Carbon fiber reinforced tin-superconductor composites

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(Received 14 February 1989; accepted 6 July 1989)

Unidirectional and continuous carbon fiber tin-matrix composites were used for the packaging of the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ by diffusion bonding at 170 °C and 500 psi. Tin served as the adhesive and to increase the ductility, the normal-state electrical conductivity, and the thermal conductivity. Carbon fibers served to increase the strength and the modulus, both in tension along the fiber direction and in compression perpendicular to the fiber layers, though they decreased the strength in compression along the fiber direction. Carbon fibers also served to increase the thermal conductivity and the thermal fatigue resistance. At 24 vol. % fibers, the tensile strength was approximately equal to the compressive strength perpendicular to the fiber layers. With further increase of the fiber content, the tensile strength exceeded the compressive strength perpendicular to the fiber layers, reaching 134 MPa at 31 vol. % fibers. For fiber contents less than 30 vol. %, the compressive ductility perpendicular to the fiber layers exceeded that of the plain superconductor. At 30 vol. % fibers, the tensile modulus reached 15 GPa at room temperature and 27 GPa at 77 K. The tensile load was essentially sustained by the carbon fibers and the superconducting behavior was maintained after tension almost to the point of tensile fracture. Neither T_c nor J_c was affected by the composite processing.

I. INTRODUCTION

The high T_c superconductors are brittle, hard to shape, and high in normal-state electrical resistivity. On the other hand, metals are in general ductile, formable, and have low electrical resistivity and high thermal conductivity. In contrast to metals, polymers in general have high electrical resistivity and low thermal conductivity. Therefore, the combination of a superconductor and a metal in the form of a composite[1–4] is more attractive than the combination of a superconductor and a polymer.[5]

Powder metallurgy has been used by a number of workers to fabricate superconductor-metal composites.[1–4] This method involves mixing superconductor powder and metal powder and then sintering[1–3] or mixing metallic Y, Ba, Cu, and Ag and oxidizing. The main drawback of this method includes the following:

(a) The metal content is limited to 50 vol. % or below in order to have a continuous superconducting path in the composite. This limits the ductility of the composite.

(b) The choice of metal is limited to metals that are stable at the sintering temperature in oxygen and do not react with the superconductor at the sintering temperature (typically 950 °C for $YBa_2Cu_3O_{7-\delta}$).

Yet another method that has been used in forming a superconductor-metal composite involves (i) packing a superconductor powder in a metal tube, (ii) drawing the tube to a smaller diameter, and (iii) sintering.[6–8] The main drawback of this technique is that the choice of metal is limited to metals that are stable at the high sintering temperature required by the superconductor.

In this paper, we have developed a diffusion bonding technique for fabricating superconductor-metal composites. This method solves both of the problems described above for powder metallurgy and metal tube drawing.

Because brittle ceramics are much stronger in compression than in tension, it is necessary to strengthen the composite further, particularly in tension. For this purpose, we have used carbon fibers, because carbon fibers are very strong (especially in tension). They have a nearly zero thermal expansion coefficient (valuable for thermal fatigue resistance), very high thermal conductivity (better than copper), and quite low electrical resistivity and are corrosion resistant. We report here that carbon fiber reinforced tin-superconductor composites provide an effective way of packaging ceramic superconductors (in bulk, film, or wire form) so that the package exhibits good mechanical, electrical, and thermal properties, for applications in superconducting cables or tapes. The high strength will be particularly valuable for applications under high magnetic field. The fabrication and characterization of these composites are presented in Secs. II and III.

II. FABRICATION

The superconductor was $YBa_2Cu_3O_{7-\delta}$. It was prepared by pressing $YBa_2Cu_3O_{7-\delta}$ powder (W. R. Grace and Co., Davison Chemical Division, super T_c-123, code: S-001) at a pressure of 137 MPa and then sintering at 950 °C for 12 h, followed by annealing at 420 °C in flowing oxygen for 1 h.

The tin used was in the form of foils (Fisher Scientific Co.) containing at least 99.8 wt. % Sn.

The carbon fibers used were continuous, PAN-based (Celion GY-70) and sized, with a tensile modulus of 517 GPa, a tensile strength of 1862 MPa, and a tensile ductility of 0.36%. (Desized fibers were found to give similar results as the sized fibers.)

The carbon fiber reinforced tin-superconductor composite was prepared by using a two-step process. The first step involved the preparation of a tin-matrix unidirectional carbon fiber composite (abbreviated MMC) by laying up carbon fibers and tin foils in the form of alternate layers and consolidating by hot pressing (by using a hydraulic press) at 5 °C above the melting temperature of tin and at a pressure in the range from 8000 to 10 000 psi (from 55 to 69 MPa) for 10–20 s. The minimum pressure for the first step is about 55 MPa. The second step involved hot pressing a layer of superconductor sandwiched by two layers of MMC at 170 °C and 500 psi (4 MPa) for 15 min in order to achieve diffusion bonding. Note that 170 °C is below the melting point of tin (232 °C). The minimum temperature for the second step is 150 °C for composites containing carbon fibers and 100 °C for those containing no carbon fibers. The minimum pressure for the second step is about 500 psi (4 MPa).

III. CHARACTERIZATION

Figure 1 shows the optical micrograph of a portion of a polished section of a Sn–$YBa_2Cu_3O_{7-\delta}$–Sn three-layer composite containing 33.3 vol. % Sn (no carbon fibers). The bright region is Sn; the dark region is $YBa_2Cu_3O_{7-\delta}$. As shown in Fig. 1, no void or crack was observed between the tin and the superconductor, even though the superconductor surface was rough.

The toughness was measured by carrying out the Izod Test using a Tinius Olsen plastic impact tester. The toughness was 3.25 in. lb for a composite containing 18.8 vol. % Sn (no fibers) and was 5.50 in. lb for a composite containing 25.5 vol. % Sn (no fibers). Hence, the tin greatly enhanced the toughness.

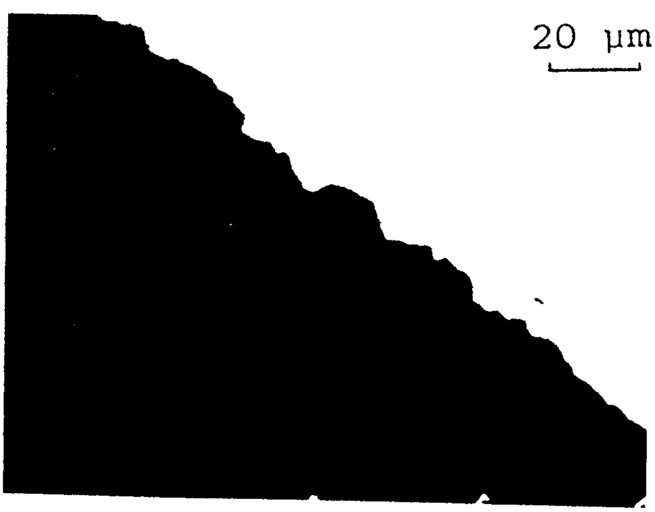

FIG. 1. Optical micrograph of a portion of a polished section of an Sn–$YBa_2Cu_3O_{7-\delta}$–Sn three-layer composite containing 33.3 vol. % Sn. The bright region is tin; the dark region is $YBa_2Cu_3O_{7-\delta}$.

Figure 2 shows a scanning electron microscope (SEM) photograph of a portion of a polished section of an MMC–$YBa_2Cu_3O_{7-\delta}$–MMC three-layer composite containing 32.1 vol. % fibers and 50.2 vol. % Sn. The left half of the photograph is the MMC; the right half is the superconductor. No void or crack was observed between the MMC and the superconductor or between the tin and the carbon fibers in the MMC.

Figure 3 shows the dependence of the electrical resistivity on temperature for the plain superconductor (solid

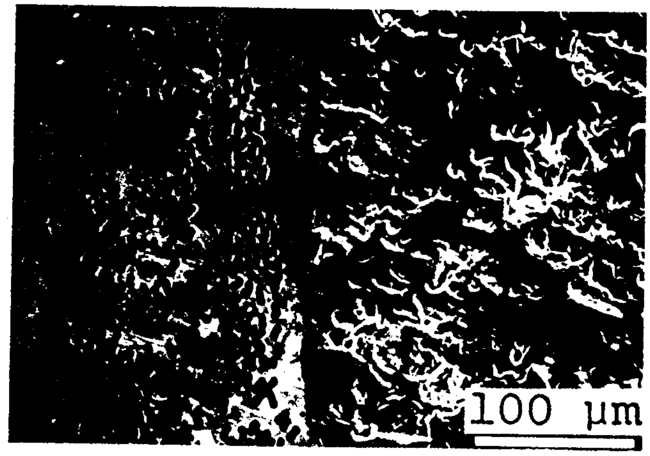

FIG. 2. SEM photograph of a portion of a polished section of an MMC–$YBa_2Cu_3O_{7-\delta}$–MMC three-layer composite containing 32.1 vol. % fiber and 50.2 vol. % Sn. The left half is the MMC; the right half is the superconductor. The dumbbells in the MMC are the tips of carbon fibers.

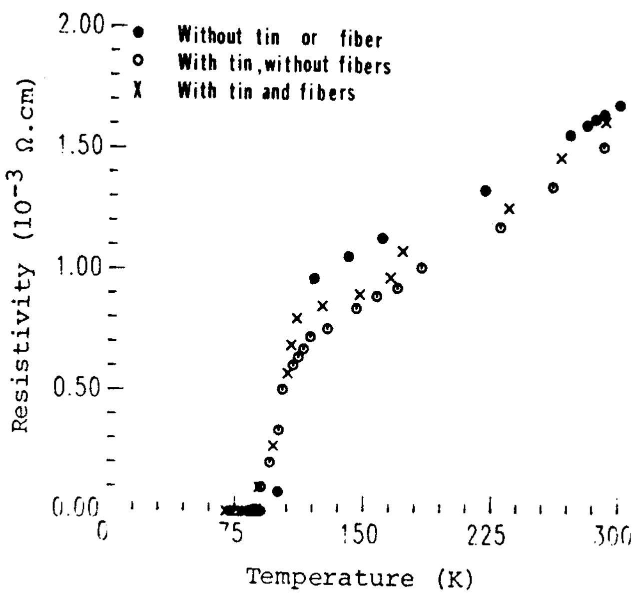

FIG. 3. Dependence of the electrical resistivity on temperature for the plain superconductor (solid circles), for a composite containing 80.1 vol. % Sn and no fibers (open circles), and for a composite containing 32.1 vol. % fibers and 50.2 vol. % Sn (crosses).

circles), for a composite without fibers but containing 80.1 vol. % Sn (open circles), and for a composite containing 32.1 vol. % fibers and 50.2 vol. % Sn (crosses).

The electrical resistivity was measured with the four-probe technique by using a Keithley 181 nanovoltmeter and a Keithley 224 programmable current source, such that the current was around 10^{-3} A. A thermocouple was placed so that it almost touched the sample. In the case of composites containing fibers, the electrical resistivity was measured in the direction of the fibers. (However, the electrical resistivity in the direction perpendicular to the fiber axis was comparable to that in the direction parallel to the fibers.) The critical temperature T_c is essentially the same for the plain superconductor and either composite, though the drop to zero resistivity is slightly less sharp for either composite than the plain superconductor. Carbon fibers have a lower electrical resistivity than the plain superconductor above T_c, but its value is higher than that of tin. Therefore, the normal-state electrical resistivity of the composite with tin and fibers is lower than that of the plain superconductor and higher than that of the composite with tin and no fiber.

The critical current density J_c was measured at 40 K. Its value was determined by taking the slope of the current-voltage plot at 0.1 μV and extrapolating this slope to zero volt. Table I lists the J_c values obtained for the plain superconductor (1.13 mm thick), a composite containing 37 vol. % superconductor (1.82 mm thick), and 63 vol. % tin (3.13 mm thick), and a composite containing 19 vol. % superconductor (1.21 mm thick), 51 vol. % tin, and 30 vol. % carbon fibers (4.81 mm thick for the MMC). The J_c values are typical of those of superconductors prepared by the sintering of powders. Table I shows that the composite processing does not degrade J_c.

Mechanical testing was performed using a hydraulic Materials Testing System (MTS). The strain in compressive testing was measured by the displacement of the crosshead. The strain in tensile testing was measured by using a strain gauge (Measurements Group, Inc., gauge type EA-13-120LZ-120, resistance = 120.0 (±0.3%) ohms, gauge factor = 1.095 ± 0.5% at 75 °F). The gauge length was 34.7 mm for tensile testing and 6 mm for compressive testing. Compressive testing was performed with the force perpendicular to the laminate layers and with the force along the fiber direction. Tensile testing was performed with the force parallel to the fibers in the plane of the laminate. At least three samples were run and the data were averaged for each composite composition in each type of test.

TABLE I. Critical current densities (J_c).

Material	J_c (A/mm^2)[a]
Superconductor	1.47
Superconductor + tin	1.45
Superconductor + MMC	1.44

[a]Each number is the average of three samples, with a data scatter of ±2%.

Figure 4 shows the compressive stress-strain curves (up to fracture) for a composite containing tin (24 vol. % Sn) but no fibers (open circles) and a composite containing 51.1 vol. % Sn and 26.2 vol. % fibers (solid circles).

Figure 5 shows the effect of tin content on the compressive ductility of composites without fibers. Tin greatly increased the ductility. Figure 6 shows the effects of both

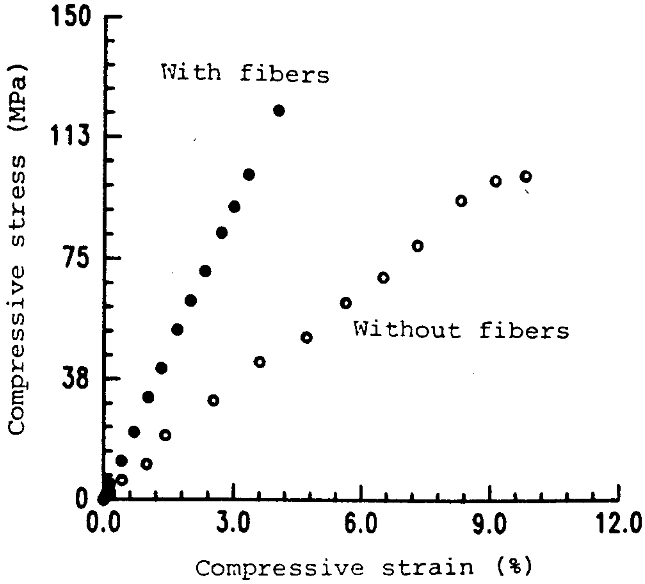

FIG. 4. Compressive stress-strain curves (up to fracture) for a composite without fibers (24 vol. % Sn) (open circles) and a composite with fibers (51.1 vol. % Sn and 26.2 vol. % fibers) (solid circles).

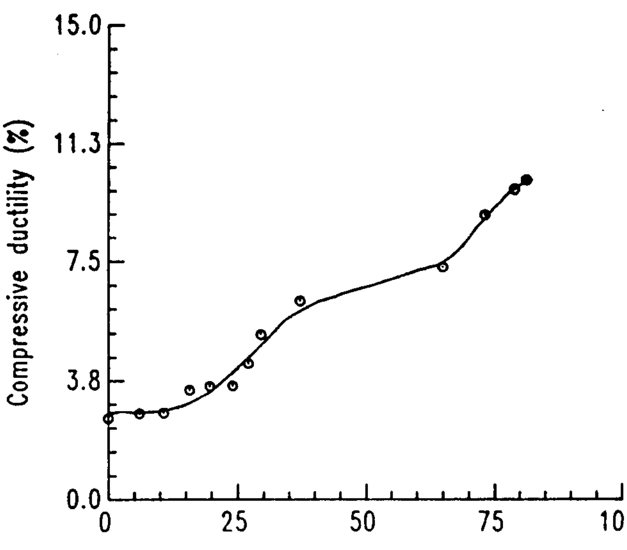

FIG. 5. Effect of tin content on the compressive ductility of composites without carbon fibers; each data point is the average value for three samples and the scatter is ±7%.

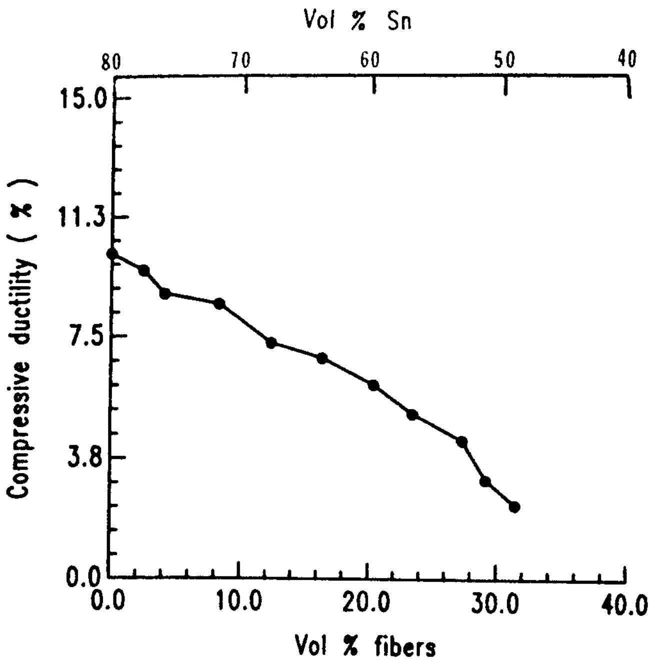

FIG. 6. Effects of tin and fiber contents on the compressive ductility; each data point is the average value of three samples and the scatter is ±5%.

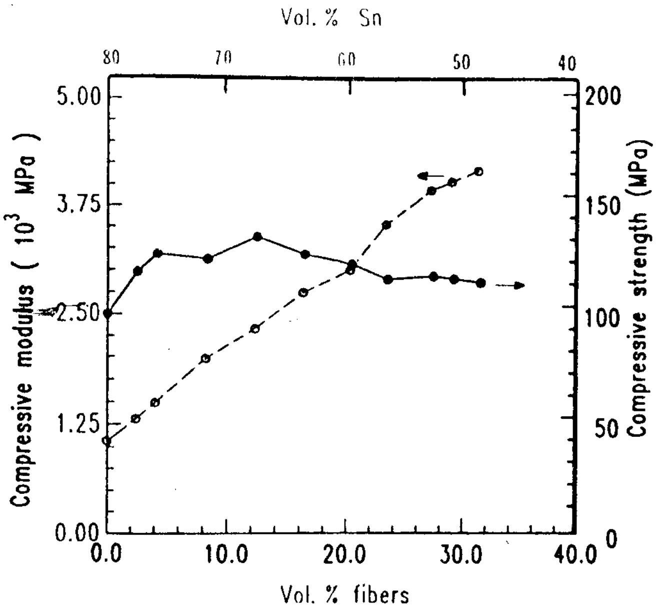

FIG. 8. Effects of tin and fiber contents on the compressive elastic modulus; each data point is the average value of three samples and the scatter is ±8%. Effects of tin and fiber contents on the compressive strength; each data point is the average value of three samples and the scatter is ±9%.

fiber and tin contents on the compressive ductility. Tin greatly increased the ductility, but the fibers decreased the ductility.

Figure 7 shows an SEM photograph of the compressive fracture surface of a composite containing 19.5 vol. % Sn and no fiber. The right one-third of the photograph is tin; the left two-thirds of the photograph is the superconductor. Cracks are observed to extend from the tin/superconductor interface inward into the superconductor. We observed a similar fracture in a composite with both fibers and tin. In contrast, the plain superconductor (without tin or fiber) shatters and disintegrates into particles upon fracture. Hence, the fracture behavior is dramatically different between either composite and the plain superconductor.

Figure 8 shows the effects of both tin and fiber contents on the compressive elastic modulus and compressive strength. The decrease of the modulus with increasing tin content and decreasing fiber content is significant. For the compressive strength, no systematic trend was found, because the strength is very sensitive to small flaws that are bound to be present in the superconductor.

Figure 9 shows the tensile stress-strain curves (up to fracture) for a composite containing tin (24 vol. % Sn)

FIG. 7. SEM photograph of the compressive fracture surface of a composite containing 19.5 vol. % Sn and no fibers. The right one-third of the photograph is tin; the left two-thirds of the photograph is the superconductor.

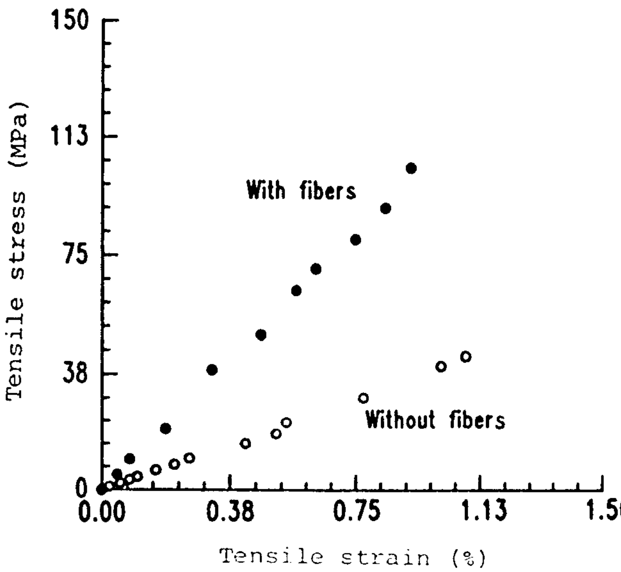

FIG. 9. Tensile stress-strain curves (up to fracture) for a composite without fibers (24 vol. % Sn) (open circles) and a composite with fibers (51.4 vol. % Sn and 27.2 vol. % fibers) (solid circles).

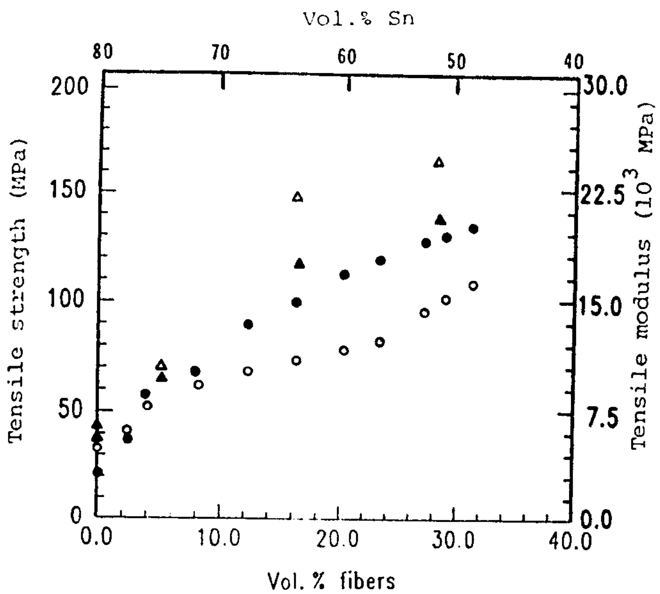

FIG. 10. Effects of tin and fiber contents on the tensile strength at room temperature (●) and 77 K (▲); each data point is the average value of three samples and the scatter is ±8%. Effects of tin and fiber contents on the tensile modulus at room temperature (○) and 77 K (△); each data point is the average value of three samples and the scatter is ±7%.

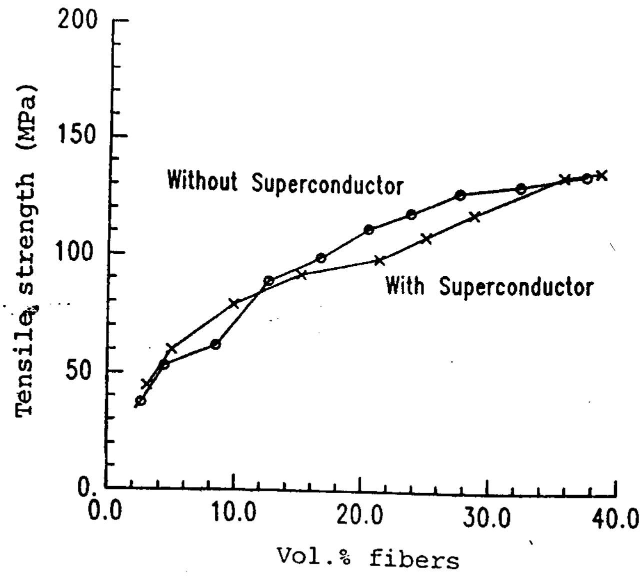

FIG. 12. The dependence of the tensile strength on the carbon fiber content in vol. % fibers, such that the volume of the superconductor is not counted in calculating the vol. % fibers. Circles: without superconductor (MMC alone); crosses: with superconductor. Each data point is the average of three samples and the scatter is ±9% for points indicated by both circles and crosses.

but no fibers (open circles) and a composite containing 51.4 vol. % Sn and 27.2 vol. % fibers (solid circles).

Figures 10 and 11 show the effects of tin and fiber contents on the tensile test results. The tensile test was performed along the fiber direction. The addition of carbon fibers greatly improved the tensile strength (Fig. 10), but decreased the ductility slightly (Fig. 11). The tensile modulus was increased by increasing the fiber content. Debonding between the MMC and the superconductor and some fiber pull-out were observed from the fracture surface after the tensile test.

Figures 12, 13, and 14 show the effects of the superconductor on the tensile test results. Data obtained with

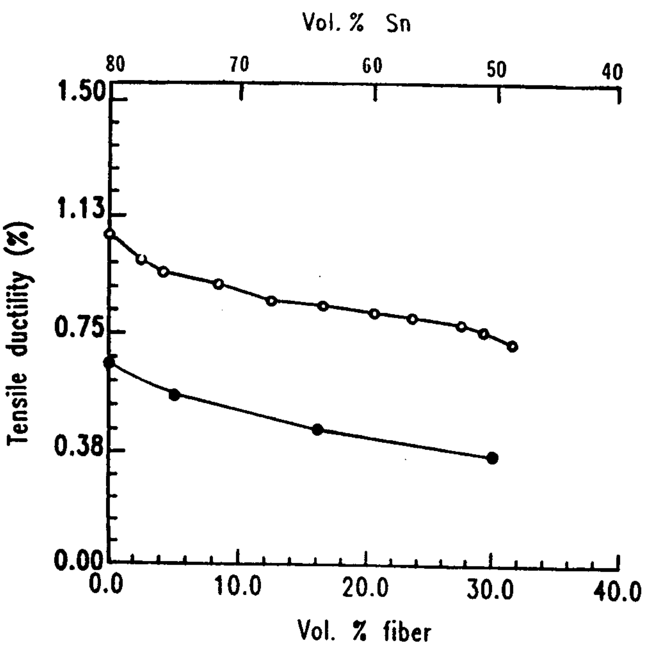

FIG. 11. Effects of tin and fiber contents on the tensile ductility at room temperature (○) and 77 K (●); each data point is the average value of three samples and the scatter is ±5%.

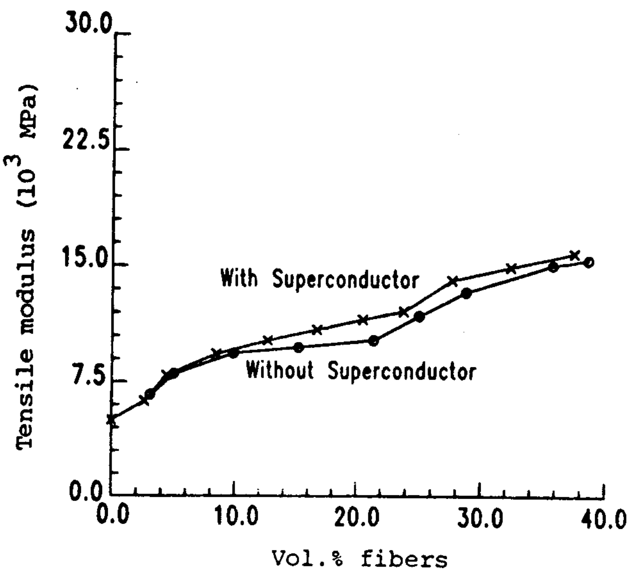

FIG. 13. The dependence of the tensile modulus on the carbon fiber content in vol. % fibers, such that the volume of the superconductor is not counted in calculating the vol. % fibers. Circles: without superconductor (MMC alone); crosses: with superconductor. Each data point is the average of three samples and the scatter is ±8% for points indicated by circles and ±7% for points indicated by crosses.

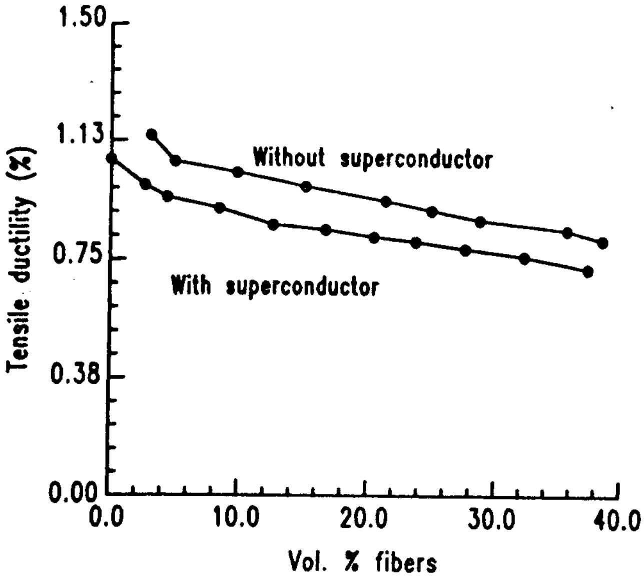

FIG. 14. The dependence of the tensile ductility on the carbon fiber content in vol. % fibers, such that the volume of the superconductor is not counted in calculating the vol. % fibers. Circles: without superconductor (MMC alone); crosses: with superconductor. Each data point is the average of three samples and the scatter is ±6% for points indicated by circles and ±5% for points indicated by crosses.

the presence of the superconductor (in the form MMC-superconductor-MMC) are shown by circles. Data obtained with the absence of the superconductor (i.e., MMC alone) are shown by crosses. The horizontal scale of Fig. 12, 13, or 14 shows the vol. % fibers such that the volume of the superconductor was not counted in the volume of the composite. (Note that this scale is different from the horizontal scale of Fig. 5, 6, 8, 10, or 11, in which the volume of the superconductor was counted in calculating the volume percent fibers.) The similarity of data with and without the superconductor in Figs. 12 and 13 shows that the tensile load was almost totally sustained by the MMC. Figure 14 shows that the tensile ductility is somewhat diminished by the presence of the superconductor.

The tensile test for the plain superconductor (without tin or fibers) did not give very reliable results because of the difficulty of gripping the superconductor, which was hard in the absence of tin. Nevertheless, the tensile strength was about 5.2 MPa, the tensile modulus was roughly 1.3 GPa, and the tensile ductility was roughly 0.5%.

A composite containing 31.0 vol. % fibers and 50.2 vol. % tin was subjected to tension up to a tensile stress of 90.6 MPa and a tensile strain of 0.57% (below the stress or strain required for fracture) and then the load was released (allowing the strain to return to essentially zero) and the electrical resistivity was measured as a function of temperature. It remained superconducting, with $J_c = 1.41\ \mathrm{A/mm^2}$.

Composites containing from 0 to 30 vol. % fibers were subjected to compression along the fiber direction. Table II shows the compressive strength, modulus, and ductility thus obtained. The compressive failure was due to delamination at the interface between the superconductor and the tin (or MMC). The presence of the fibers decreased the compressive strength, showing that the fibers weakened the bonding between the superconductor and the tin (or MMC). The presence of the fibers increased the compressive modulus slightly and decreased the compressive ductility slightly.

Comparison of Table II and Fig. 8 shows that the compressive strength and modulus values perpendicular to the fiber direction are higher than those along the fiber direction for the same volume percent fibers. Comparison of Table II and Fig. 6 shows that the compressive ductility along the fiber direction is lower than that perpendicular to the fiber direction for the same volume percent fibers.

Composites of various fiber contents were subjected to thermal cycling between room temperature and liquid nitrogen temperature (77 K) by immersion in liquid nitrogen for 20 min, followed by room temperature equilibration for at least 30 min, and repeating. After every cycle, each specimen was observed under an optical microscope to look for delamination (slight cracking) between the superconductor and the MMC. Table III shows the number of cycles for the start of delamination for each composite composition. The higher was the carbon fiber content, the greater was the number of cycles for the start of delamination.

Because the superconductors are used at liquid nitrogen temperature (77 K) in practice, the mechanical properties of the composites were tested at 77 K also. The tensile testing was performed using the same materials testing system at the same strain rate. However, the sample was held with a fixture (OSW-1, Comten Industries), with very severely serrated wedges, that was a positive clamp, becoming tighter as force was applied. The fixture and the sample

TABLE II. Mechanical properties of superconducting composites upon compression along the fiber direction.

Carbon fiber content (%)	Sn content (%)	Compressive strength (MPa)	Compressive modulus (GPa)	Compressive ductility (%)
0	54.7	87.12	2.35	3.63
0	62.3	91.12	2.29	3.91
3.0	52.1	71.82	2.46	3.42
7.0	54.3	73.63	2.49	3.32
30.1	51.3	66.23	2.53	3.24

TABLE III. Thermal fatigue due to cycling between room temperature and liquid nitrogen temperature.

Carbon fiber content (vol. %)	Sn content (vol. %)	No. of cycles for delamination to start[a]
0	43.2	63 (±4%)
3.0	39.4	86 (±3%)
8.3	40.1	102 (±5%)
12.0	43.1	116 (±2%)
15.3	48.3	123 (±5%)
20.1	50.2	127 (±2%)

[a]Each number is the average of three specimens.

were completely immersed in the liquid nitrogen in a cryostat during the testing. The results are shown in Figs. 10 and 11, where each data point is the average of those of three specimens. The modulus was significantly increased while the strength was slightly increased when the temperature was lowered from room temperature to 77 K (Fig. 10). The ductility was decreased when the temperature was lowered from room temperature to 77 K (Fig. 11). In particular, with 29.4 vol. % fibers and 50.3 vol. % Sn, the tensile strength was 140.7 MPa, the modulus was 26.4 GPa, and the ductility was 0.40%. This effect of temperature is attributed to the effect of temperature on the mechanical properties of carbon fibers and of tin, both of which have higher moduli at 77 K than room temperature. These results show that the superconducting composites are mechanically sound at 77 K.

IV. DISCUSSION

Comparison of Figs. 8 and 10 shows that, without fibers, the tensile strength (parallel to the fiber direction) was much less than the compressive strength (perpendicular to the fiber layers), but with about 24 vol. % fibers, the tensile strength was approximately equal to the compressive strength. With further increase of the fiber content, the tensile strength exceeded the compressive strength.

The tensile strength of the plain superconductor was roughly 5.2 MPa. The presence of tin (without fibers) increased the value to about 20 MPa (Fig. 10). Further addition of carbon fibers significantly increased the tensile strength, up to 134 MPa for 31 vol. % fibers at room temperature and 141 MPa for 29 vol. % fibers at 77 K. The tensile modulus was 16 GPa at room temperature for 31 vol. % fibers and was 26 GPa at 77 K for 29 vol. % fibers.

Carbon fibers increased the compressive strength and compressive modulus perpendicular to the fiber layers, and also increased the tensile strength, tensile modulus, and compressive modulus along the fiber direction, but they decreased the compressive ductility perpendicular to the fiber layers, the compressive strength and ductility along the fiber direction, and the tensile ductility. However, because tin was also present and tin is a soft metal, the compressive ductility perpendicular to the fiber layers for the case of 31 vol. % fibers was approximately equal to that for the plain superconductor (without tin or fiber). For carbon fiber contents less than 30 vol. % fibers, the compressive ductility perpendicular to the fiber layers exceeded that of the plain superconductor. In general, the carbon fibers decreased the tensile ductility (Fig. 11) and the compressive ductility along the fiber direction (Table II) much less than the compressive ductility perpendicular to the fiber layers (Fig. 6).

The superconducting behavior (T_c and J_c) of the composites was maintained after tension almost to the point of tensile fracture.

The fabrication of the composites involved low temperatures. The simplicity of this process makes it possible for an operation to be set up for fabricating continuous superconducting cables which are both shielded and toughened by tin and strengthened by carbon fibers. In contrast to powder metallurgy, the diffusion bonding method allows the metal to be the major phase while still maintaining a continuous superconducting path in the composite. Furthermore, carbon fibers, with their nearly zero thermal expansion coefficient, help match the thermal expansion coefficients of the MMC layer and the superconductor layer. This matching is necessary in order to enhance the durability of the composite to thermal cycling (i.e., thermal fatigue). In addition, carbon fibers are excellent in thermal conductivity (both at ambient and cryogenic temperatures), wear resistance and corrosion resistance, and are low in electrical resistivity.

The process described in this paper can be applied to package multiple layers of ceramic superconductors (separated by tin) in bulk, film, or wire form, although only a single layer of bulk superconductor was used here. It can also be applied to package superconductor-metal composites prepared by powder metallurgy and to package superconductors prepared by melt texturing or other techniques. Low temperature metals other than tin (such as tin-lead, indium, etc.) can also be used.

V. CONCLUSION

The combination of tin and continuous carbon fibers was found to be effective for packaging ceramic superconductors so as to render them mechanically durable and electrically and thermally stable, with no degradation of T_c or J_c. The process involved diffusion bonding of the superconductor between two layers of a tin-matrix carbon fiber composite. Tin served as the adhesive and also served to increase the ductility, the normal-state electrical conductivity, and the thermal conductivity. Carbon fibers served to increase the strength and the modulus, both in tension (parallel to the fibers) and in compression (perpendicular to the fiber layers); they also served to increase the thermal conductivity and the thermal fatigue resistance. The tensile load was essentially sustained by the carbon fibers, and the superconducting behavior was maintained after tension almost to the point of fracture.

ACKNOWLEDGMENTS

The authors are grateful to Mr. Shy-Wen Lai of SUNY/Buffalo and Mr. Scott Cooper of Union Carbide Corp. (Linde Division) for technical assistance. This research was supported by an award from the New York State Institute on Superconductivity in conjunction with the New York State Energy Research and Development Authority.

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