements, which were conducted in air to 1300°C in a Theta Industries, Inc., Dilatronic II dilatometer.

From sintering data, microstructural observations, CTE data, and the equations shown above to estimate the residual stress, alumina with 10 vol.% TZ3Y and 50 vol.% alumina/50 vol.% mullite were selected as the materials for core and sheath, respectively, of a duplex FM cell. Tapes of these materials were prepared by techniques that have been discussed elsewhere [13,15].

The tapes were then stacked, pressed, heated in air to remove binder, and sintered in air at temperatures of 1500–1600°C for 3 h. To develop the technology for fabricating three-phase FMs, we used a dip-coating procedure to coat duplex filaments and form the cell-boundary phase. An Al_2O_3/mullite plastic mass was extruded to produce the filament that was used to evaluate the dip-coating procedure. Mullite, which is more difficult to sinter than Al_2O_3/mullite was selected as the cell-boundary phase. A mullite slurry, similar to that used for tape casting, was prepared. Filaments were then coated, dried, sectioned, and stacked, and then pressed uniaxially to form green bars. The bars were subjected to binder burnout and were then sintered in air at 1550°C for 3 h.

RESULTS AND DISCUSSION

Additions of ZrO_2 to Al_2O_3 increase CTEs, whereas additions of mullite decrease CTEs. Representative residual stress (σ) values that would be expected in a sandwich structure with a higher-CTE core and a lower-CTE sheath, calculated by a rule of mixtures, are shown in Table 1; in this table ZTA(10%) = 90 vol.% Al_2O_3/10 vol.% ZrO_2 and AM(50%) = 50 vol.% Al_2O_3/50 vol.% mullite.

Table 1. Calculated residual stresses for Al_2O_3-based laminates.

Core/sheath	Volume fraction	Core σ (MPa)	Sheath σ (MPa)
Al_2O_3/mullite	90/10	100	−900
	80/20	220	−870
	70/30	350	−820
Al_2O_3/AM(50%)	90/10	90	−810
	80/20	190	−740
	70/30	290	−670
ZTA(10%)/AM(50%)	90/10	100	−920
	80/20	210	−850
	70/30	330	−760

The calculated residual stresses indicate a need to maximize within the FM cell the volume fraction of the phase that is in tension. For the system that we selected for the duplex cell in the three-phase FMs, i.e., a core of ZTA(10%) and an outer sheath of MA(50%), the tensile residual stresses become quite large for sheath volume fractions that are significantly >10%. These calculations have been supported recently by direct measurements of residual stresses in Al_2O_3/ZrO_2 laminates in which residual stresses >500 MPa were measured [16].

Most duplex FMs that have been fabricated contain ≈20 vol.% or more of the cell boundary [1-8]. (The cell boundary in a duplex FM closely coincides with the outer cell sheath in a three-phase FM.) We believe that the volume fraction of the sheath in our current FMs can be reduced by 50%, but we have not yet succeeded in doing so.

Because the three-phase FMs are to be sintered at atmospheric pressure, in addition to producing specific ratios of phases, one must match the shrinkages of the phases during firing. Basic sintering data are shown in Fig. 1, which reveals that ZrO$_2$ additions were much more effective than mullite additions in promoting densification of Al_2O_3. Relatively good densities could be obtained for both ZTA(10%) and AM(50%) by sintering in air at ≈1550–1600°C for 3 h. The average grain size of each composite was ≈ 1 μm (Fig. 2).

To ensure compatibility, laminated structures of ZTA(10%)/AM(50%) were produced by tape casting and sintering at 1550°C. No significant cracking and sharp interfaces were observed for laminates with 70/30, 80/20, and 90/10 ZTA(10%)/AM(50%) volume ratios.
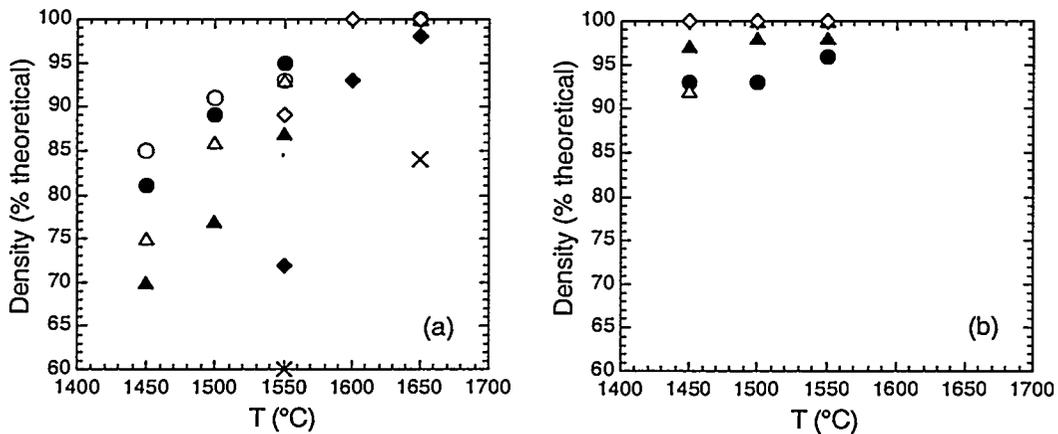

Figure 1. Densities of composite specimens sintered in air for 3 h at various temperatures: (a) Al_2O_3/mullite and (b) Al_2O_3/ZrO_2; x = mullite, O = 2% addition, ● = 5% addition, △ = 10% addition, ▲ = 20% addition, ✧ = 50% addition, and ◆ = 80% addition.
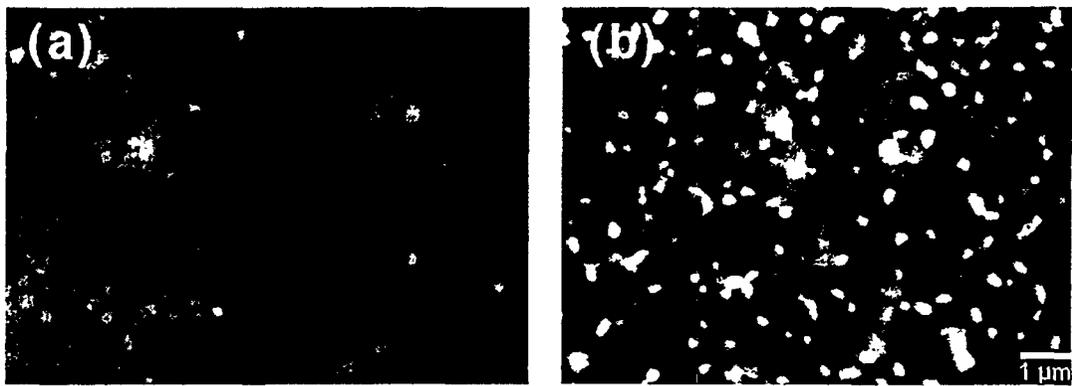
Figure 2. Scanning electron microscopy photomicrographs of thermally etched (a) MA(50%) and (b) ZTA(10%) specimens that were sintered in air at 1550°C for 3 h.

We have assumed that extrusion of a duplex oxide filament will not present a problem. We have had, for example, considerable success extruding duplex $ZrSiO_4/ZrSiO_4$ filaments [13,17]. To allow us to focus on the dip-coating procedure being developed to create the mullite cell boundary, we extruded monofilaments of AM(50%), which would be the material in contact with the cell boundary in the three-phase FM. The dip-coating formulation was a diluted version of that used for extrusion; its constituents are listed in Table 2. The solvent was an organic azeotrope of moderate vapor pressure. The binder was a thermosetting acrylic polymer, with a butyl benzyl phthalate as the plasticizer.

Green extruded filaments were dipped into the mullite slurry and allowed to dry in air. Subsequent re-dipping produced coatings of various thicknesses. After the filaments were essentially dry, they were sectioned, laid up unidirectionally, pressed in a bar die, and heat treated [13]. To date, air drying has produced filaments that are slightly brittle. Consequently, microfracture of these filaments generally occurred during pressing. The binder was burned out of the green bars in flowing O_2 of $\approx$4 torr total pressure. These FM bars were then sintered in air at 1600°C for 3 h.

Table 2. Approximate formulation for dip-coating MA(50%) filaments.

Constituent	Mass (g)
Mullite powder	50
78% xylene/22% butanol	30
Monsanto AT-51 binder	30
Rohm & Haas S-160 plasticizer	2-3
Fishoil	1-3

5

Specimens were cut, polished, thermally etched in air at 1500°C for 1 h, and examined by optical microscopy and SEM (Fig. 3). The mullite near the AM(50%) cell appeared to be denser than the other mullite within the cell boundary, but not as dense as the cell phase (Fig. 4). Chemical analysis of this area indicated that it had the same composition as that of the mullite further from the AM(50%); no Al_2O_3 was present. The nearby cell phase may have promoted densification through some sort of cooperative shrinkage.
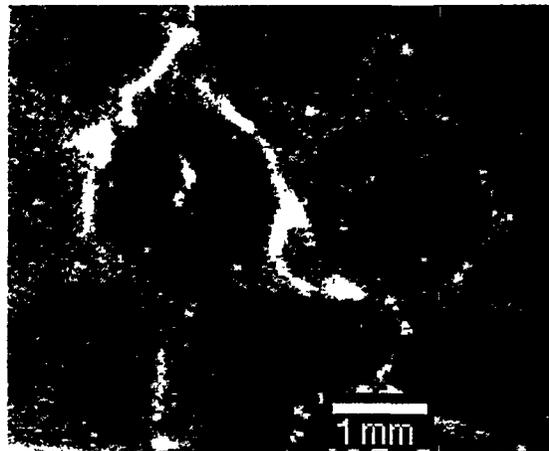

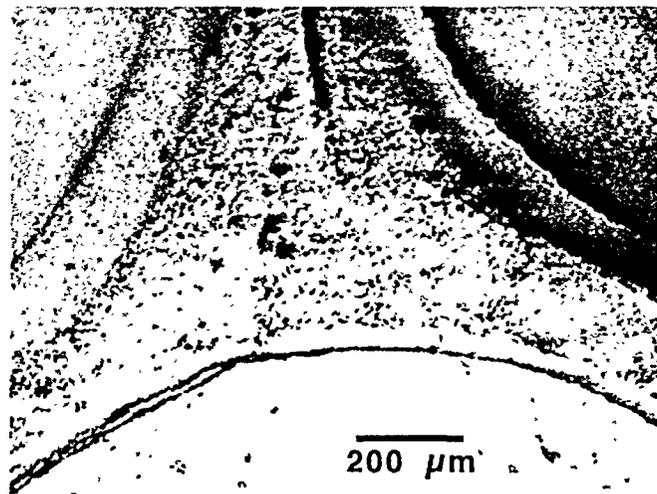Figure 3. Optical photomicrograph showing prototype Al_2O_3/mullite FM.

Figure 4. Optical photomicrograph of mullite cell boundary and AM(50%) cell, showing enhanced densification of mullite near the cell.

The bonding between the cell and cell boundary appeared to be only partial. Mechanical testing is required to determine how successful the current approach will prove to be. Future work on this FM system will focus on producing duplex filaments with a ZTA(10%) core that is ≈90% of the total cell volume, reducing the brittleness of the filaments, reducing the thickness of the cell boundary, and characterizing the microstructures and mechanical properties of the FMs.

CONCLUSIONS

Three-phase FM structures, based on Al_2O_3 modified with ZrO_2 or mullite to create favorable residual stresses, are being developed. Calculations indicate that compressive stresses can exceed 500 MPa. Mullite is being used as a porous cell-boundary phase that is designed to promote crack deflection and delamination. Prototype FMs have been produced by sintering of coated filaments, but mechanical properties have not yet been studied.

ACKNOWLEDGMENTS

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