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ABSTRACT

Fibrous monoliths (FMs) based on mullite combined with Al_2O_3 and Y_2O_3-stabilized ZrO_2 have been produced. These FMs incorporate duplex cells in which compressive residual stresses were engineered into the surfaces of the cells. The residual stresses should increase average cell strength, which may allow them to achieve mechanical properties comparable to those of Si_3N_4/BN FMs. The expected residual stresses have been calculated, and data on sintering and thermal expansion have been gathered. Prototype FMs were produced and their microstructures examined.

INTRODUCTION

Ceramic fibrous monoliths (FMs) consist of a strong cellular phase surrounded by a weaker phase that is designed to dissipate energy during fracture. FMs are produced in-situ from powders, and thus have inherent cost advantages over fiber-reinforced ceramic composites. Moreover, FMs fail gracefully in flexure and can support significant loads to large strains [1-9].

FMs can be produced from many materials systems, including nitrides, carbides, borides, and oxides [7]. Commercial products available through Advanced Ceramics Research (Tucson, AZ) include Si_3N_4/BN, SiC/graphite, various carbides and borides, and cermets [7]. The best room-temperature mechanical properties to date (fracture strengths to $\approx$700 MPa and work-of-fracture values to $\approx$9 kJ/m^2) have been obtained from FMs in which BN is the cell-boundary phase [6,7]. These FMs offer promise for exceptional performance at elevated temperature, also, although an effective coating is required for long-term service in oxidizing environments.

Oxide FMs have generally contained porous cell boundaries to promote debonding and crack deflection during fracture [10]. Recently developed, porous-matrix, oxide-fiber composites and multilayers have exhibited excellent mechanical properties [11,12], and the expectation is that analogous FMs can be fabricated. FMs produced from oxides such as Al_2O_3 and $ZrSiO_4$ have been somewhat successful: they fail gracefully, but generally at stresses of <150 MPa [6,10].

In an attempt to produce stronger and more creep-resistant oxide FMs, the focus is now on mullite-based composites. Several oxides composites that contain regions of high compressive residual stress have exhibited remarkable fracture properties [13-15]. To tailor the residual stresses in the cell, promote densification during sintering, and improve creep resistance at elevated temperature, 50 vol.% mullite/50 vol.% Al_2O_3 for the sheath of the cell and 50 vol.% mullite/50 vol.% Y_2O_3-stabilized ZrO_2 (YSZ) for the core of the cell were selected. In some of the FMs, we have incorporated a porous mullite matrix to promote crack deflection [11,12]. Work to date, which includes calculations of expected residual stresses, basic sintering and thermal-expansion studies, fabrication of prototype FMs, and examination of microstructural development will be summarized.

RESIDUAL-STRESS ESTIMATIONS

FMs are assembled from round, coextruded filaments. Commercial FMs are hot-pressed, resulting in a cell with a flattened hexagonal cross section [4]. The oxide FMs produced in this study are sintered rather than hot-pressed, which reduces the distortion (Fig. 1); the cell cross section can be approximated reasonably well by a circle.

Residual stresses that arise from differences in thermal expansion between constituents have been calculated for cylindrical composites [16,17]. It is assumed that, if present, the porous matrix has little influence on residual stresses, and therefore that the stresses arise from differential contraction between the cell core and sheath with cooling. The temperature difference (ΔT) is assumed to be $\approx$1200°C. The data required to estimate residual stresses are shown in Table I [18].

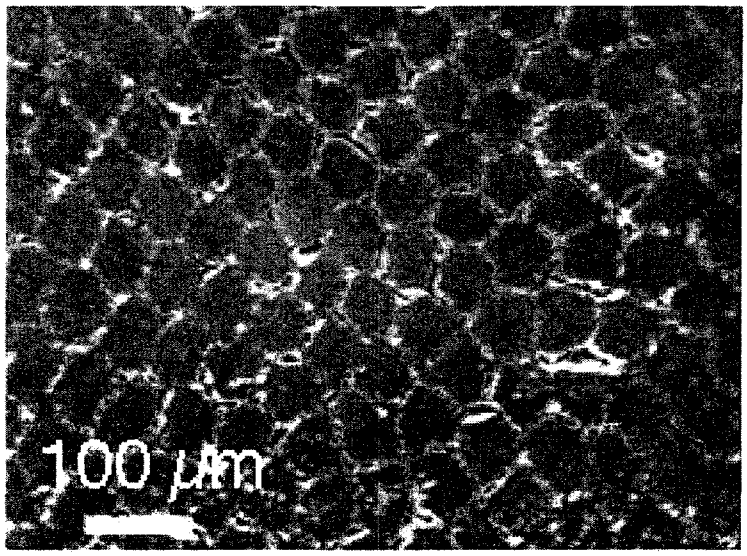

Fig. 1. SEM photomicrograph of transverse cross section of typical $ZrSiO_4$-based FM.

Table I. Coefficient of thermal expansion (α), Young's modulus (E), and Poisson's ratio (ν) for FM constituents

Oxide	α ($°C^{-1}$)	E (GPa)	ν
Mullite	5.9×10^{-6}	145	0.25
Al_2O_3	9.2×10^{-6}	380	0.26
YSZ	11.6×10^{-6}	205	0.23

The configuration for the residual-stress calculations is shown in Fig. 2. Values for the axial stress at the surface of the duplex cell ($\sigma_{z,2}$), the tangential stress at the surface of the sheath ($\sigma_{t,1}$), and the tangential stress at the outer sheath surface ($\sigma_{t,2}$) can be been calculated from:

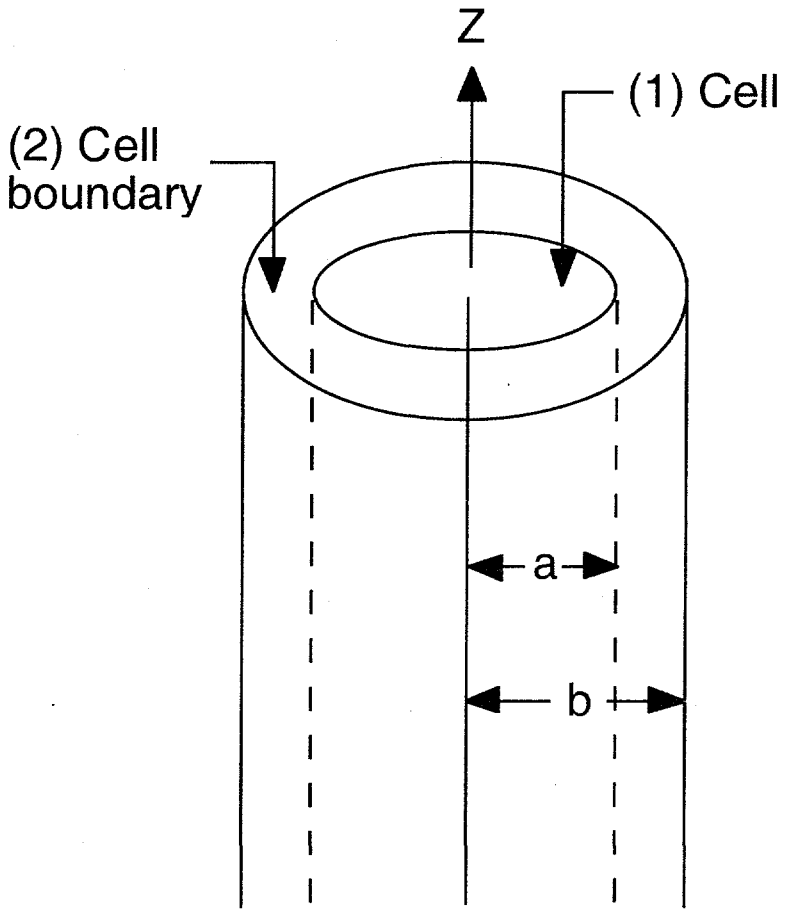

Fig. 2. Schematic diagram of composite cylinder.

$$P = \left(\frac{\beta_2 + \beta_3}{\beta_1\beta_3 - 2\beta_2^2} \right)(\alpha_2 - \alpha_1)\Delta T \quad ,$$

$$\sigma_{t,1} = -\frac{1 + V_1}{V_2} P \quad ,$$

$$\sigma_{t,2} = -\frac{2V_1}{V_2} P$$

$$\beta_1 = \frac{1 - \upsilon_1}{E_1} + \frac{\upsilon_2}{E_2} + \frac{1 + V_2}{V_1 E_2} \quad ,$$

$$\beta_2 = \frac{\upsilon_1}{E_1} + \frac{V_1\upsilon_2}{V_2 E_2} \quad ,$$

$$\beta_3 = \frac{1}{E_1} + \frac{V_1}{V_2 E_2} \quad ,$$

$$\sigma_{z,2} = -\frac{V_1}{V_2}\left(\frac{\beta_1}{\beta_2} \frac{\beta_2 + \beta_3}{\beta_1\beta_3 - 2\beta_2^2} - \frac{1}{\beta_2} \right)(\alpha_2 - \alpha_1)\Delta T \quad ,$$

where V is the volume fraction, the subscript 1 refers to the core and the subscript 2 refers to the sheath, and the other terms are defined in Table I [17].

Residual-stress values were calculated for three volume fractions of core/sheath, with the core being 50 vol.% mullite/50 vol.% YSZ and the sheath being 50 vol.% mullite /50 vol.% Al_2O_3 (Table II). The residual stresses are a strong function of the core/sheath volume fraction. The goal is to fabricate a duplex cell with a core/sheath ratio of ≈80/20, which has been shown to be approximately optimal for Si_3N_4/BN FMs [6]. Ratios of ≈70/30 have been obtained in $ZrSiO_4$-and Al_2O_3-based FMs [10,19].

Table II. Calculated residual stresses in duplex FM cell; negative values are compressive

Core/sheath ratio	$\sigma_{z,2}$ (GPa)	$\sigma_{t,1}$ (GPa)	$\sigma_{t,2}$ (GPa)
90/10	–6.7	–7.1	–2.0
80/20	–1.7	–1.9	0.5
70/30	–0.8	–1.0	1.8

EXPERIMENTAL PROCEDURES

Powders were obtained from commercial sources: KM101 mullite, from Kyoritsu Ceramic Materials Co. (Nagoya, Japan); RC-HP-DBM Al_2O_3, from Malakoff Industries (Malakoff, TX); and TZ-3Y Y_2O_3-stabilized ZrO_2 (YSZ), from Tosoh Ceramics (Bound Brook, NJ). The average particle sizes were 0.8 μm for the mullite, 0.5 μm for the Al_2O_3, and 0.3 μm for the YSZ.

The powders were mixed with organics (Table III) and vibratory-milled for 24 h. The resultant mixtures were de-aired, tape-cast to a thickness of ≈0.6 mm, and partially dried for 2 h. The tapes were then stripped, compacted, and mixed in a Brabender high-shear mixer (South Hackensack, NJ) to ensure homogeneity. Each plastic mass was then fed into a separate extruder hopper and forced into a coextrusion die to produce an initial duplex filament [10].

Segments of some of the duplex filaments were dip-coated with a mullite slurry [19]. The mullite powder was preheated in air at 1400°C for ≈6 h to reduce its surface area slightly. The slurry composition was similar to that used for extrusion, but the solvent and binder concentrations were increased because lower viscosity and added shrinkage during firing were required. Coated filaments were suspended and dried overnight in a xylene/butanol-containing atmosphere.

Dried filaments, either coated or uncoated, were sectioned, stacked, and pressed into bars, which were then heat-treated in air. For comparison, a few multilayer specimens were fabricated from tape castings and fired along with the FMs. Organics were removed by heating to 600°C at 6°C/h and holding for 6 h. After binder burnout, the bars were sintered in air at ≈1600°C for 3 h. The FM filaments were not bundled and extruded a second time, as has been reported previously [10]. Thus, the average final cell size was ≈2 mm, as opposed to the 100–150 μm cells that are generally observed. The individual layers in the multilayers were 100–150 μm thick.

The fired FMs were too irregularly shaped to allow reliable mechanical testing; a few were fractured by impact so that their surfaces could be examined by scanning electron microscopy (SEM). Cross sections were also mounted, polished, and examined.

Table III. Composition of plastic mixes used for coextrusion of duplex cell in mullite-based FMs

Constituent	Mullite/YSZ (g)	Mullite/Al_2O_3 (g)
Ceramic powders	200	200
Rohm & Haas AT-51 binder	78	78
78 wt.% xylene/22 wt.% butanol	12	12
Monsanto S-160 plasticizer	14	14
ICI Americas Solsperse 9000	10	10
Carbon powder		1

RESULTS AND DISCUSSION

The performance of commercial Si_3N_4/BN FMs at room and elevated temperatures is excellent, so long as environmentally induced degradation does not occur [4-8]. Development of oxidation-resistant FMs that can match this performance is a daunting challenge because, in general, oxides are weaker at all temperatures [20]. Room-temperature strength can perhaps be improved by engineering favorable residual stresses into oxide FMs [13-15]. Elevated-temperature strength must be addressed by selection of creep-resistant oxides. Within this program, focus has settled on mullite and yttrium aluminum garnet (YAG) systems. The YAG work is being conducted at the University of Illinois at Urbana-Champaign (see, for example, [21]); progress in the mullite work will be reported here.

Pure mullite is difficult to sinter completely unless novel techniques or temperatures >1600°C are applied [22-24]. Additions of Al_2O_3 or YSZ improve mullite's sintering response significantly. For the first set of prototype FMs, 50 vol.% alloys were selected because of expectations of minimal grain growth during sintering and good creep resistance in service. As shown in Table II, these alloys in a composite structure should establish residual stresses greater than 1 GPa.

The multilayers and duplex FMs could be fired without cracking. The FMs in which a porous mullite matrix was incorporated exhibited significant cracking (Fig. 3).

Although only a few rudimentary FMs that contained a mullite matrix were processed, it is likely that the porous mullite (Fig. 3b) cannot provide sufficient constraint to prevent the cell from cracking because of the large stresses generated during cooling. It appears that the thermal expansions of the constituents of the duplex cell will have to be better matched so that the maximum residual stresses are

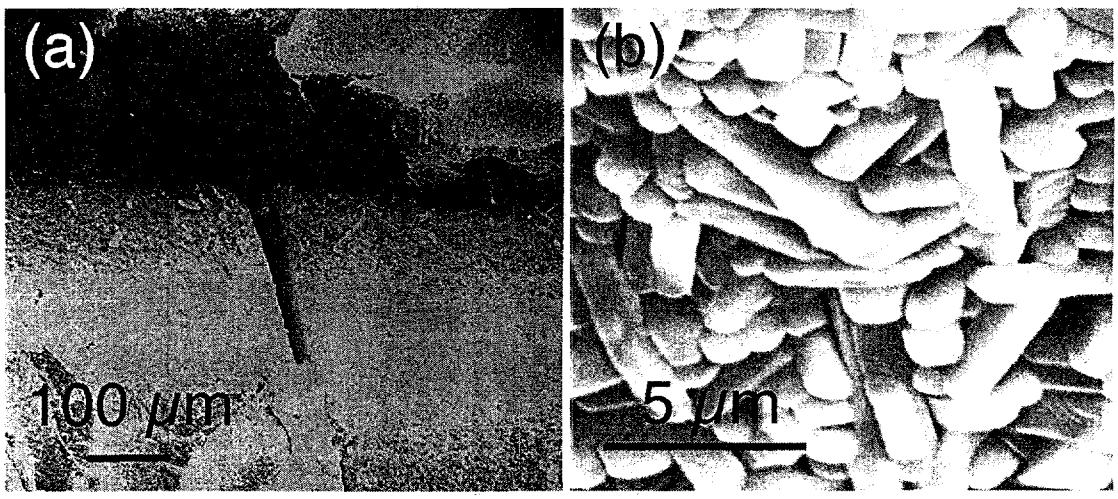

Fig. 3. SEM photomicrographs of FM containing porous mullite matrix: (a) cracks induced by heat treatment (matrix at top, duplex filament at bottom of image) and (b) mullite matrix.

lower or that the matrix phase will have to be eliminated. For a dual-phase FM in which the cell-boundary phase is under compression it is not clear that the residual-stress state that are so effective in improving the fracture properties of multilayers will be as effective. No mechanical tests have been conducted on any of these new FMs.

SEM examinations revealed that the composites without the porous mullite matrix sintered together well. The mullite/Al_2O_3 phase was >95% dense and the mullite/YSZ phase was >99% dense. The average mullite grain size was ≈2 μm in all locations; that of the Al_2O_3 was ≈5 μm; and that of the YSZ was ≈1 μm (Fig. 4). The interfaces between the cell and cell boundary or between layers in the multilayers were sharp and well bonded (Fig. 5). Based on sintering and microstructural considerations only, these mullite-based FMs appear to exhibit promise. However, substantially more work is required before an informed assessment can be made.

Future work will focus on fabrication of dense FM billets. The emphasis will be on FMs without a porous mullite matrix. Once FMs can be produced reliably and in quantity, mechanical testing will commence. Strength tests at >1000°C are of particular interest because the benefits of residual stresses are likely to be negligible.

SUMMARY

Mullite-based FMs, with or without a porous mullite matrix, were fabricated by coextrusion, lay-up, and sintering. FMs that contained the porous matrix exhibited significant cracking after heat treatment. FMs without the porous mullite were dense and exhibited sharp interfaces between the mullite/Al_2O_3 and mullite/YSZ regions. Only moderate grain growth occurred during sintering. Mechanical testing is pending; thus, how effective these FMs will be in structural applications is uncertain.

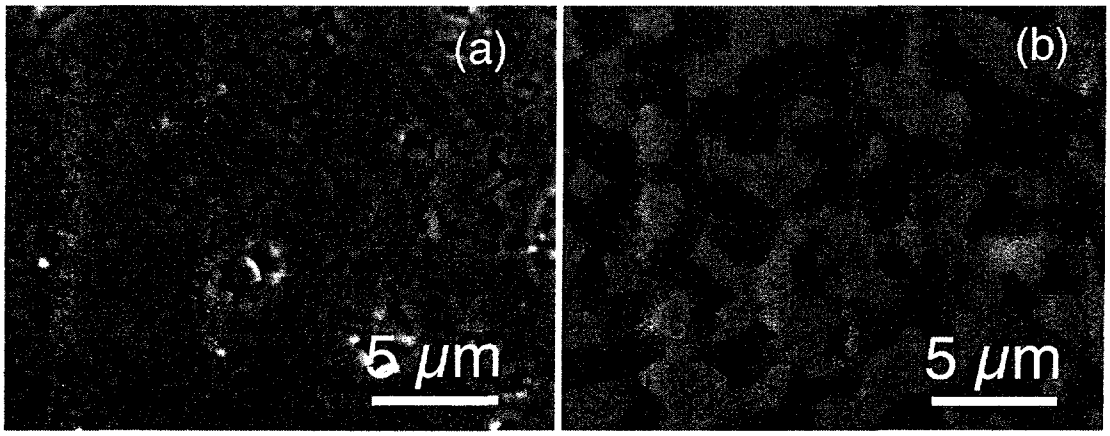

Fig. 4. SEM photomicrographs of (a) 50 vol.% mullite/50 vol.% Al_2O_3 phase and (b) 50 vol.% mullite/50 vol.% YSZ phase; the Al_2O_3 exhibits moderate grain growth.

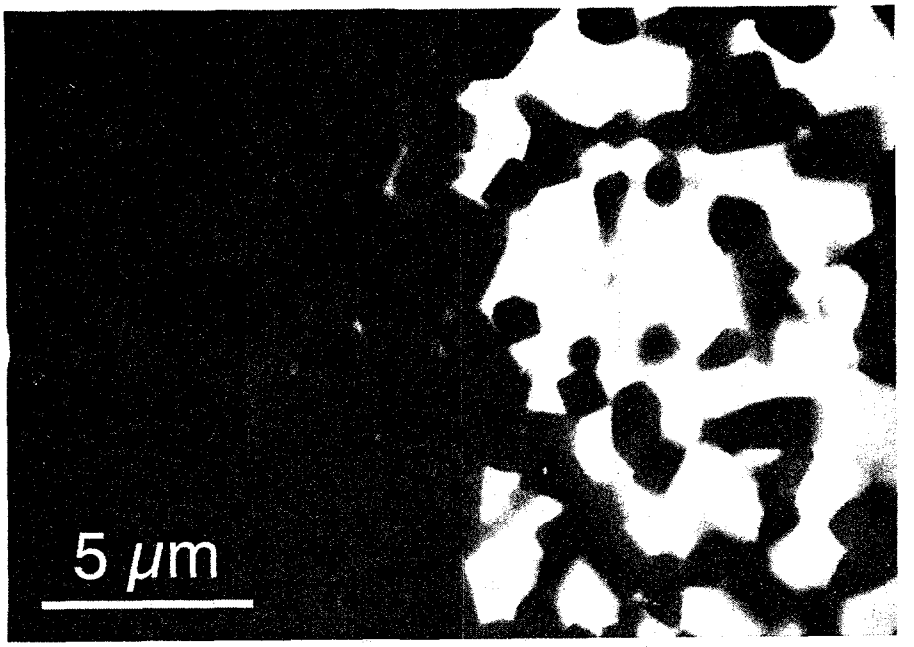

Fig. 45. Interface in multilayer between (right) 50 vol.% mullite/ 50 vol.% Al_2O_3 phase and (left) 50 vol.% mullite/50 vol.% YSZ phase; interface is sharp and free of defects.

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