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COATED-WIRE-IN-TUBE PROCESSING OF BISMUTH-2223  
SUPERCONDUCTORS\*

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## COATED-WIRE-IN-TUBE PROCESSING OF BISMUTH-2223 SUPERCONDUCTORS

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### ABSTRACT

A coated-wire-in-tube (CWIT) process greatly increases the silver/superconductor interface area in silver-sheathed Bi-2223 superconductors. When the performance of CWIT samples is compared to that of conventional monofilaments made with the same powder, critical current density increases significantly with increased silver/superconductor interface area. Benefits of increasing the silver/superconductor interface area are realized only when there is good continuity of the coated wires, and this requires a mechanical deformation sequence to preserve good continuity of the wires.

### INTRODUCTION

Abundant evidence [1-5] suggests that a large fraction of the current in silver-sheathed Bi-2223 conductors is carried by dense, well-aligned material at the silver/superconductor interface. In an effort to improve the performance of Bi-2223 conductors, a coated-wire-in-tube (CWIT) process has been developed to greatly increase the silver/superconductor interface area. In CWIT processing, fine silver wires (0.003-0.020 in. diameter) are coated with Bi-2223 precursor powder (coating thickness  $\approx$ 25-100  $\mu$ m) by either a slurry method [6,7] or electrophoresis [8]. In the slurry method, the Bi-2223 coating is tough and adherent due to

its relatively high concentration of organics ( $\approx 25$  vol.%), but the removal of organics may be difficult. Coatings made by electrophoresis are not as adherent as those made by the slurry method, but they contain much lower concentrations of organics and therefore removal of the organics is not as difficult. With either method, 100-600 coated wires are bundled and then loaded into a silver tube and drawn and rolled into a tape in a manner similar to the powder-in-tube (PIT) method.

In addition to increasing the silver/superconductor interface area, CWIT processing has several other possible advantages over alternative methods for fabricating silver-sheathed conductors. The matrix of CWIT conductors consists of superconductor, whereas silver forms the matrix of multifilament conductors, another type of conductor with an increased silver superconductor interface area. As a result, percolation through CWIT conductors may be better than that in multifilament conductors, in which small-scale disruptions such as second-phase particles or cracks may force transport through silver. In addition, the superconductor layer thickness can be reduced in CWIT conductors, and the silver/superconductor interface area increased, by decreasing the initial coating thickness. This means that thinner superconductor layers can be made without additional mechanical deformation. By comparison, the filaments of a multifilament conductor are made finer by subjecting them to additional mechanical deformation, which can roughen the interface and cause misalignment of grains in the interface layer. Other expected benefits of CWIT processing include good strain tolerance due to the distribution of silver on a fine scale, and the ease of adapting it to the fabrication of long-length-conductors, perhaps even by a continuous process.

## EXPERIMENTAL

Bundles of coated wires were prepared, some from wires made by slurry coating, others from wires coated by electrophoresis. The bundles, each containing 125-150 coated wires, were loaded into silver tubes (4.35 mm I.D. x 6.35 mm O.D. x 250 mm ); the organics were then removed from the coating by heating ( $5^{\circ}\text{C}/\text{h}$  up to  $720^{\circ}\text{C}$ , then hold for 24 h) under a partial vacuum (2-3 torr of flowing oxygen). The partial vacuum facilitates removal of gaseous products and prevents decomposition of the superconductor during the process. After the tubes with the slurry-coated wires were heated, both ends of all tubes were swaged so that the coated wires were gripped during mechanical deformation. In addition to the CWIT samples, a monofilament was prepared by the conventional PIT process; this sample served as a reference for the CWIT samples. The CWIT samples and the monofilament were all prepared from the same powder,  $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{2.0}\text{Ca}_{2.0}\text{Cu}_{3.0}\text{O}_{10}$  prepared by Argonne's two-powder process [9].

Mechanical processing consisted of drawing the tubes from 0.635 cm to 0.2 cm at a 10% reduction in diameter per pass, which corresponds to  $\approx 19\%$  reduction in area per pass and  $\approx 23\%$  elongation. The resulting wires were then rolled to the final tape thickness at 10-12% reduction in thickness per pass, with annealing for 5 min at 400°C after each drawing and rolling reduction. The final tapes were  $\approx 250 \mu\text{m}$  thick and  $\approx 4 \text{ mm}$  wide. For later reference, this deformation sequence is called the "harsh" process. To reduce the failure of silver wires during mechanical deformation, a "gentle" process was developed for processing subsequent CWIT samples. In this process, wires were drawn to 0.2 cm diameter at 3% reduction in diameter per pass (6% reduction in area and  $\approx 6\%$  elongation per pass), then rolled to  $\approx 250 \mu\text{m}$  at  $<10\%$  elongation per pass. All samples made by the gentle process were prepared from wires by electrophoresis.

Samples ( $\approx 3 \text{ cm}$  long) were cut from the tapes and heated for 50 h at 818-823°C in 8%  $\text{O}_2$ /balance  $\text{N}_2$ , after which the tapes were uniaxially cold-pressed at  $\approx 2 \text{ GPa}$ . Following pressing, the tapes were annealed for an additional 100 h at 818-823°C, pressed one more time, then heated for 100 h at 818-823°C. Critical current,  $i_c$ , was measured by the four-probe method at 77 K in zero applied field with a  $1 \mu\text{V/cm}$  criterion. Superconductor area was measured by digital image analysis of transverse sections. To calculate critical current density,  $J_c$ , of Bi-2223,  $i_c$  was divided by the superconductor area determined by digital image analysis. The engineering critical current density,  $J_e$ , was calculated by dividing  $i_c$  by the cross-sectional area of the tape (sheath + core).

## RESULTS

Figure 1 shows  $i_c$  versus total heat treatment time for tapes prepared by the harsh mechanical deformation sequence. Each data point represents the average of measurements from three individual tapes. For each tape thickness, monofilaments had the highest  $i_c$  and CWIT samples made by slurry-coating had the lowest  $i_c$ . For each tape thickness, the CWIT sample made by electrophoresis had an  $i_c$  that was  $\approx 50\%$  higher than the  $i_c$  of slurry-coated CWIT samples. While there is no conclusive evidence that removal of organics degraded the performance of slurry-coated samples, the microstructures of those samples were similar to those of previous PIT samples that had high carbon contents, exhibiting larger and more abundant second phases in addition to significant amounts of Bi-2212. This suggests that organic removal may have been a factor in decreasing the  $J_c$  values of slurry-coated CWIT samples relative to those of the electrophoresis samples. For this reason, subsequent study of the CWIT process focused on wires coated by electrophoresis.

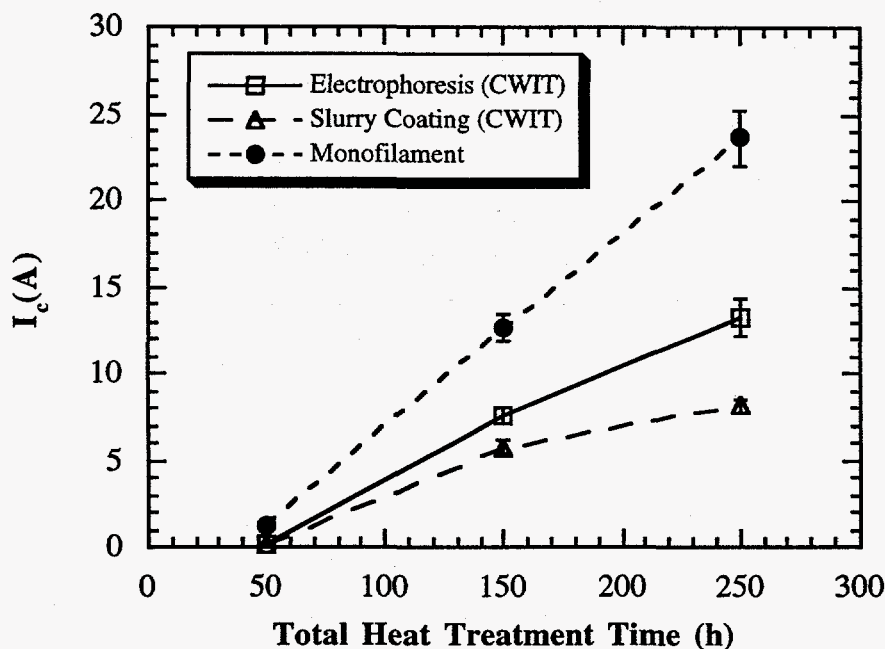


Fig. 1. Critical current,  $i_c$ , vs. total heat treatment time for samples processed by "harsh" mechanical deformation sequence. Tape thickness before heat treatment was 0.010 in. Each data point represents average of measurements from three individual tapes.

The  $i_c$  of the CWIT electrophoresis sample was  $\approx 50\%$  of that of the  $i_c$  of the monofilament sample (Fig. 1). Digital image analysis of transverse sections showed that the superconductor area was  $\approx 50\%$  smaller in the CWIT sample than in the monofilament, so  $J_c$  of the superconductor was approximately the same in the CWIT and monofilament tapes, indicating that the silver wires had not enhanced superconductor performance. Examination of longitudinal sections revealed a thin (1-2  $\mu\text{m}$ ), dense layer of Bi-2223 at the interface with the silver wires, but the wires were broken in many places (Fig. 2) and were separated from one another by many grain lengths. This suggested that current was forced through regions with randomly oriented grains in order to pass from one well-aligned region to the next. In turn, this led to speculation that such a microstructure may reduce or eliminate the benefit of the silver wires and that the silver wires would be beneficial only if they were continuous, i.e., if failure of the silver wires could be prevented.

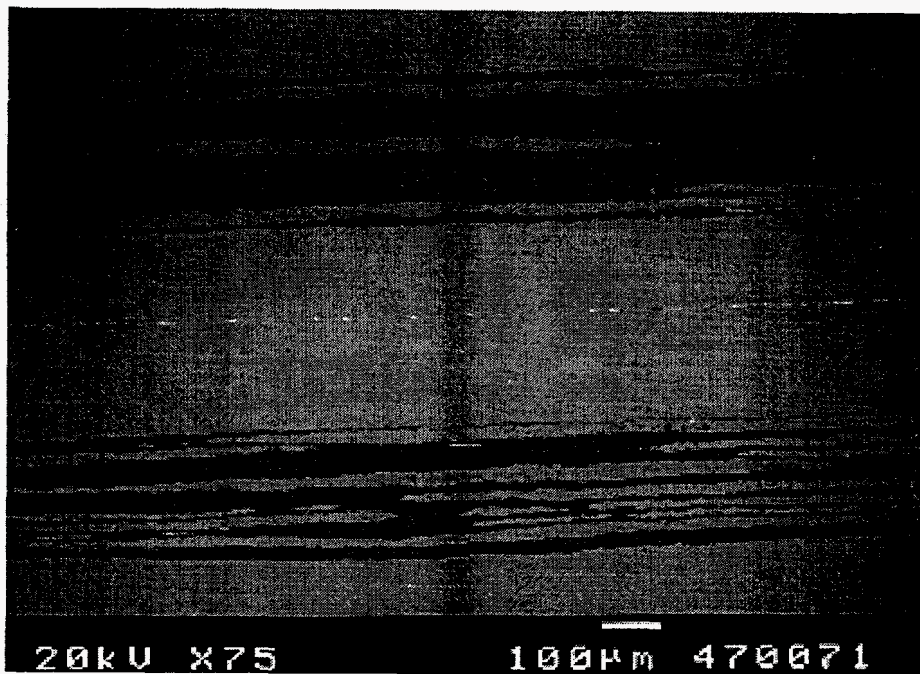


Fig. 2. Secondary electron image of CWIT sample (longitudinal section) prepared by "harsh" mechanical processing. Dark gray regions are Bi-2223; light gray regions are silver sheath along edges, and silver wires in core (which are broken in many places).

Figure 3 suggests that the silver wires inside CWIT conductors may have broken because of excessive deformation between annealing and/or inadequate annealing. Figure 3a plots ductility (represented by percent elongation per 2-in. sample) as a function of degree of cold-working (represented by percent reduction in area of 0.091-in.-diameter fine silver wire) [10]. For wire that has undergone a 19% reduction in area, an elongation of  $\approx 20\%$  is expected, and this is approximately the elongation experienced by CWIT wires during a single reduction. This suggests that the silver wires are in a critical regime after the first reduction and that subsequent elongation must be carefully limited to prevent failure of the wires. Figure 3b shows ductility versus annealing temperature (annealing time = 0.5 h) for silver wire subjected to 50% cold-working [10]. Annealing for 0.5 h at  $400^\circ\text{C}$  clearly imparts sufficient ductility to the silver wires to withstand 20% elongation, but annealing for 5 minutes (as done in "harsh" processing) may be inadequate, especially considering that the wires are embedded in a porous ceramic matrix that impedes thermal conduction.

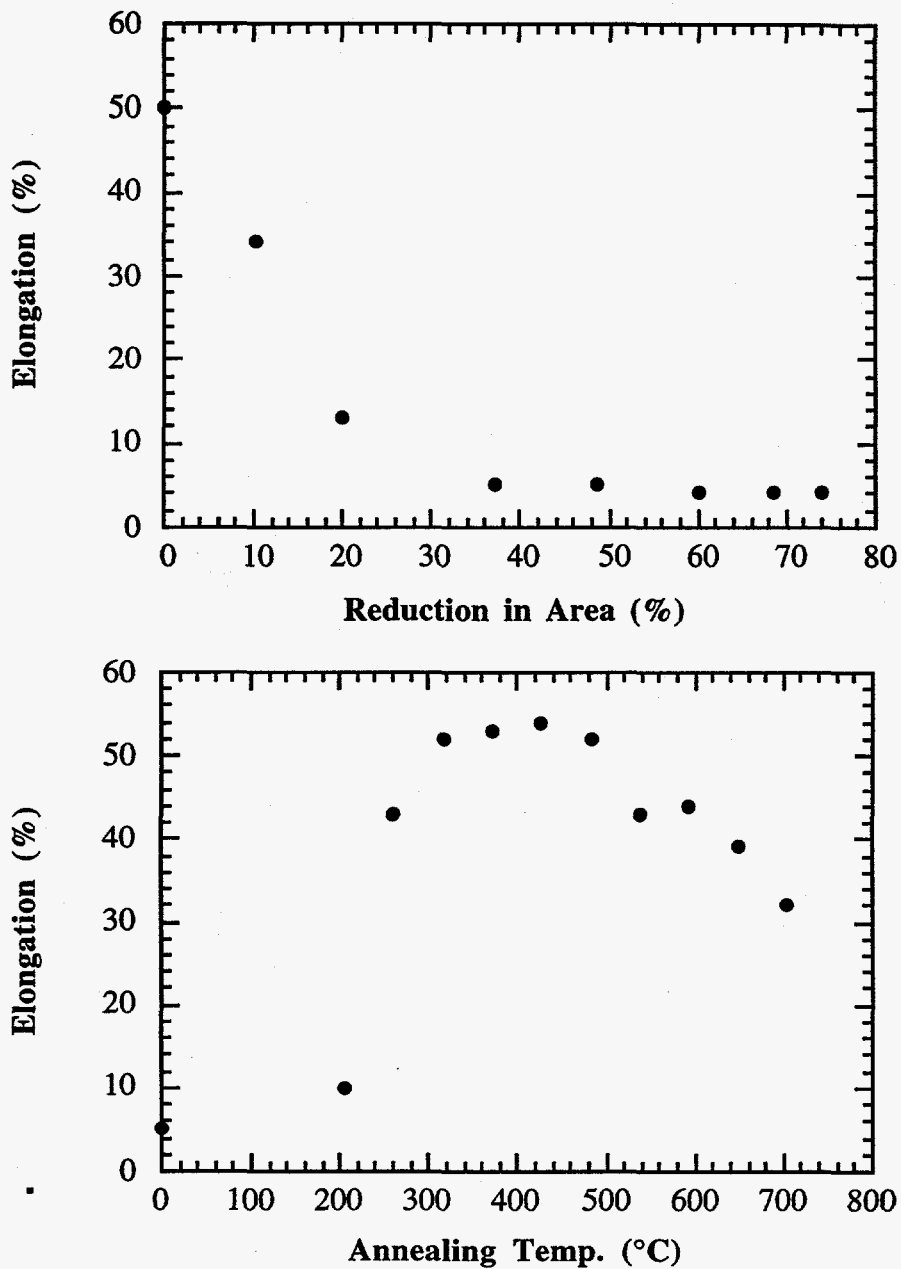


Fig. 3. Ductility of 0.091-in.-diameter fine silver wire, given as percent elongation for a 2-in. specimen, vs. (a) degree of cold-working, given as reduction in area (%), and (b) annealing temperature, where a sample subjected to 50% cold-working is annealed for 0.5 h at various annealing temperatures. Data taken from Ref. (10).



To prevent failure of the silver wires, the gentle mechanical deformation process was developed in which the reduction per pass was reduced and the annealing time was increased. Details of the gentle process are described in the experimental section. As seen in Fig. 4, the gentle deformation sequence nearly eliminated the failure of silver wires in CWIT conductors. Figure 5 compares transverse views of typical CWIT and monofilament conductors. Measuring the total silver/superconductor interface (measured as a length in the two-dimensional transverse view) and dividing by the area of superconductor showed that the interface per unit area of superconductor increased from  $\approx 40 \text{ mm}^{-1}$  in the monofilament to  $\approx 450 \text{ mm}^{-1}$  in the CWIT conductor. The core areas (including superconductor and silver wires) are approximately the same for the two conductors, but the superconductor area is  $\approx 50\%$  smaller in the CWIT conductor because silver accounts for  $\approx 50\%$  of the CWIT core. Despite the smaller superconductor area,  $i_c$  was  $\approx 50\%$  higher in the CWIT conductor, showing that superconductor performance had been enhanced.

$J_c$  is plotted in Fig. 6 as a function of initial tape thickness (i.e., before heat treatment).  $J_c$  (Bi-2223) was  $\approx 150\%$  higher in the CWIT sample than in the monofilament;  $J_e$  was  $\approx 50\%$  higher for the CWIT conductor. These results support the idea that material at the silver/superconductor interface has improved properties relative to material at the core interior, and demonstrate that  $J_c$  and  $J_e$  of tape conductors can be enhanced by increasing the silver/superconductor interface area. In addition, because the CWIT conductor had a higher  $J_c$  than the monofilament when the silver wires remained continuous, but a lower  $J_c$  when the wires were broken, the silver wires are required to have good continuity in order for the CWIT approach to be beneficial.

## CONCLUSIONS

A coated-wire-in-tube (CWIT) method greatly increases the interface area between silver and superconductor in Bi-2223 silver-sheathed superconductors. Using this CWIT process, we increased the silver/superconductor interface area by more than one order of magnitude. As a result, critical current density ( $J_c$ ) was  $\approx 150\%$  higher in the CWIT sample than in a monofilament made with the same powder, and engineering critical current density was  $\approx 50\%$  higher in the CWIT conductor. These results clearly indicate that the performance of silver-sheathed Bi-2223 superconductors can be enhanced by maximizing the interface area between silver and superconductor. We also demonstrated that the mechanical deformation sequence is important to the success of the CWIT process. "Harsh" mechanical processing caused many breaks in the silver wires, and consequently the

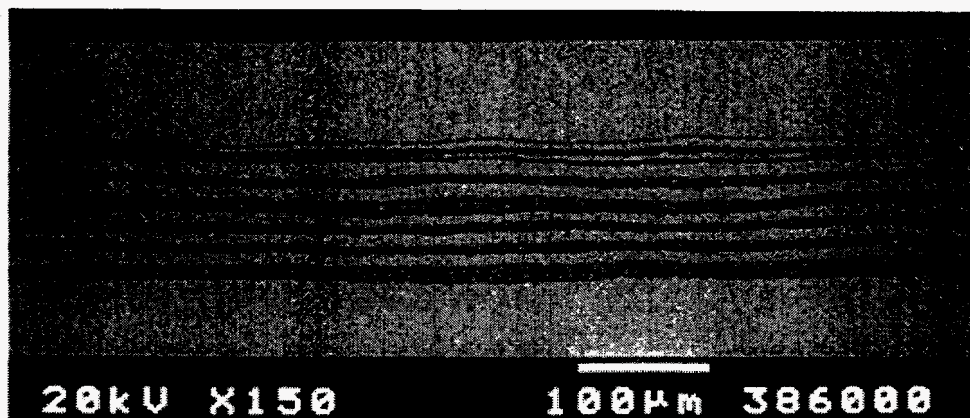


Fig. 4. Secondary electron image of CWIT sample (longitudinal section) prepared by "gentle" mechanical processing. Dark gray regions are Bi-2223; light gray regions along edges are silver sheath, and light gray regions in core are silver wires.

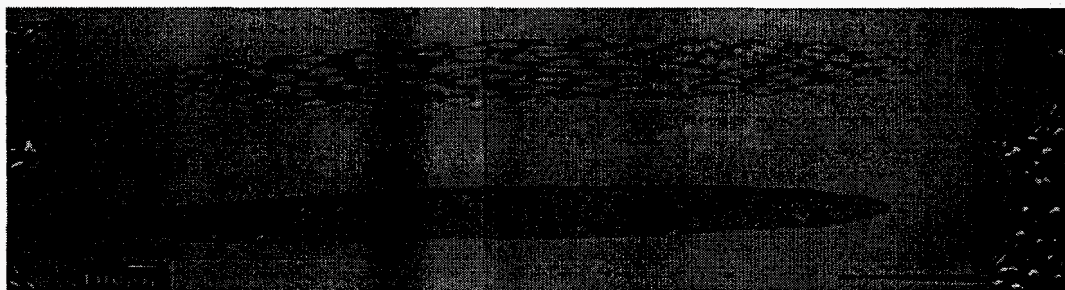


Fig. 5. Secondary electron image (transverse sections) of monofilament and CWIT tapes prepared by "gentle" mechanical processing. Dark gray regions are Bi-2223; light gray regions along the edges are silver sheath, and light gray regions in core are silver wires.

well-aligned superconductor at the interface was not continuous. As a result, incorporation of the silver wires did not enhance the performance of the superconductor. By contrast, "gentle" mechanical processing preserved the continuity of the silver wires, and incorporation of the silver wires increased the superconductor  $J_c$ .

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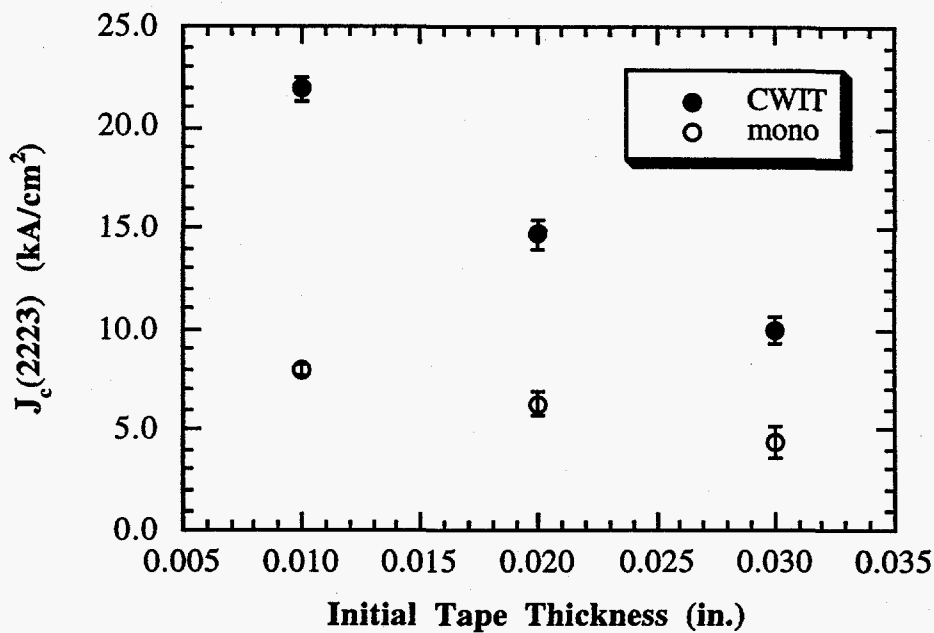


Fig. 6. Critical current density,  $J_c$ , vs. initial tape thickness (i.e., before heat treatment) of monofilament and CWIT tapes made by "gentle" mechanical processing.

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