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Damage tolerant oxide/oxide fiber laminate composites

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Abstract

Oxide-fiber/oxide-matrix composites were developed using non-infiltrated woven fiber layers between matrix-infiltrated fiber layers in order to achieve damage tolerant behavior. A fiber interface coating was not used. This technique enables damage tolerance in materials with strong fiber-matrix bonding and under oxidizing conditions. Fabrication of composites was carried out through a slurry infiltration technique. Slurries for fiber (Nextel™ 720, 3M) infiltration were prepared using a submicron α-Al_2O_3 powder coated with an amorphous SiO_2-layer through a sol–gel process. Hot-pressing was used to densify and bond the laminate layers together, followed by pressureless heat-treatment to allow mullite to form. Room temperature three-point bending tests were performed on as-received samples and on samples which underwent long-term annealing at high temperatures (1200–1300°C) in air. Subsequent examination revealed that due to the lack of a fiber interface coating, matrix-infiltrated fiber layers behaved in a quasi-monolithic manner with little or no crack deflection. Layers of non-infiltrated fibers, however, provided damage tolerance by deflecting cracks in the plane of the laminate and by serving as a mechanical bond between matrix-infiltrated layers. The laminate composites demonstrate reasonable room-temperature fracture strength both in the as-received state (88 MPa) and after exposure to 1300°C air for 200 h (72 MPa) along with extensive fracture deflection through the layers of non-infiltrated fiber. Composite properties, specifically fracture strength and damage tolerance, can be tailored by varying lay-up and processing parameters such as fiber-matrix ratio and type of fiber weave.

Keywords: Aluminosilicate fibers; Composites; Laminates; Mechanical properties; Mullite matrix

1. Introduction

In the most traditional sense, a fiber-reinforced ceramic-matrix composite consists of ceramic matrix material, fiber reinforcement and a tailored interface between the two. While the fiber and matrix determine for the most part the strength of the material, without a suitable interface the possibility of achieving a reasonable level of fracture toughness is limited. Such an interface can be tailored through in-situ reactions between fiber and matrix, but normally an interface coating is deposited on the fiber before matrix infiltration. Regardless of how it is applied, a weakened interface enables the necessary debonding and pullout mechanisms by deflecting cracks and dissipating crack energy. Coatings such as carbon and boron nitride are quite suitable for this purpose because of their easy-to-cleave laminate structures.[1] Many other non-oxide coatings also can provide damage tolerance but all function at the expense of one of the most valued properties of oxide-oxide composites, namely oxidation resistance.[1] Since ceramic matrix composites are of particular interest for use as thermal protection tiles in the combustion chambers of jet engines, a sensitivity to oxidation is a distinct drawback to a material with a non-oxide interface. Therefore, the development of an all oxide-based composite system is a priority.

There are some candidate oxide-based interface coatings,[2] but the selection is limited: due to high diffusion rates of oxides and the associated reaction with fibers and matrices, the deposition of such coatings on multiple filament yarns is often complicated and costly. For these reasons, it is worthwhile to explore other possible techniques to obtain damage tolerance in oxide-based ceramics. Many studies have explored the use of novel construction techniques to achieve high strength and damage tolerance, including several papers investigating laminate construction using monolithic and fiber-reinforced ceramic layers.[3,4] Of particular interest is the work of Tu et al.[5]

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who demonstrated the concept of "H-cracking", in-plane crack deflection resulting from inter-laminar elastic mismatches and residual stress. Also of interest is the research involving porous laminate layers, again using discontinuities in the material properties between laminate layers to obtain crack deflection.

2. Fabrication

This paper presents initial investigations of a concept based upon the use of non-infiltrated woven-fiber layers in a laminate to achieve crack deflection, but with the added feature that the fiber layers provide a degree of crack bridging as well. In this composite, layers of matrix-infiltrated fibers (hereafter referred to as "CMC layers") are separated by non-infiltrated fiber cloth layers (hereafter referred to as "fiber layers") and are hot-pressed together. The general method used to process fiber-laminate composites is outlined in Fig. 1.

2.1. Synthesis of microcomposite Al_2O_3–SiO_2 powder

These initial investigations of the fiber laminate composite concept were conducted concurrently with the development of a mullite-based matrix material. This matrix material is based upon the microcomposite-powder reaction-sintering technique developed by Sacks et al.[6] and advanced by Bartsch et al.[7] The Al_2O_3–SiO_2 microcomposite uses particles of α-alumina (AKP-50, Sumitomo Corp) which were coated with amorphous silica through a sol–gel process, the hydrolysis of TEOS. The ratio of TEOS to AKP-50 was selected so as to produce a final alumina/silica ratio slightly higher than the stoichiometric composition of mullite ($3Al_2O_3{\cdot}2SiO_2$) producing some excess α-Al_2O_3 after composite processing. Residual alumina was accepted in order to avoid the degradation of high-temperature properties caused by residual glassy silica.[8]

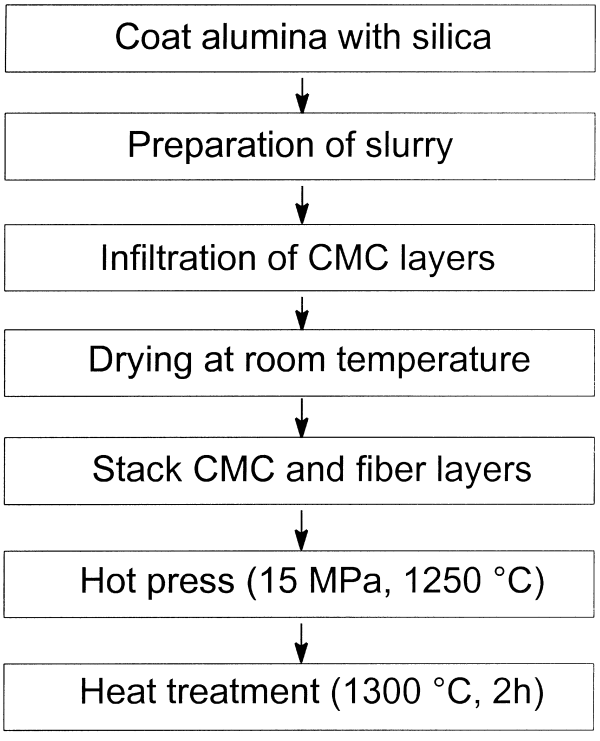


Fig. 1. Flowchart of processing steps used to fabricate fiber laminate composites.

Because the initial sintering characteristics of this coated powder are dominated by the sintering properties of the outer silica coating, a compact, high-density solid can be achieved at temperatures below 1300°C through transient liquid-phase sintering of SiO_2. In the case of reaction-sintered α-Al_2O_3/SiO_2 powder, however, mullite normally begins to form in significant amounts only at temperatures well above 1400°C. It is known that commercial alumina and aluminosilicate fibers show a severe degradation in properties due to the grain growth that occurs at these temperatures; therefore, other techniques need to be developed which allow mullite to form at lower temperatures.[9,10] Mechnich et al. have shown that the addition of CeO_2 as a sintering aid can significantly reduce the mullite formation temperature down to around 1300°C.[11] This reduction in processing temperature enables the use of the current state-of-the-art polycrystalline aluminosilicate fibers, albeit with some reduction in fiber strength due to crystal growth and microstructural changes in the fibers at high temperatures.[10] Improvements in the thermal stability of oxide-based ceramic fibers would be an important step into the development of even stronger and more usable CMCs.

2.2. Composite fabrication

Slurries containing microcomposite Al_2O_3–SiO_2 powder (α-Al_2O_3 particles coated with non-crystalline SiO_2) were prepared with added CeO_2 and mullite precursor powder (Siral, Condea, Brunnsbüttel, Germany.) CeO_2 and mullite precursors were added in order to accelerate sintering and to improve mullite formation. Powders were ball milled for 30 min. Nextel 720 (3M, Minnesota, USA) woven cloth (atlas eight-harness satin weave) was cut into squares approximately 50 by 50 mm. These squares were dipped into the slurry material, manually manipulated while immersed, allowed to absorb slurry, removed and allowed to dry. Altering the matrix solids content of the slurry along with repeated dipping allowed infiltrated fiber layers of varying matrix content and distribution to be produced. This simple dipping technique added a uniform and controlled amount of matrix to the fiber cloth — the matrix content among individual CMC layers (prepared from a given slurry mixture) varied less than 5%.

Laminate pre-forms were prepared by stacking in an alternating fashion CMC layers and fiber layers, as

illustrated in Fig. 2. A total of 13 layers (seven CMC and six fiber layers) provided an adequate specimen thickness of between 2.5 and 3.8 mm, depending on the matrix formulation. The composite lay-up was placed in a hot-press and heated to 1250°C in air without applied pressure. At 1250°C, a pressure of 15 MPa was applied and the temperature held constant for a period of 30 min to allow the material to consolidate and sinter. After 30 min, pressure was removed and the specimen was heated to a temperature of 1300°C. This temperature was held for a period of 2 h to allow the components in the microcomposite powder to undergo reaction sintering to form mullite. Samples were subsequently cut into three-point bend samples 4.0–4.5×50 mm in size. Some samples were exposed to high temperatures in air for 200 h.

After hot-pressing and subsequent heat treatment at 1300°C, the laminate structure of the composite was readily apparent to the eye. Though the outermost fibers in the fiber layers were bound to the matrix phase in the CMC layers, the "uninfiltrated" nature of the fiber layers was not compromised and a clear laminar discontinuity in the composite was present.

In order to ascertain a baseline for comparisons of strength values, monolithic samples were prepared by casting the matrix material into plaster molds. Once dried, the green material was processed under identical pressure, temperature and time parameters as the fiber laminate composites.

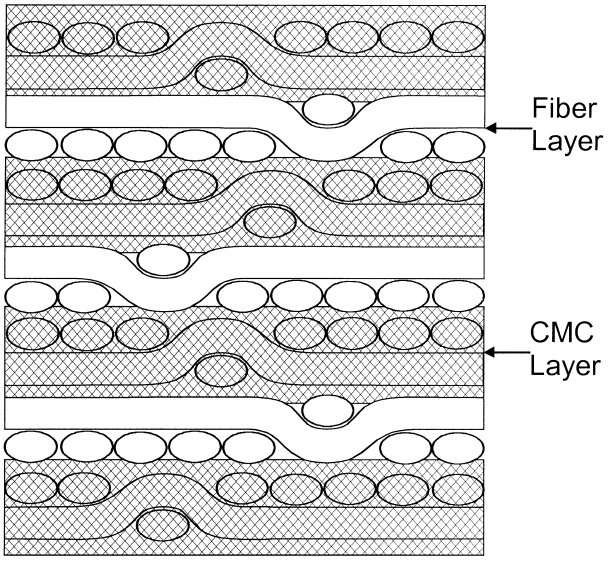


Fig. 2. Conceptual drawing of fiber laminate composite. Note connection between CMC layers (matrix-infiltrated fiber layers) and fiber layers.

3. Characterization of laminate composites

Three series of samples, each with a different matrix content as described in Table 1, were tested in three-point bending at room temperature (RT) using a UTS 10 Universal Test Machine (UTS Instruments, Inc) in order to determine the effects of matrix content. The effects of longterm exposure to high-temperature oxidizing atmospheres were also measured. For the sake of simplicity, only one series of samples was used for these tests. Fiber laminate composites were prepared using a 50 wt% slurry and a double infiltration step. Three-point bend samples were cut and annealed for 200 h in air at 1200, 1250 or 1300°C. Bend testing was conducted at room temperature. Monolithic samples were tested as-received using three-point bending.

Mullite formation was examined by X-ray diffraction in the 10 to 80° 2θ range using CuK_α radiation (Siemens D-5000 X-ray diffractometer, Siemans AG, Karlsruhe, Germany). Differential scanning calorimetry was carried out on a Netsch 404 DSC. After three-point bend testing at RT, fracture surfaces were examined using a Philips 525M SEM.

4. Results

4.1. Mechanical properties

Representative load-displacement curves for as-received and heat-treated samples (Fig. 3) clearly illustrate the strength and damage-tolerance behavior of the material, even after exposure to high-temperature oxidation. The maximum strength values of the samples treated at 1200, 1250 and 1300°C were 63, 64 and 72 MPa, respectively. These values decreased slightly compared with the 88 MPa strength of the as-received samples. The area below the load–displacement curves which corresponds to the degree of pseudoplastic behavior (damage tolerance) significantly increased with temperature treatment. Monolithic samples were also tested in three-point bending in the as-received condition. Strength was determined to be 124 MPa.

Table 1
Summary of data for three slurry preparations

Sample description (# infiltration, solids wt%)	CMC layer thickness (mm)	CMC layer fibre/matrix ratio	Strength (three-point bend) (MPa)	Photo of sample
1 infiltration, 20% slurry	0.28	85/15	38	Fig. 5a
1 infiltration, 50% slurry	0.30	62/38	73	Fig. 5b
2 infiltrations, 50% slurry	0.38	41/59	88	Fig. 5c

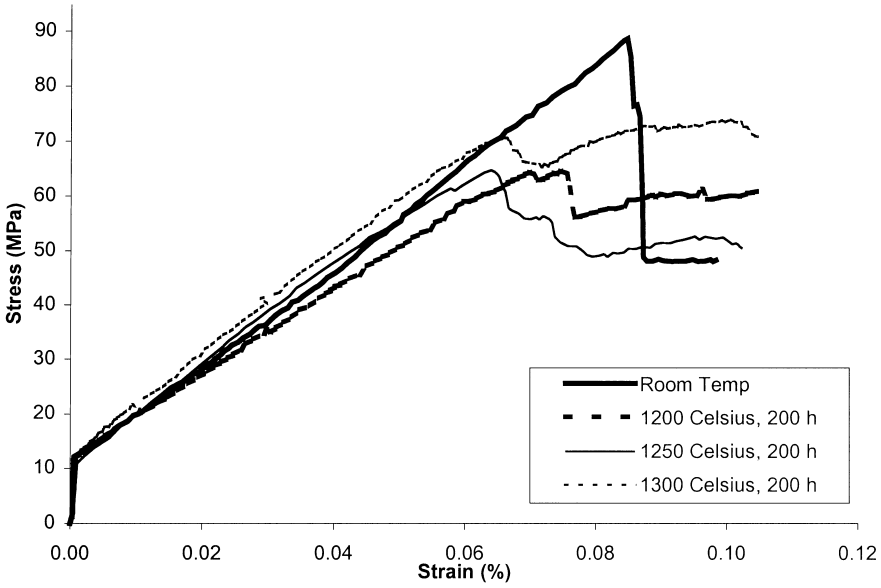


Fig. 3. Stress–strain curves for heat-treated samples. All samples prepared using 50 wt% solid slurry and two infiltration steps.

Fig. 4 shows a representative three-point bend sample after testing. The extent of crack deflection through the sample clearly shows the brittle fracture mechanism of the CMC layers and the crack bridging and deflection properties of the fiber layers. The wide crack separation shown in the sample did not normally occur during testing. Rather, the sample had to be cyclically manipulated by hand in order to cause the composite to separate. This illustrates an important advantage of fiber laminate composites, namely that even after failure the composite remains intact, a desired property in a material used in aircraft engines.

4.2. Microstructural observations

Differential scanning calorimetry (DSC) and XRD results determined that mullite formation began to occur in appreciable amounts only at 1300°C, Powder samples hot-pressed for 30 min at 1250°C/15 MPa and then annealed without pressure at 1300°C showed almost complete mullite formation. XRD analysis revealed that less than 5% SiO_2 remained unreacted with Al_2O_3. Matrix properties are given in details elsewhere.[7,11]

SEM photos of the three different series of samples are shown in Fig. 5(a)–(c). Fig. 5(a) is a sample whose CMC layer was prepared by a single infiltration step into a slurry with a 20 wt% solids content. CMC layers contain on average 14 wt% matrix and are easy to differentiate from fiber layers due to a somewhat planar fracture surface perpendicular to the laminate plane and due to the absence of loose individual fibers. CMC layer thickness is approximately 0.28 mm. Fig. 5(b) shows a sample where a slurry with 50 wt% solid was used. In this case, differentiation between pure fiber layers and matrix-containing layers is easy due to a marked increase in the amount of retained matrix. Most of this matrix occupies the inter-fiber spaces, so that despite a 37% increase in matrix content, the CMC layers, with a thickness of 0.30 mm, are only 0.02 mm thicker than those prepared above with the thinner slurry. Fig. 5(c) also shows a sample prepared with 50 wt% solid slurry, but in this case the individual fiber layers were infiltrated, allowed to dry and then infiltrated a second time. The photo shows a marked increase in CMC layer thickness; not so clearly illustrated is the increased distribution of this matrix on the surface of the layers as opposed to in the inter-fiber and inter-bundle spaces. Layer thickness was approximately 0.38 mm. Table 1 summarizes the data for these three preparations.

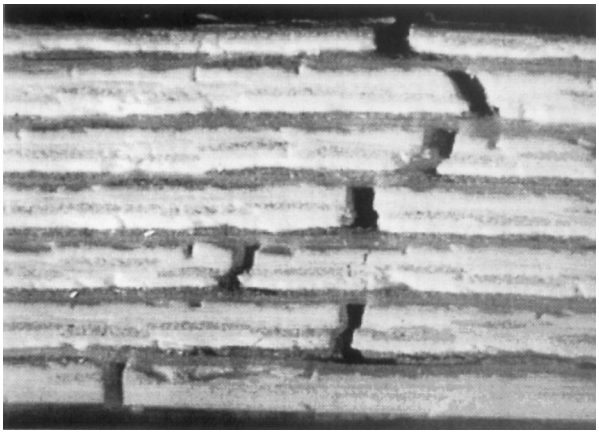


Fig. 4. Photo of broken three-point bend sample. Sample was prepared with a double infiltration step and using a slurry with 50% solids content (see Table 1). Sample was tested in as-received condition.

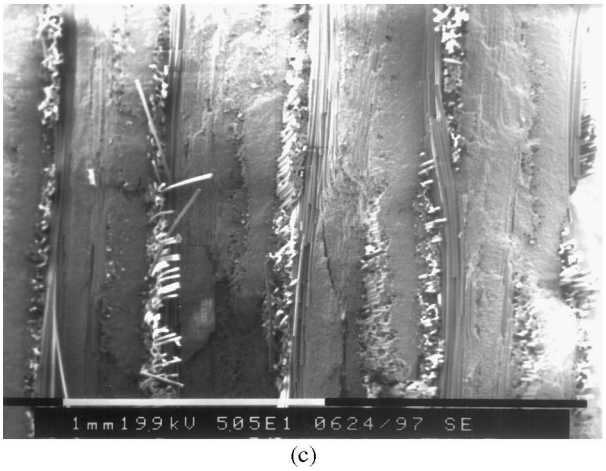
4.3. Discussion

Because of the strong bonding between fiber and matrix and the lack of an interface coating, the CMC

layers of this fiber laminate composite form a stiff material with a brittle fracture mechanism. Little or no damage tolerance results from the inclusion of fibers in CMC layers, nor would any such behavior be expected in the absence of an interface coating. Rather, in the CMC layers, fiber is used to assist in producing thin, quasi-monolithic layers, preventing excessive macro-scale cracking which can occur during the hot-pressing of thin monolithic tapes. Initial attempts to produce a fiber laminate composite using ceramic tapes instead of CMC layers failed due to this macro-scale cracking.

(a)

(b)



(c)

Fig. 5. Fiber laminate composites of varying matrix content and preparation technique: (a) 2% slurry solids, 1 infiltration; (b) 50% slurry solids, 1 infiltration; (c) 50% slurry solids, 2 infiltrations.

The characteristics of the matrix in the CMC layers affect the composite properties in several ways. The amount of matrix on the surfaces of the CMC layers influences the bonding between CMC and fiber layers arising from hot-press sintering and annealing. Insufficient matrix on the surfaces prevents bonding between CMC layers and fiber layers. In addition, the amount of matrix and its distribution within each CMC layer affect the strength and stiffness of that layer and, as a result, those of the composite. Specimens with thicker CMC layers (i.e. with higher matrix content) tended to have higher strength and a sharper drop in strength after initial matrix cracking. Samples with less matrix had a fairly flat load–displacement curve after initial matrix cracking.

The fiber layers function to modify the interaction between the CMC layers and to provide damage tolerance to the material. Through hot-pressing, the outermost fibers in the bundles of the fiber layers are bonded to the CMC layers. The woven bundles in the fiber layers serve as a mechanical connection between the overlying and underlying CMC layer, transferring loads and bridging inter-laminar and intra-laminar cracks. The layers provide a planar discontinuity in the matrix, adding a local anisotropic weakness which serves as an fracture path, thus improving damage tolerance.

Investigations to improve microcomposite-powder-derived mullite slurries need to be extended, so that slurry infiltration can be optimized and RT-and high-temperature (HT) strength increased. Fig. 6 illustrates several potential causes of CMC layer weakness. Clearly

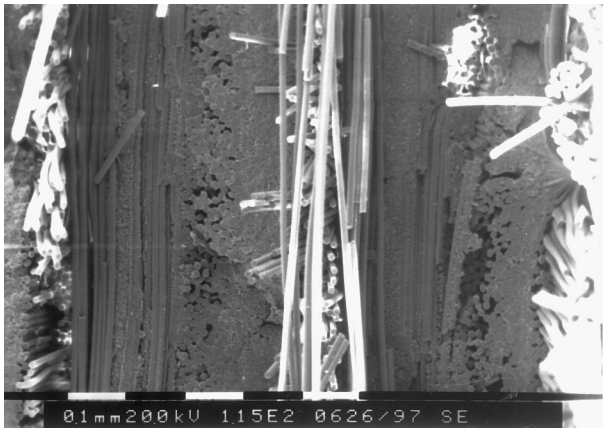


Fig. 6. Typical oxide/oxide fiber laminate composite with arrows showing areas of sub-optimum matrix infiltration and fiber-to-fiber contact. Sample was prepared with single infiltration step in slurry with 50% solids (see Table 1).

present are areas of incomplete matrix infiltration into the center of the fiber bundles and areas of fiber-to-fiber contact. Not visible is the small amount of macro-scale matrix cracking in the CMC layer green body which occurs on the outermost surfaces as the slurry dries. HT-test results also show that a small amount of glass containing silicates was present, somewhat affecting the high temperature properties of the fiber laminate composites. It is likely that a better-infiltrated CMC layer will improve the properties of a fiber laminate composite. Also of high importance is the weave characteristics of the fiber cloth. An eight-harness satin weave was used for convenience, as this is the weave provided by the manufacturer. It is in large part, however, the woven nature of the fiber cloth that provides a mechanical connection between the adjacent CMC layers. This is easily seen by visualizing a fiber laminate composite with fiber layers comprised of matrix-free 0°/90° unidirectional fiber layers instead of woven cloth — without woven bundles, the peel strength of the fiber layers would be very low, a fact proven by experiment. Because of the strong impact of the fiber layer on total composite properties, it is expected that increasing the woven nature of the cloth (using four-harness, plain weave, etc.) would strongly affect the material properties. This is currently being investigated.

Nonetheless, in a straight comparison, fiber laminate composites prepared with the current slurry formulation and dip infiltration technique and using eight-harness satin woven fabric compare well with regards to the monolithic samples. Fiber laminate composites retain about 70% of the baseline monolithic strength (126 MPa) while adding a significant level of damage tolerance. In applications where weight is a strong concern, fiber laminate composites show improved performance. When normalized according to weight, fiber laminate composite samples retain 83% of the baseline monolithic strength. This is because the low density fiber layers add to the bulk of the material, but add little to the weight. Weight is usually considered to be more important than size in the specific application of jet engine combustion chamber.

5. Conclusion

Fiber laminate composites, a new type of laminate material which uses no fiber interface coating but displays damage tolerant fracture, were fabricated. The effect that the individual components of the composite had on fracture behaviour and strength values were investigated. Composites exhibited moderate strength values at RT and at HT (up top 1300°C), retaining their strength after 200 h at HT in air. Properties of the fiber composites described in this paper most likely can be improved by changing the chemical composition of microcomposite particles, by improving the infiltration of the CMC layers with these slurries prepared by using microcomposite particles and by changing the type of weave of the fibers.

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