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Mechanical Properties of Fiber–Reinforced $YBa_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_x$ Bars*

K. C. Goretta, L. J. Martin, R. B. Poeppel, Nan Chen, C.-Y. Chu, and J. L. Routbort

Argonne National Laboratory, Argonne, IL 60439 USA

R. A. Gleixner
Babcock & Wilcox, Alliance, Ohio 44601 USA

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MECHANICAL PROPERTIES OF FIBER-REINFORCED $YBa_2Cu_3O_x$ AND $Bi_2Sr_2CaCu_2O_x$ BARS*

K. C. Goretta, L. J. Martin, D. Singh, R. B. Poeppel, Nan Chen,[a] C.–Y. Chu,[b] J. L. Routbort, and R. A. Gleixner[1]

Argonne National Laboratory, Argonne, Illinois 60439
[1]Babcock & Wilcox, Alliance, Ohio 44601

ABSTRACT

Strength in four–point bending and fracture toughness of $YBa_2Cu_3O_x$ (123) and $Bi_2Sr_2CaCu_2O_x$ (2212) were examined at room temperature. The 123 was reinforced with 15 vol.% Y_2BaCuO_5 (211) fibers and was processed to 90–91% density by cold pressing and sintering. The 2212 was reinforced with 15 vol.% 2212 fibers and was processed to ≈90% density by sinter forging. The 123/211 composites had a fracture toughness of 1.9 MPa(m)$^{0.5}$, which is 20–30% higher than that of corresponding monoliths, but exhibited no improvement in strength. The strength and fracture toughness of the 2212/2212 composites were 102 MPa and 2.7 MPa(m)$^{0.5}$, respectively, which were slight improvements over the monoliths. Transport critical current densities at 77 K were only slightly affected by the fiber additions.

INTRODUCTION

Mechanical properties of bulk high-temperature superconductors have received considerable attention. Good strength and flexibility are required in most bulk applications (Alford et al., 1990). The mechanical properties of $YBa_2Cu_3O_x$ (123) and $Bi_2Sr_2CaCu_2O_x$ (2212) are in general rather poor, and various composite systems have been developed to improve both strength and fracture toughness (e.g., Singh et al., 1990).

There are several factors to consider in design of a composite. Fracture toughness, K_{IC}, can be improved by addition of components that dissipate

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[a]Nan Chen is now with Illinois Superconductor, Evanston, IL.
[b]C.–Y. Chu is now with Elan Technologies, Belleville, NJ.

energy from the moving crack front. In general, fiber reinforcement improves K_{IC} by mechanisms related to fiber sliding, crack deflection, crack bowing, or microcrack formation (Rice, 1981). Crack deflection and bowing are also applicable to self-reinforced ceramics. For example, composites consisting of a mixture of elongated Si_3N_4 grains within a matrix of equiaxed Si_3N_4 grains are commerically available and offer K_{IC} values as high as 12 MPa(m)$^{0.5}$, a factor of 2.5–3 higher than that of the monolithic Si_3N_4. (e.g., Li and Yamanis, 1989).

However, in many instances the increase in toughness can be accompanied by an undesired decrease in strength. Fabrication of dense composites is complicated by the additions that inhibit sintering, agglomerate to form extended flaws in the sintered body, or introduce unwanted impurity phases. Chemical reactions between the matrix and the reinforcing phase, which could degrade electrical or mechanical properties, must be avoided. Therefore, care must be taken in selection of the type of reinforcement, its dispersion within the parent phase, and in the consolidation process. Design of superconductor composite systems is complicated by the fact that virtually all materials react to some extent with 123 and 2212. Those exhibiting little reaction include Ag (Singh et al., 1990), oxide glasses (Seino et al., 1989; Imam et al., 1989), and MgO (Soylu et al., 1992). Even these materials, however, interact with high-temperature superconductors in subtle ways. For example, Ag alters the Cu valence (Meyer et al., 1989) and Cu diffuses from the superconductor into the ceramics (Wu et al., 1993).

Ideal reinforcements for high-temperature superconductors would be fully chemically compatible and mechanically strong. Long fibers would be likely to improve strength and fracture toughness most significantly (Evans, 1989). Y_2BaCuO_5 (211) is in equilibrium with 123 at processing temperatures (Hinks et al., 1987) and is stronger, more stable, and more refractory than 123 (De Arellano-López, 1991; Goretta et al., 1991). In addition, it has been demonstrated that 211 particles within grains of melt-textured 123 improve fracture toughness (Fujimoto et al., 1990). 211 may be an excellent reinforcement in fiber form. In the Bi-Sr-Ca-Cu-O system, alkaline earth cuprates such as $(Sr,Ca)_2CuO_3$ are in equilibrium with 2212 during processing (Holesinger et al., 1992; Schartman et al., 1993). These phases tend to be highly hygroscopic, however, and their successes as reinforcements are not assured (Phillips et al., 1991). High-quality 2212 fibers are available (Miller et al., 1991) and polycrystalline 2212 may be reinforced with fibers of the same or different composition.

Bulk 123 can be sintered at atmospheric pressure to high density through proper control of oxygen partial pressure and temperature (Singh et al., 1992). Under some conditions, strengths can exceed 200 MPa (Goretta et al., 1993a), with fracture toughness generally being ≈1.5 MPa(m)$^{0.5}$ (Singh et al., 1990). 2212 requires pressure to achieve full density because of highly anisotropic grain growth (Johnson and Rhodes, 1989; Chu et al., 1992). Strengths for well-textured microstructures are typically 100–110 MPa (Murayama et al., 1992; Goretta et al., 1993b).

No candidate fiber available was available for 123 when this work was begun. Experimental fibers made from 211 powder were provided by SKY Fibretech (1992). The 2212 fibers used for 2212 reinforcement have been described previously (Miller et al., 1991). The goals of this work were to fabricate dense bars of 123/211 and 2212/2212 composites and to determine whether the reinforcements increased strength or fracture toughness. The reinforcement schemes employed in this study will, in all probability, be of use only in applications in which high critical current density (J_c) is not required. In such applications, for example current leads or cryogenic fluid level sensors, J_c values at 77 K need only be 10^3 A/cm^2 or less.

EXPERIMENTAL PROCEDURES

123 and 2212 powders were synthesized from mixtures of oxides and carbonates. Final grinding in a tungsten carbide rotary mill produced powders 2–5 μm in average size. Details of the procedures have been published (Balachandran et al., 1989; Bloom et al., 1991; Chu et al., 1992).

Representative fibers are shown in Fig. 1. The 211 fibers were obtained as a tangled mass. Individual fibers were ≈50–1000 μm long and ≈3–5 μm in diameter. The 2212 fibers were initially amorphous and were longer, thinner, and much smoother than the 211 fibers.

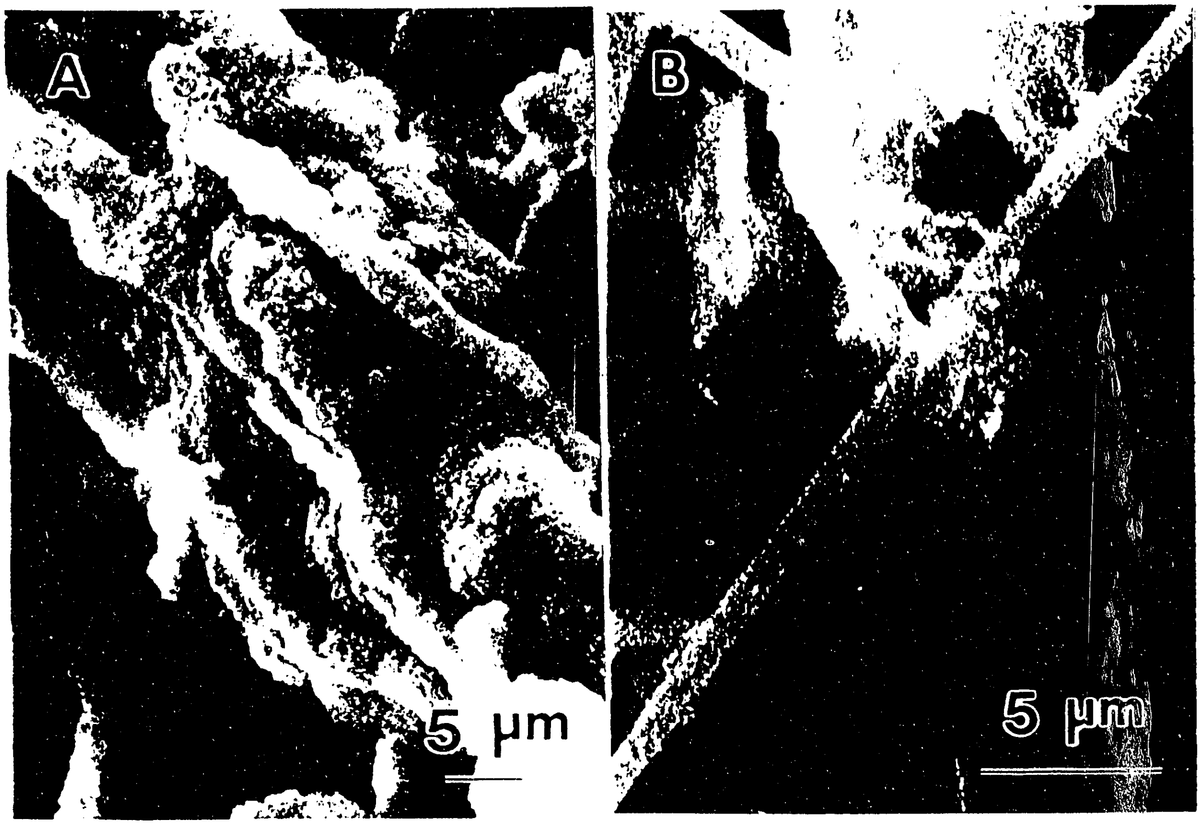

Figure 1. SEM photomicrographs of as-received (a) 211 and (b) 2212 fibers.

The strengths of the fibers were estimated by the sizes of the mirrors on the fracture surfaces. Such features form around the failure-initiating flaw and can be related to the fracture strength as follows (Kirchner and Gruver, 1973):

$$\sigma_f r_f^{1/2} = A \quad (1)$$

where σ_f is the fracture strength, r_f is the fracture mirror radius, and A is an empirical constant. For polycrystalline ceramics with very small grain size, it is reasonable to take A = 3.5 $MPa{\cdot}m^{0.5}$ (Thouless et al., 1989).

For the 211 fibers, no mirror could be observed by scanning electron microscopy (SEM). Therefore, no estimate of the fiber strength was made, although the combination of small diameter and fine grain size implies that the strengths were relatively high. For the 2212 fibers, only the larger fibers could be handled easily. They were heat treated in air at 825°C to form the 2212 phase, as confirmed by X-ray diffraction. A typical fracture mirror size was ≈7 μm (Fig. 2). The estimated fracture strength was

$$\sigma_f = 3.5 \times 10^6/(7 \times 10^{-6})^{1/2} = 1.3\ \text{GPa} ,$$

which is much stronger than the expected strength of the unreinforced 2212 matrix (Goretta et al., 1993b).

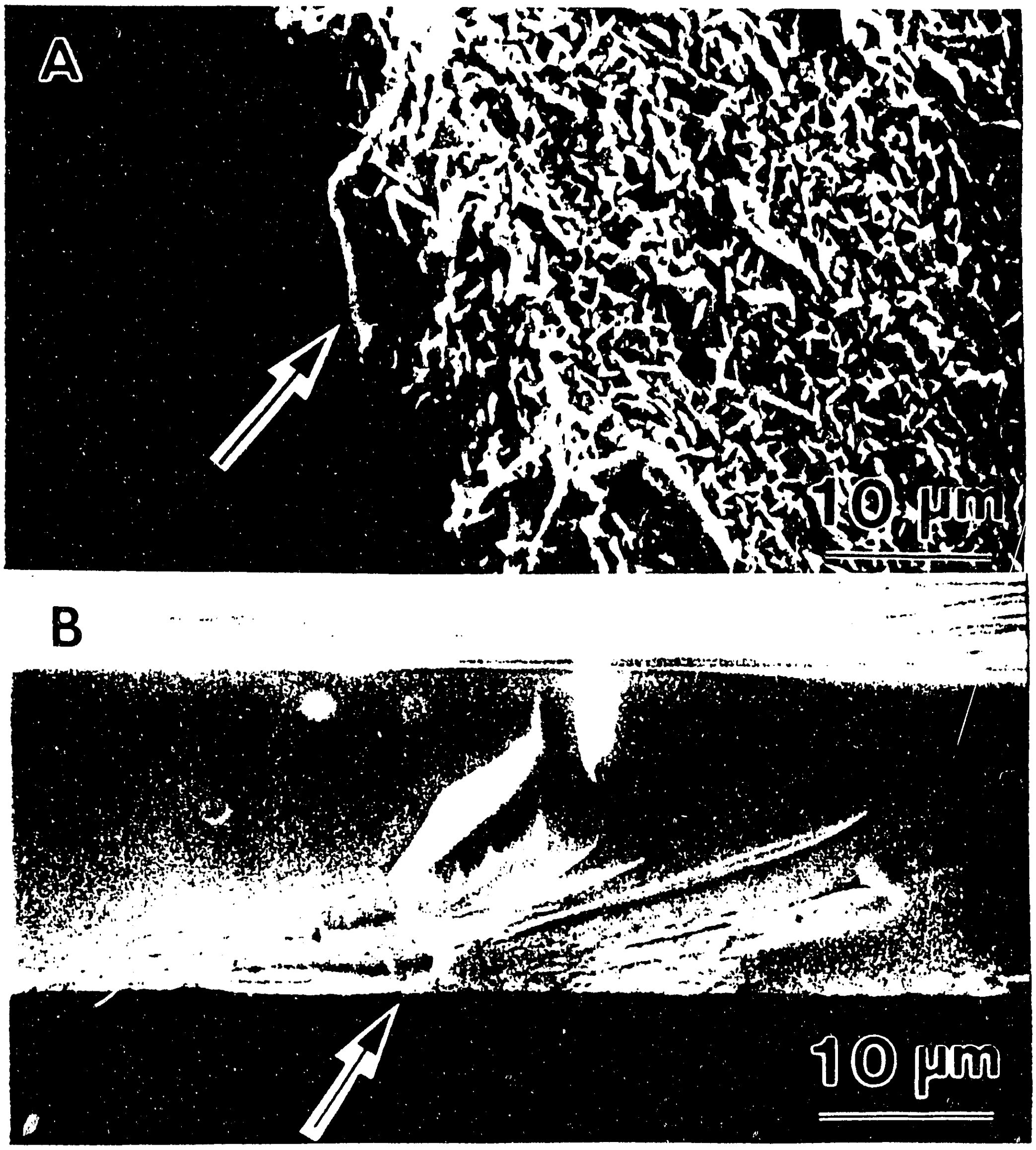

Figure 2. SEM photomicrographs of large heat-treated 2212 fiber: (a) side of fiber near failure (arrow), note fine grain size; and (b) fracture surface at initiation site (arrow).

The fibers were mixed in 15 vol.% concentrations with the matrix powders and isopropyl alcohol. They were blended either by ball milling with ZrO_2 media for 2 h or by ultrasonic agitation for 1 h. Ball milling reduced the fiber lengths substantially, but most of the fibers remained longer than 50 μm. The mixed powders were pan dried and cold pressed into bars.

The 123/211 bars were sintered in air for 4 h at 990°C. The final densities were 90–91% of theoretical. Unreinforced and reinforced 2212 bars were sinter forged in air at 840°C. Compression rates were 0.001–0.01 mm/min and the total deformation time was ≈3 h. Final densities were ≈90% of theoretical.

Strengths were measured in four-point bending. The inner and outer load spans were 9.6 and 19.2 mm, respectively. The tensile surfaces of the bars were polished to a 1μm finish. Fracture toughness (K_{IC}) was measured by indentation for the 123/211 bars (Evans and Charles, 1976) and by the single-edge notched beam method for the 2212 (Brown and Srawley, 1967). Details of the testing procedures can be found in Chu et al. (1992) and Goretta et al. (1993b). Indentation was chosen for 123/211 because of the large amount of data available for pure 123 (Alford et al., 1990; Ochiai et al., 1988; Goyal et al., 1992). This method could not be used for the 2212 bars, however, because of inability to generate consistent cracks at the corners of the indentation.

Small pieces were cut from the processed bars and transport J_c was measured with a 1 μV/cm criterion. The 123/211 was measured at 77 K, the 2212 and 2212/2212 at 4.2 K. The 123/211 bars were annealed in O_2 at 450°C prior to testing.

RESULTS AND DISCUSSION

Data for strength and K_{IC} are summarized in Table 1. For these sets of samples, which were all ≈90% dense, the fiber additions imparted modest improvements. Critical current densities were all rather low. The 123 and 123/211 bars had values at 77 K of ≈200 A/cm^2, which is typical of bulk 123. The 2212 and 2212/2212 had values at 4.2 K of 100–500 A/cm^2. It is unknown why the current carrying capacities of the sinter-forged 2212 bars were so low. Similarly processed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223) bars have attained J_c values at 77 K of 3000–8000 A/cm^2 (Chen et al., 1993).

Table 1. Summary of property data for monolithic and fiber/composite bars.

Sample	Strength [MPa]	K_{IC} [MPa(m)$^{0.5}$]
123	100–120	1.4 ± 0.4
123/211	100 ± 30	1.9 ± 0.3
2212	80–105	1.5 ± 0.3
2212/2212	102–113	1.8 ± 0.4

SEM of fracture surface failed to reveal evidence of significant fiber pullout. It is most likely that the small improvements in strength and toughness can be attributed to crack bridging and crack deflection. It is noted that none of these samples achieved either a strength or toughness that was more than about half the record values for these materials. The highest strengths in bulk 123 (Goretta et al., 1993a) and 2212 (Alford et al., 1990) were obtained on fine, plastically extruded wires. Viscously processed ceramics generally have relatively small flaws and thus high strengths (Alford et al., 1986). The flaws in cold-pressed compacts are generally much larger. Some of the problems with the samples of this study are undoubtedly related to the fact that they were only about 90% dense and that their flaws tended to be rather large. A disadvantage of fiber additions is that their presence retards densification during processing. Relatively large flaws may result. As second problem was breakage of the fibers during processing (this was observed by SEM). Clearly, as the fiber length approaches the grain size, little benefit from fiber addition can be realized.

The fibers used in this work were experimental. Improvements in uniformity, strength, and length can be achieved. If these improvements can be made and the fibers can be produced economically, composites of the type studies here may have some application. It seems to be unlikely, however, that high-J_c composites of this type can be made because of the limitations on J_c in conventionally sintered high-temperature superconductors (Jin and Graebner, 1991). It may be possible to use fibers in partial-melt processing in which strong textures and good J_c values are obtained.

Recent work on fully dense, sinter-forged 2212 and 2223 bars has confirmed that strength and toughness are strong functions of density (Martin, 1993). For dense bars, strengths for both materials were 140–150 MPa and K_{IC} values were 3 MPa. We have yet to succeed in making fully dense composites, and thus direct comparisons of data cannot be made.

CONCLUSIONS

Addition of 15 vol.% 211 fibers to 123 and 15 vol.% 2212 fibers to 2212 improved the strength and fracture toughness in each case. The increases in strength and toughness were, however, relatively modest. Longer, more uniform fibers must be developed before substantial additional improvements can be realized.

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