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Interface engineering in mullite fiber/mullite matrix composites

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Abstract

Mullite fiber/mullite matrix composites are attractive because of their inherent oxidation resistance at high temperatures. Mullite has better creep resistance than alumina. However, chemical interactions between oxides are often very severe; with the result no gain is made over monolithic mullite in terms of toughness. Even in the absence of chemical bonding, a strong mechanical bond component may be present. This originates from radial compressive stress due to thermal expansion mismatch and/or the surface roughness of interface. Thus, the microstructure and behavior of the interface region are the key factors in obtaining an effective control of damage in composites and enhancement of toughness. This body of work on mullite/mullite composites shows the feasibility of producing fully dense, tough oxide/oxide composites by interface engineering. Coatings such as BN alone or SiC/BN double coating function effectively for mullite fiber/mullite matrix composites in that they provide a nonbrittle fracture and increased work of fracture at room temperature. It would appear that for use at high temperatures in air, one needs to identify structural analogs of BN among oxides.

Keywords: Fibers; Mullite; Composites; Fracture; Toughness and toughening

1. Introduction

Mullite fiber/mullite matrix composites form an important subpart of the oxide fiber/oxide matrix compsites.[1–3] Mullite-based composites are attractive because of their inherent oxidation resistance at high temperatures and their favorable thermal shock and damage tolerance properties. In fiber reinforced ceramic matrix composites, the local response of the fiber/matrix interface during fracture is of great importance. The microstructure and behavior of the interface region are the key factors in obtaining an effective control of damage in composites and enhancement of toughness. When a crack moves through a matrix containing unidirectional fibers, a variety of failure mechanisms may come into play as shown in Fig. 1:

- matrix fracture;
- interfacial debonding at the crack tip, followed by crack deflection;
- interfacial debonding in the crack wake, followed by crack deflection;
- frictional sliding between the fiber and matrix;
- fiber failure;
- fiber pullout.

It has been amply suggested that reinforcement with continuous fibers such as carbon, alumina, silicon carbide, and mullite fibers in brittle matrices can result in toughening.[3] It is not necessary for all these failure mechanisms to operate simultaneously for a given fiber/matrix system and often in many composite systems only one or two of these toughness contributions will dominate the total fracture toughness. Interface engineering approach involves incorporation of fiber coatings that can bring into play energy absorbing processes such as crack deflection and fiber pullout, and thus make the composite damage-tolerant. It would appear that the debonding of the fiber/matrix interface is a prerequisite for phenomena such as crack deflection, crack bridging by fibers, and fiber pullout.

2. Criteria for interfacial debonding

There are two main criteria for interfacial bonding. Both of them are difficult to use in practice. We indicate a third one that is relatively simple and involves only radial stress (i.e., normal to the fiber/matrix interface) component. A brief description of these criteria follows:

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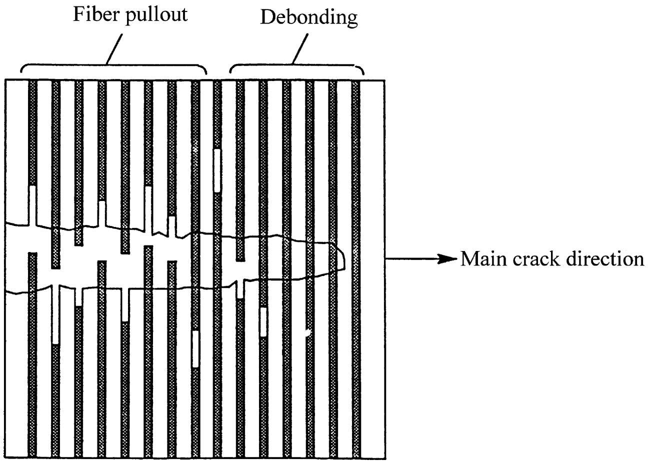

Fig. 1. A schematic of different failure mechanisms that may come into play when a crack moves through a matrix containing unidirectional fibers.

2.1. Strength-based criterion

Debonding of the fiber/matrix interface appears to be a prerequisite for phenomena such as crack deflection, crack bridging by fibers, and fiber pullout. Cook and Gordon first proposed crack deflection or the formation of a secondary crack at a weak interface.[4] For the case of a fiber/matrix system having identical elastic constants (i.e., identical materials), Cook and Gordon, estimated the strength of the interface necessary to cause a diversion of the crack from its original direction. For any given crack, either a triaxial state of stress (plane strain) or a biaxial stress (plane stress) is present at the crack tip. The applied principal stress component, σ_y, has a very high value at the crack tip, which decreases sharply with distance from the crack tip as it must be because the surface of a crack is a free surface. σ_x, the stress component normal to the fiber/matrix interface, is 0 at the crack tip. σ_x then rises quickly to a maximum a short distance away from the tip and then quickly decreases with distance in a fashion similar to that seen with σ_y. If the fiber/matrix tensile interface strength is less than the maximum value of σ_x, fracture should occur at the interface ahead of the approaching crack tip. Cook and Gordon estimated that if the interface had strength of about 1/5 or less than that of the main stress component, σ_y, it will debond in front of the crack tip. Again, it should be noted that they studied a system with identical components.

2.2. Energy-based criterion

An energy-based criterion has been proposed for interfacial debonding by He and Hutchinson.[5] If Γ_{i} is the interfacial (debond) energy and Γ_2 is the fracture energy of the second material or fiber in Mode I, then interfacial debonding and sliding will occur rather than brittle cracking through the fiber, when the following inequality is satisfied:

$$\Gamma_{\mathrm{i}} \leq \left(\frac{1}{4}\right) \Gamma_2 \quad \text{for } \alpha = 0 \tag{1}$$

where α is the elastic mismatch parameter and is defined as:

$$\alpha = \frac{E'_2 - E'_1}{E'_2 - E'_1}, \quad \text{where } E' = \frac{E}{(1 - \upsilon^2)} \tag{2}$$

where E is the elastic modulus and υ is the Poisson's ratio for each material of interest. For debonding and sliding to occur, the interfacial energy, Γ_{i} must not exceed an upper bound relative to the fracture energy of the second material, Γ_2. Unfortunately, reliable Γ_{i} and Γ_2 are usually not readily available for many systems, making this criterion difficult or impossible to use when exploring new material systems.

3. Importance of interfacial characteristics for debonding

A rough fiber/matrix interface results in strong mechanical keying, which can prevent interfacial debonding and fiber pullout. A smooth interface, on the other hand, results in weak keying, which is conducive to fiber pullout. Fig. 2 shows a schematic of a periodic roughness at the fiber/matrix interface. Many investigators have found that interfacial roughness has a pronounced effect on the interfacial sliding stress. The radial strain at the fiber/matrix interface consists of two parts: one is due to the thermal mismatch between the fiber and matrix, which can be either tensile or compressive, and the other one comes from the roughness induced clamping, which is always in compression or zero. The important point to note here is that even when the coefficients of thermal expansion of the coating, fiber, and matrix are such that a radial tensile stress exists at the fiber/coating interface, fiber pullout may not occur because of a strong mechanical bonding due to a roughness induced clamping at the fiber/matrix. Thus, in CMCs having an extremely rough interface, the pullout would not be expected, and they would likely fail like monolithic materials.

The two sources that contribute to the radial stress component acting normal to the fiber/matrix interface are:

(i) thermal mismatch induced radial compressive stress;
(ii) mechanical gripping induced by the fiber surface roughness.

In ceramic matrix composites, interfacial roughness induced interface stresses, especially the radial stress, will affect the interface debonding, the sliding friction of debonded fibers, as shown in Fig. 1, and the fiber pullout length. Fiber pullout is one of the important energy dissipating fracture processes in fiber reinforced ceramic or glass matrix composites. An absence of strong chemical bond and a purely mechanical bond at the fiber/matrix interface is highly desirable for the fiber pullout to occur. Even when the coefficients of thermal expansion of the coating, fiber, and matrix are such that a radial tensile stress exists at the fiber/coating interface after cooling from an elevated processing temperature, fiber pullout may not occur because of a strong mechanical bonding due to a roughness induced clamping at the fiber/matrix interface. The radial stress resulting from the surface roughness of the fiber during fiber pullout,

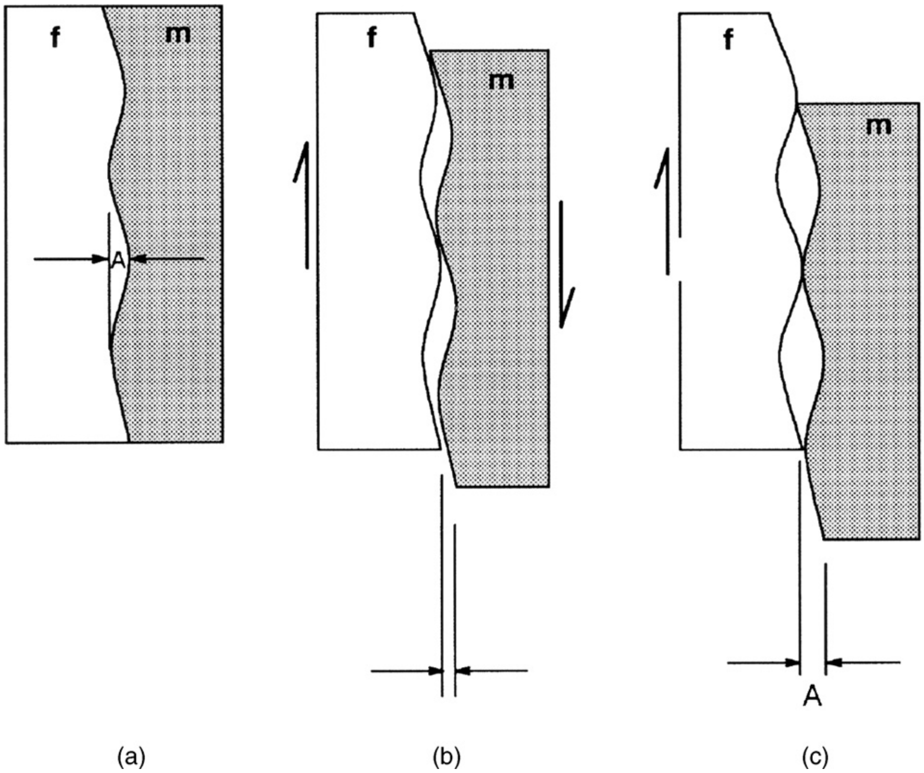

Fig. 2. Schematic of periodic interfacial roughness. The fiber and matrix are indicated by f and m, respectively. *A* is the amplitude of the interfacial roughness.

should be added algebraically to the radial thermal stress, i.e., the effect of surface roughness of the fiber along the debonded interface on the radial stress at the interface needs to be considered together with the thermal stresses. The sense of the two can be the same or opposite. The surface roughness of the available oxide fibers can be varied significantly. In ceramic matrix composites, roughness-induced interfacial gripping, especially in the radial direction, will affect the interface debonding, the sliding friction of debonded fibers, and the fiber pullout length.[1,3]

The objective of this paper is to show that by applying the principle of interfacial engineering in mullite fiber reinforced mullite matrix composites, one can get fully dense but tough, damage tolerant composites. Thus, approaches involving a porous matrix or interlace are not considered here. Thin film coatings on fibers are used to modify and control the interface behavior in CMCs. In particular, BN can be a weak interphase between the mullite fiber and mullite matrix because of its graphite-type layer structure.[6–8] A major disadvantage of BN coatings is their poor oxidation resistance at high temperatures. There are two ways around this problem. One possible way is to use a thick BN coating so a portion of the coating can be sacrificed during processing. The other possibility is to protect the BN coating it by a second coating with better oxidation resistance, such as SiC, i.e., use SiC/BN double coating. That still retains a nonoxide interphase in an oxide fiber/oxide matrix composite. It should be recognized here that both BN and SiC/BN coatings are nonoxides and thus susceptible to oxidation at high temperatures in air.

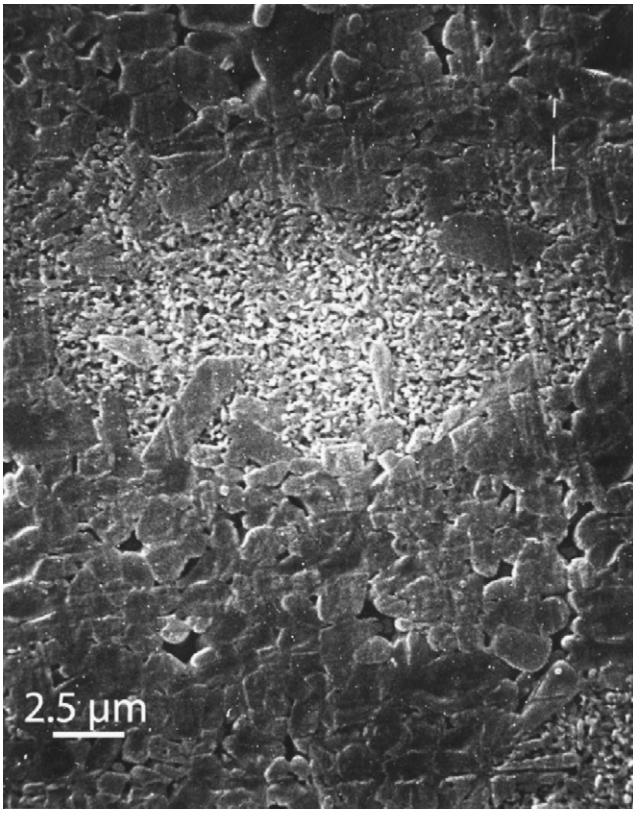

Fig. 3. A mullite fiber/mullite matrix composite processed without an interphase coating. The etched cross-section shows that mullite fiber in the center was lost after processing.

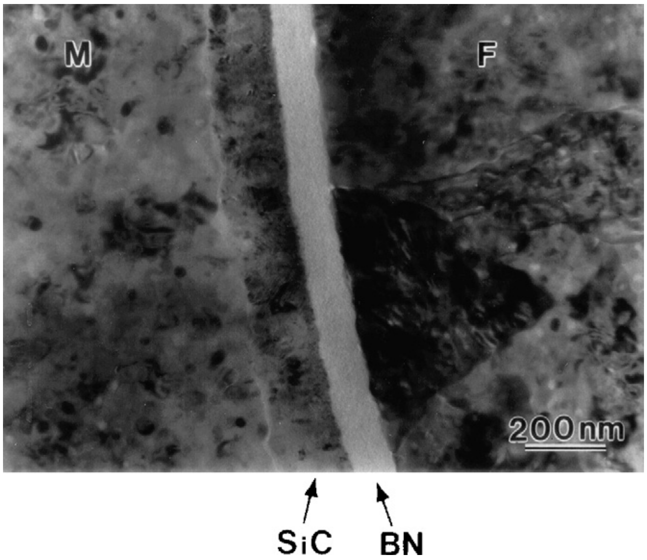

Fig. 4. A cross-section of the composite showing the mullite matrix (M) and mullite fiber (F) with the double coating of SiC and BN in between.

4. Materials and experimental procedure

3M Company has developed a series of oxide fibers.[9] This series of fibers, called the Nextel fibers, mainly consists of alumina and mullite-type fibers. Nextel ceramic oxide fibers are continuous and polycrystalline. These fibers are typically transparent, nonporous, and have a diameter of 10–12 μm. Two mullite-based fibers from this series, Nextel 480 and Nextel 550 were used. Nextel 480 fibers have 70 wt.% Al_2O_3, 28 wt.% SiO_2, and 2 wt.% B_2O_3 and are currently not produced. BN coatings on Nextel 480 were produced by CVD. Nextel 550 fibers have 70 wt.% Al_2O_3, 30 wt.% SiO_2, i.e., compared to Nextel 480, boria is missing.

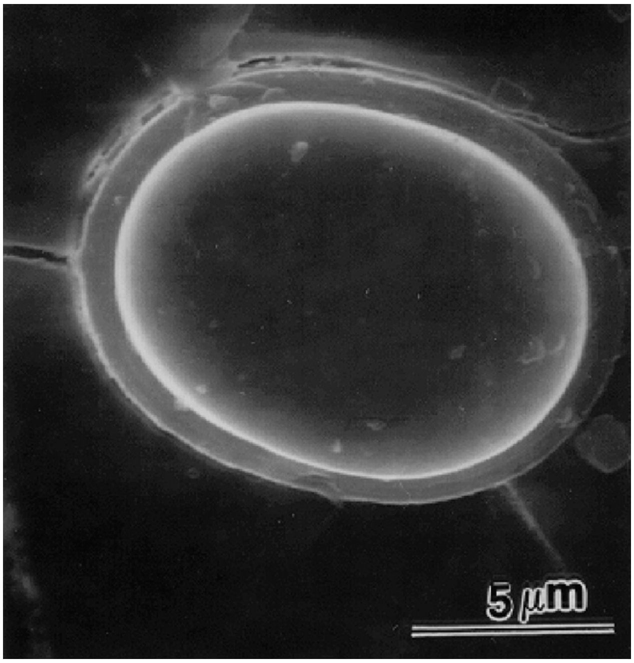

Fig. 5. An indentation induced crack deflection at the BN coating in the as-made composite.

Two of the most common interphases used in fiber composites are carbon (C) and boron nitride (BN). These materials have intrinsic low fracture toughness. The graphitic form of carbon has easily cleavable basal planes. This makes it ideal as a weak interface for crack deflection. The problem with carbon is that it is readily oxidized at temperatures above 400 °C in air. Boron nitride also has a layer structure like that of graphite. Boron nitride, although a nonoxide, is more oxidation resistant than carbon, but its oxidation resistance is a function of its stoichiometry.

Double coatings of BN (inner)/SiC (outer) double layer were produced by CVD.

An interfacial testing system with a flat-bottomed, diamond indenter was used to obtain the interface characteristics. Three-point flexural tests were done to examine the load-displacement characteristics of the composites.

Mullite fiber/mullite matrix composites were made via a sol–gel route. Mullite gels can be single-phase or diphasic according to the scale of component mixing, depending upon the nature of the alumina and silica precursors. Single-phase

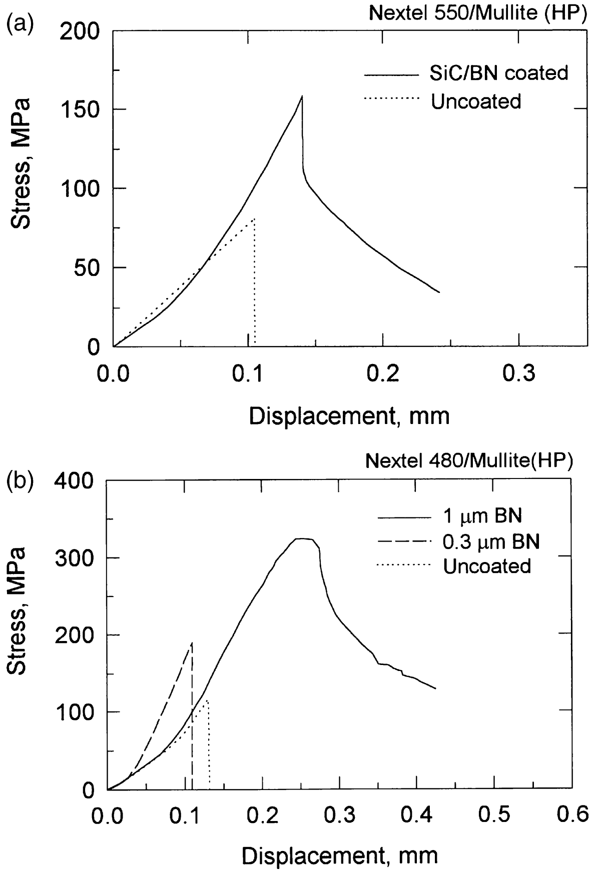

Fig. 6. (a) Stress vs. displacement for a mullite fiber (Nextel 550)/mullite matrix composite with no coating and double coating of SiC/BN. The composite with the double coating shows a damage-tolerant behavior. (b) Stress vs. displacement for a mullite fiber (Nextel 480)/mullite matrix composite with no coating and two composites with different coating thicknesses of BN. The uncoated composite and the composite with 0.3 μm BN coating show catastrophic, brittle fracture while the composite with 1 μm BN coating shows a damage tolerant behavior.

gels are prepared from aluminum and silicon alkoxides or salts; they have molecular-scale mixing because of a polymerized-oxide network formed by hydrolytic condensation. Diphasic gels involve mixing of sols of boehmite and silica or mixing of one colloidal component with alkoxide or salt of other. The two routes are quite different, mainly because of the different scales of component mixing. The single-phase and diphasic gels show different types of mullite crystallization behavior during heating. Single-phase gels have a very short interdiffusion distance because of the molecular-scale mixing, and therefore, mullite crystallization can occur at temperatures as low as 1000 °C. In diphasic gels, however, the diffusion distance is much longer, so mullite crystallization does not occur until above 1250 °C. Retardation of mullite crystallization in the diphasic gels provides a useful processing window.[10] This is a key point. With diphasic gels, >95% of theoretical density (TD) can be obtained through one of the following two methods:

- Sintering times of more than 1 h between 1200 and 1300 °C, with carefully controlled heating;
- Sintering for 1 h with a low heating rate (2° C/min) and a high compaction pressure (441 MPa) for a green body.

Compared to this, in single-phase gels, crystalline mullite forms at very low temperatures, which makes densification difficult because of the high degree of covalent bonding in crystalline mullite. The result is that the densities obtained at the same hot pressing temperature are much lower than with the viscous-phase processing.

5. Results and discussion

As expected, no fiber pullout was observed in the uncoated mullite/mullite composites as shown in Fig. 3. A cross-section of the composite showing the mullite matrix (M) and mullite fiber (F) with the double coating of SiC and BN in between is shown in Fig. 4. We used two types of coatings, a thicker BN (1 μm) and a BN/SiC double coating. The thicker coating allows for a part of the coating to be sacrificed by oxidation during processing. The objective of using an SiC coating was to provide oxidation protection to BN during processing. The efficacy of BN coating to deflect an oncoming crack is shown in Fig. 5. The crack, introduced by means of an indentation, can be seen to deflect at the BN coating and go around the fiber rather than penetrate it. In the BN interphase, which is isostructural to C, the orientation of the basal planes parallel to the substrate surface is attributed to low surface energy perpendicular to the basal planes. The orientation of (0 0 0 2) BN basal planes parallel to the fiber surfaces is the favorable for the damage tolerance of composites properties.[11] It enables easy sliding along these planes thus producing a weak fiber/matrix interface.

In both cases, thick BN coating or SiC/BN double coating, a noncatastrophic failure mode was observed. The stress-displacement curves obtained in a three-point bend tests for composites containing interfacial coatings of BN and SiC/BN-coated as well as uncoated composites are shown in Fig. 6a and b. Fig. 7a shows the fracture surfaces of the composites containing 1 μm BN-coated fibers and while Fig. 7b shows the fracture surface of a composite containing SiC/BN-coated fibers. In both cases, the phenomenon of fiber pullout occurred; which led to a

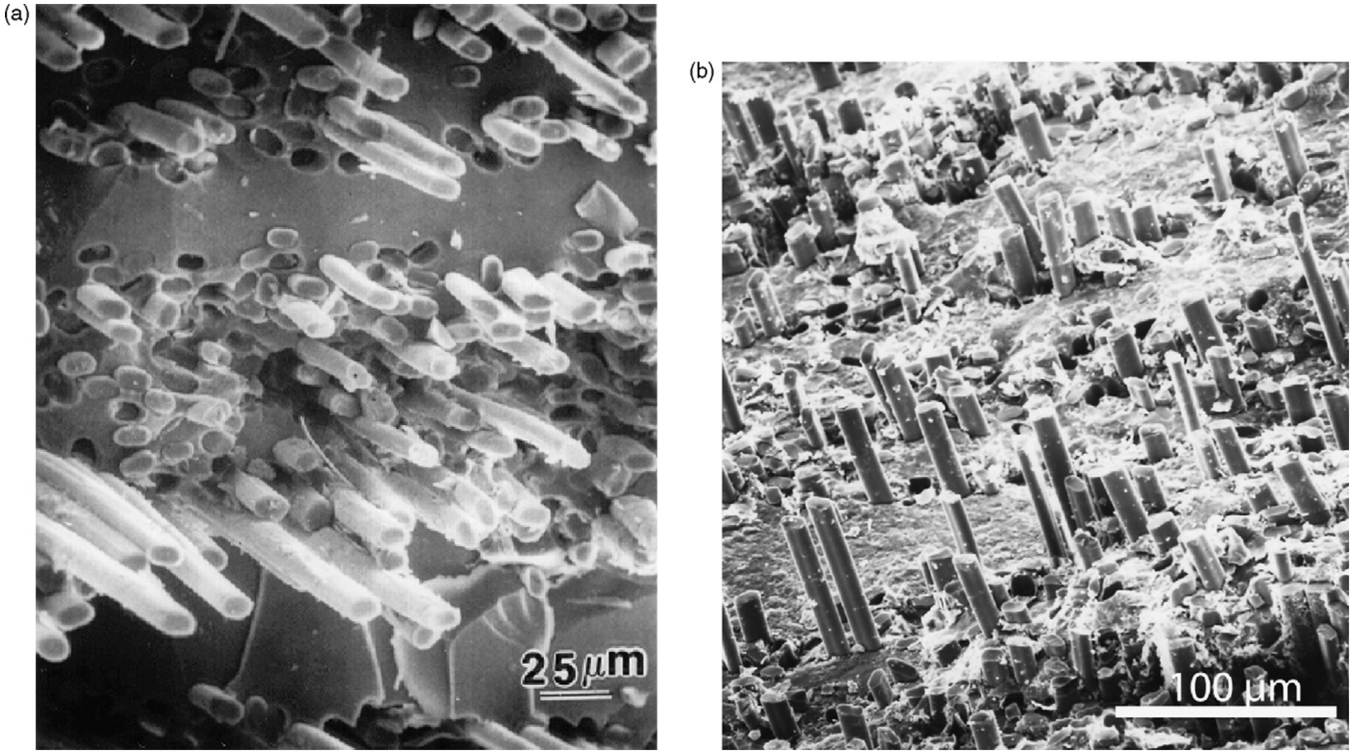

Fig. 7. Fiber pullout (a) in thick BN-coated and (b) SiC/BN-coated mullite fiber/mullite matrix composite.

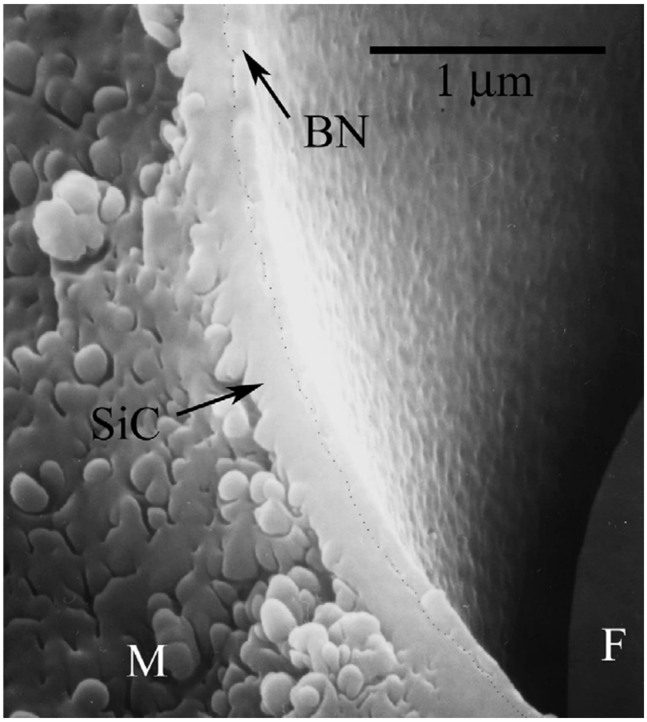

Fig. 8. Fracture surface of mullite fiber, Nextel 550 (F) with double coating of SiC/BN in a mullite matrix (M). The interface between BN and SiC is highlighted with a dotted line. Note the sliding occurred along the fiber/BN coating. The SiC coating remained bonded to the mullite matrix.

higher work of fracture in the coated fiber composites than in the uncoated fiber composite. The BN/SiC double coating system consists of 0.08 μm BN and 0.16 μm SiC-layers. In this case BN is rather turbostractic,[11] and does not undergo any microstructural change up to 1300 °C. An interesting high magnification micrograph of the fracture surface of mullite fiber, Nextel 550 (F) with double coating of SiC/BN in a mullite matrix (M) is shown in Fig. 8. The interface between BN and SiC is highlighted with a dotted line. Note the sliding occurred along the fiber/BN coating. The SiC coating remained bonded to the mullite matrix. The outer thin SiC layer of the double coating system improves the oxidation resistance of BN up to 1200–1300 °C in spite of a partial oxidation of SiC to SiO_2.

A word of caution is in order here. The application of a coating on fiber can affect its strength. If the thermal mismatch can result in a residual tensile strength in the fiber, it will weaken the fiber. The tensile strength of Nextel 480 fiber increased with increasing BN coating thickness until 0.2 μm. For coatings greater than 0.2 μm in thickness, the fiber strength decreased. There are two factors affecting the strength of the coated fiber simultaneously. One is the smooth boron nitride coating which heals the surface defects of such fiber, and thus, contributes to strength enhancement. The second one is the volume fraction of the coating material which is a weak material. When coating thickness is below 0.2 μm, the first factor plays a dominant role in the strength enhancement. When coating thickness is above 0.2 μm, the second factor becomes dominant to reduce the fiber strength.

Coatings such as BN alone or SiC/BN double coating function effectively for mullite fiber/mullite matrix composites in that they impart damage tolerant characteristics to mullite fiber/mullite matrix composites. However, both BN and SiC/BN coatings are nonoxides, and thus are susceptible to oxidation at high temperatures in air. Of course, SiC is more resistant to oxidation than BN. What this points to is the need for oxide analogs of BN that would function as interphase materials at high temperatures. Beta-aluminas or micas are possible candidate materials. Layered oxides having β-alumina and magnetoplumbite structures should be explored as possible easy cleavage coatings in mullite-based composites.

6. Conclusions

- Chemical interactions between oxides are often severe such that selection of possible mullite-based composites or oxide fiber/oxide matrix composites, in general, is limited.
- Even in the absence of chemical bonding, a strong mechanical bond component may be present. This originates from radial compressive stress due to thermal expansion mismatch and/or the surface roughness of interface.
- Coatings such as BN alone or SiC/BN double coating function effectively for mullite fiber/mullite matrix composites in that they provide a nonbrittle fracture and increased work of fracture at room temperature.
- Need oxide analogs of BN that would function as interphase materials at high temperatures. Beta-aluminas or micas are possible candidate materials. Layered oxides having β-alumina and magnetoplumbite structures should be explored as possible easy cleavage coatings in mullite-based composites.

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References

1. Chawla, K. K., Coffin, C. and Xu, Z. R., *Int. Mater. Rev.*, 2000, **45**, 165.
2. Schneider, H. and Komarneni, S., ed., *Mullite*. Wiley-VCH, Weinheim, 2005.
3. Chawla, K. K., *Ceramic Matrix Composites* (*2nd ed.*). Kluwer, Boston, 1998.
4. Cook, J. and Gordon, J. E., *Proc. R. Soc. Lond.*, 1964, **A228**, 508.
5. He, M.-Y. and Hutchinson, J. W., *Int. J. Solids Struct.*, 1989, **25**, 1053–1067.

6. Rice, R.W., US Patent 4,642,271 (1987).
7. Thomas, J., Watson, N. E. and O'Conner, T. E., *J. Am. Chem. Soc.*, 1963, **84**, 4619.
8. Wyckoff, R. W. G., *Crystal Structures, vol. 1* (*2nd ed.*). R.E. Kreiger Publishing Co, Malabar, FL, 1982.
9. Chawla, K. K., *Fibrous Materials*. Cambridge University Press, Cambridge, UK, 1998.
10. Chawla, K. K., Xu, Z. R., Ha, J. S., Schmücker, M. and Schneider, H., *Appl. Comp. Mater.*, 1997, **4**, 263.
11. Chawla, K. K., Xu, Z. R. and Ha, J.-S., *J. Euro. Ceram. Soc.*, 1996, **16**, 293.