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# Sandwiching of superconductor by carbon fibre metal matrix composite for improving the mechanical properties, air stability and thermal cycling resistance

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The sandwiching of $YBa_2Cu_3O_{7-\delta}$ by two layers of continuous copper-coated carbon fibre Sn-Pb matrix composite was found to (i) increase the tensile and compressive strengths in the direction parallel to the fibres, such that both strengths increased with increasing fibre volume fraction, (ii) increase the resistance to thermal cycling between room temperature and 77 K and (iii) increase the stability in air. The sandwich composites were made by diffusion bonding at 110°C and 0.34 MPa, or by hot roll bonding at 240°C and 7.0 cm $s^{-1}$. Copyright © 1996 Elsevier Science Limited

**(Keywords: superconductor; metal matrix composite; sandwich; carbon fibre; tin; lead; $YBa_2Cu_3O_{7-\delta}$; mechanical properties; air; stability; thermal cycling)**

## INTRODUCTION

As for ceramics in general, the ceramic superconductors are mechanically poor, especially under tension. The desire for a large grain size for the sake of a high critical current density ($J_c$) worsens the mechanical problem. For ceramic superconductors in the form of films supported by substrates, the substrates provide strengthening. For bulk superconductors (such as those made by sintering), the strengthening requires composite material development, which is complicated by (i) the tendency of the superconductor to have its superconducting properties (e.g. $J_c$) degraded after heating to moderate temperatures (e.g. 200°C) due either to oxygen loss or reaction with the surrounding materials, (ii) the requirement that the superconducting phase be continuous, (iii) the requirement for easy cooling to 77 K or below (i.e. high thermal conductivity) and good resistance to thermal cycling between room temperature and 77 K (or below) and (iv) the need for reasonably high electrical conductivity when the superconductor happens to lose its superconductivity. These requirements point to a packaging material which (i) can be bonded to the superconductor at low temperatures (below about 200°C), (ii) is low in thermal expansion coefficient (as the superconductor has a low coefficient), (iii) is high in thermal conductivity and (iv) is high in electrical conductivity. These requirements are satisfied by a metal matrix composite with a low melting metal matrix and carbon fibres as the reinforcement. The sandwiching of a $YBa_2Cu_3O_{7-\delta}$ superconductor by two layers of a carbon fibre metal matrix composite has been previously shown to provide good mechanical properties and thermal cycling resistance, while retaining the superconducting properties of the superconductor[1]. The effect of the sandwiching on the air stability is also of interest, since the superconductor is inherently poor in its stability in air[2]. This paper shows for the first time that the sandwiching greatly improves the air stability. Furthermore, it provides an assessment of the effect of thermal cycling by mechanical testing before and after the cycling, in contrast to the previous use of microscopic crack observation to assess the effect of thermal cycling[1].

## EXPERIMENTAL

The superconductor was $YBa_2Cu_3O_{7-\delta}$. It was prepared from CuO 99% (Aldrich Chemical Company, Inc.), yttrium oxide 99.99% (Rare Earth Products) and $BaCO_3$ 99.79% (Fisher Scientific). The CuO was milled in a ball mill. Then $Y_2O_3$ was added to the mill and

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mixed with the CuO. After this, $BaCO_3$ was added to the mill and mixing was conducted for 2–3 h. The mixed powder was calcined in flowing oxygen at 935°C for 24 h to form a single phase $YBa_2Cu_3O_{7-\delta}$ powder. After calcination, the powder was ground and mixed. Then the powder was pressed into a pellet of 1 in diameter (25.4 mm) and 1 mm thickness. The pellet was then sintered in 1 atm oxygen at 940°C for 18 h. After sintering, the pellet was slowly cooled to 450°C under flowing oxygen over a period of 8 h and then held at 450°C for 1 h.

The carbon fibres used were continuous copper-coated carbon fibres provided by American Cyanamid Co. The uncoated carbon fibres were mesophase-pitch based graphite fibres (Thornel P-100 from Amoco Performance Products). The copper coating served to improve the wetting of the fibres by the molten Sn-Pb used to form the matrix of the composite. The coated fibre diameter was 15 $\mu$m, with the coating thickness being 2.5 $\mu$m, as shown by scanning electron microscopy (SEM) in the direction perpendicular to the fibre axis (*Figure 1a*) and in the direction parallel to the fibre axis (*Figure 1b*, in which the fibres have been embedded in a polymer mounting medium and polished). The surface of the coated fibre was granular, as shown in *Figures 1a, c,* and *d*. Some of the fibres had been partially broken, as shown in *Figures 1c* and *d*, which is a high magnification view of the cracked region of *Figure 1c*. As shown by single fibre tensile testing using a Sintech 2/D screw-type tester, the tensile strength of the coated fibres was 600 ± 120 MPa, based on the measurement of six separate fibres.

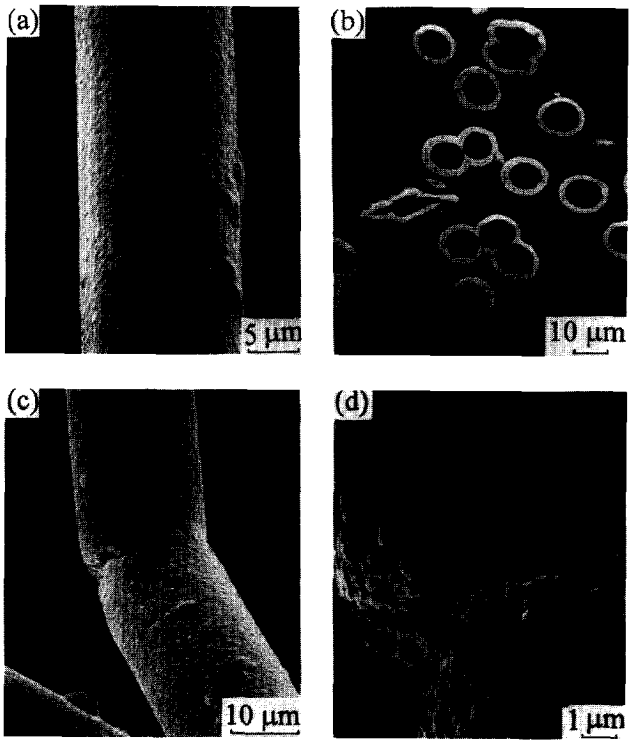


**Figure 1** SEM micrographs of: (a) single copper-coated carbon fibre in the direction perpendicular to the fibre axis; (b) a number of the fibres in the direction parallel to the fibre axis (with a polymer mounting medium between the fibres, so that the bright regions are the copper coating); (c) single copper-coated carbon fibre partially cracked by bending; (d) high magnification view of (c) at the cracked region

The metal alloy used as the matrix of the carbon fibre composite was Sn-Pb (60 wt% Sn, 40 wt% Pb). The composite (without the superconductor) was made by a modified form of squeeze casting, using a mould cavity of length 7.8 cm and width 2.1 cm. After washing the fibres consecutively in dilute hydrochloric acid, water (to remove the acid) and acetone (to remove the water), the fibres of length a little below 7.8 cm were placed along the length of the mould and then wetted with a solution of rosin (a binder as well as a flux) in acetone. Then the mould was heated on a hot plate at 200°C. Sn-Pb liquid at 280°C was poured into the mould while the mould was at 200°C. Then the mould was allowed to cool to room temperature. After that, the composite in the mould was consolidated further by heating it to 140°C and hot pressing at 27 MPa.

Composites with the superconductor (1 mm thick) sandwiched by two layers (1 mm thick each) of the Sn-Pb matrix composite were fabricated by diffusion bonding at 110°C (the minimum temperature for good diffusion bonding being 100°C) and 0.34 MPa for 24 h (the minimum time for good bonding), unless stated otherwise. Similar sandwich composites were fabricated by hot roll bonding at 240°C (the minimum temperature for good roll bonding) and a rolling speed of 7.0 cm $s^{-1}$. Hot rolling above 240°C caused excessive melting of the Sn-Pb matrix. In general, the sandwiching temperature and time were minimized so that the superconducting properties of the superconductor were not affected by the sandwiching. The advantage of hot roll bonding is in its ability to make continuous lengths of the sandwich composite, whereas diffusion bonding is limited to composites of size less than the platen size of the hot press.

$T_c$ and $J_c$ (77 K) were measured using a conventional four-probe method with a 1 $\mu$V $cm^{-1}$ criterion. Mechanical testing was conducted under tension and compression, with the force along the fibre direction in both cases. The compressive testing provides information related to the adhesion between the adjacent layers in the three-layer sandwich. The tensile testing provides information related to the reinforcing ability of the carbon fibres, as the superconductor itself is much weaker under tension than compression. No strain gauge was used.

## RESULTS

*Tables 1* and *2* give the tensile and compressive properties of the sandwich composites as well as the plain composite (without the superconductor) and the plain superconductor. The plain superconductor was extremely weak under tension (*Table 1*) and quite weak under compression (*Table 2*). The sandwiching greatly increased the tensile and compressive strengths, such that both strengths

**Table 1** Tensile properties

| | Sn-Pb content (vol.%) | Fibre content (vol.%) | Superconductor content (vol.%) | Tensile strength (MPa) | |
|---|---|---|---|---|---|
| | | | | Measured | Calculated[a] |
| Plain composite | 70 | 30 | 0 | 64 ± 5 | 218 |
| Sandwich A | 48 | 20 | 32 | 53 ± 3 | 147 |
| Sandwich B | 51 | 17 | 32 | 45 ± 3 | 128 |
| Plain superconductor | 0 | 0 | 100 | 7.8 ± 1 | – |

[a] Based on the rule of mixtures, with the tensile strengths of the superconductor, Sn-Pb and fibres being 7.8, 52.5 and 600 MPa, respectively

**Table 2** Compressive properties

| | Sn-Pb content (vol.%) | Fibre content (vol.%) | Superconductor content (vol.%) | Compressive strength (MPa) |
|---|---|---|---|---|
| Plain composite | 60 | 40 | 0 | 116 ± 5 |
| Sandwich C | 41 | 27 | 32 | 111 ± 4 |
| Sandwich A | 48 | 20 | 32 | 82 ± 4 |
| Plain superconductor | 0 | 0 | 100 | 39 ± 3 |

increased with increasing fibre volume fraction. Both strengths were slightly lower for the sandwich composites than the plain composites. The measured tensile strength was much lower than the calculated value based on the rule of mixtures, because the fibres were not exactly straight. Nevertheless, the measured tensile strength was much higher than that of the plain superconductor. The high value of the compressive strength (even higher than the tensile strength) of the sandwich composites indicates that the adhesion between adjacent layers in the three-layer sandwich composite was excellent. SEM observation of the tensile fracture surface of the sandwich composite shows the absence of delamination between the layers of the sandwich (*Figure 2a*), but severe fibre pull-out (*Figure 2b*).

*Table 3* gives the effect of 100 cycles of thermal cycling between room temperature and 77 K on the compressive strength. The compressive strength was decreased by 56% after cycling for the plain superconductor, but was decreased by 13–16% after cycling for the sandwich composites. These decreases are due to the temperature gradient and the resulting thermal stress and thermal fatigue. The improvement in thermal cycling resistance due to the sandwiching is attributed to the decreased temperature gradient within the superconductor when the superconductor was sandwiched. The good thermal cycling resistance of the sandwich composites is partly due to the reduction of the coefficient of thermal expansion (CTE) of the Sn-Pb due to the carbon fibre addition and the resulting better match with the low CTE of the superconductor.

*Table 4* gives the $T_c$ and $J_c$ (77 K) values of sandwich composite A and the plain superconductor before and after room temperature air exposure for 15 days. The cross-sectional area used to compute $J_c$ was that of the superconductor layer only. The plain superconductor was not superconducting at all after the exposure, whereas the sandwich composite remained superconducting, with

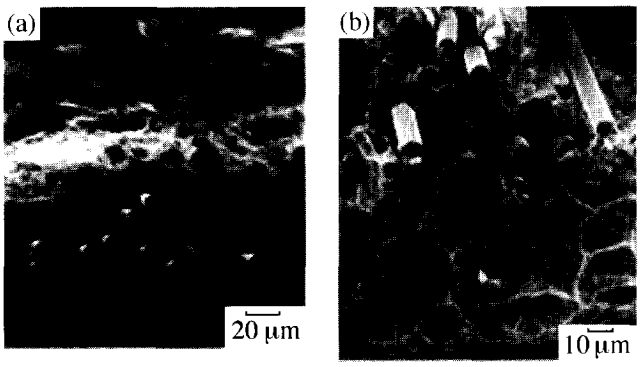


**Figure 2** SEM micrographs at two magnifications of the tensile fracture surface of a sandwich composite. (a) The upper part is the superconductor, while the lower part is the fibre composite. (b) The fibre composite region

$T_c$ and $J_c$ values decreased from the values before the exposure. Thus, the sandwiching greatly improved the stability in air. The degradation in air is a well-known effect that is due to the change in composition during air (with moisture) exposure.

Although not shown in *Table 4*, neither $T_c$ nor $J_c$ was affected by the sandwich composite processing, whether the sandwiching was achieved by hot pressing or hot roll bonding. Moreover, the tensile and compressive properties of the sandwich composites were independent of the method of sandwiching.

**Table 3** Effect on compressive strength (MPa) of temperature cycling between room temperature and 77 K for 100 cycles

| | Before cycling | After cycling |
|---|---|---|
| Sandwich C | 111 ± 4 | 96 ± 5 |
| Sandwich A | 82 ± 4 | 71 ± 5 |
| Plain superconductor | 39 ± 3 | 17 ± 3 |

**Table 4** Effect of room temperature air exposure for 15 days on $T_c$ and $J_c$

| | Sandwich | | Plain superconductor | |
|---|---|---|---|---|
| | Before | After | Before | After |
| $T_c$(K) | 87.6 ± 2.1 | 82.6 ± 3.5 | 88.1 ± 1.9 | [a] |
| $J_c$(A cm$^{-2}$) | 94 ± 3.7 | 45 ± 4.1 | 101 ± 2.5 | [a] |

[a] Not superconducting

## CONCLUSIONS

The sandwiching of the superconductor $YBa_2Cu_3O_{7-\delta}$ by two layers of Sn-Pb matrix carbon fibre composite was found to improve the mechanical, chemical and thermal properties. The mechanical properties (both tensile and compressive, parallel to the fibres) were improved greatly, indicating good load transfer to the carbon fibres and good adhesion between the layers in the sandwich. The chemical property improvement is associated with the increased stability in air, as shown by $T_c$ and $J_c$ measurements before and after a 15 day air exposure. The thermal property improvement is associated with the increased resistance to thermal cycling between room temperature and 77 K, as shown by compressive testing (parallel to the fibres) before and after cycling.

## ACKNOWLEDGEMENTS

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