RECENT DEVELOPMENTS IN FABRICATION AND PROPERTIES OF Ag-CLAD BSCCO CONDUCTORS*

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Abstract

Long-length mono- and multifilament Ag-clad BSCCO superconductors with consistent current transport properties were fabricated by the powder-in-tube technique. A critical current ($I_c$) of 42 A has been recorded in short-lengths of 37-filament conductors. Critical current density ($J_c$) up to 12000 A/cm$^2$ has been observed at 77 K in 125-m-long monocore and 850-m-long multifilament conductors. A high-$T_c$ magnet, fabricated from 770 m of monofilament conductor, generated a record high field of $\approx 1$ T at 4.2 K in a field of $\approx 20$ T. In-situ strain tests showed that multifilament conductors have better strain tolerance than monofilament conductors. The in-situ bending characteristics of the monofilament conductors indicate that their irreversible strain limit increases with decreasing superconductor/Ag ratio. Superconducting joints and multilayer Ag/superconductor composites have been fabricated with a novel chemical etching technique. Typical $I_c$ through such joints was 23 A, or $\approx 70\%$ of that carried by normal monofilament tapes and $\approx 60\%$ of that carried by multifilament tapes. Preliminary results with multilayer tapes show that continuous Ag reinforcement of the BSCCO core improves strain tolerance of the tapes so they can carry 90\% of their initial $I_c$ at 1\% bend strain in spite of a higher superconductor/Ag ratio than unreinforced tapes.

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Introduction

Most bulk applications of high-temperature superconductor (HTS) materials require that they be shaped into some form of a continuous conductor. Significant effort is underway to develop wires and tapes with these materials as a preliminary step in this direction. The powder-in-tube (PIT) process for the Bi-Sr-Ca-Cu-O (BSCCO) system of superconductors, which employs silver (Ag) as a sheathing material, is a promising technique for fabricating such long-length conductors from HTS materials. Although significant progress has been made in the past few years in fabricating PIT tapes and enhancing their critical current density ($J_c$), critical issues remain that impede successful commercialization of HTSs. For many applications, as in electromechanical machinery, continuous lengths of tape, on the order of 1 km, with uniform electrical properties are necessary. Even when such long lengths are available, for many applications, e.g., in sub-coil interconnections in large magnets or in the development of current leads, superconducting joints are needed between the tapes. The electrical properties of these conductors under strain is another important engineering issue that we must understand better. The results of our research, which is focused on these critical issues, are outlined in this paper.

Powder Synthesis and Fabrication of Long-Length Conductors

The precursor powder used to fabricate HTS conductors was obtained by solid-state reaction of high-purity oxides and carbonates of Bi, Pb, Sr, Ca, and Cu. The resulting powder was calcined at 800-850°C for ~50 h in air to obtain a partially reacted mixture of BSCCO-2212, calcium cuprate, and other secondary phases. Some of our best results were achieved with a Bi:Pb:Sr:Ca:Cu ratio of 1.8:0.4:2:2:2.3. Partially reacted precursor powder facilitates the formation of a transient liquid phase, which helps to heal microcracks that are formed during subsequent mechanical processing, and results in a dense core and higher critical-current values. The powder was characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), and inductively coupled plasma chemical analysis. The partially reacted mixture was then packed into high-purity Ag tubes by mechanical agitation. The tubes were swaged, drawn through a series of dies, and then rolled to a final thickness that ranged between 0.25 and 0.1 mm. Required lengths of the tape were then cut and subjected to a series of heat treatment cycles with intermittent pressing. The tapes were characterized by XRD, DTA, and scanning electron microscopy (SEM). Transport properties of the tapes were measured by the four-point probe method, with 1 μV/cm as the criterion, and $J_c$ of the superconducting and overall cross-sectional areas was measured.

Although the above described process has produced high-quality short-length tapes, it is not amenable to fabrication of long-length tapes. Implementing a carefully designed two-step rolling and heat-treatment procedure, researchers at Intermagnetics General Corporation, in association with Argonne National Laboratory, fabricated mono- and multifilament conductors several hundred meters in length. High transport current properties in short samples have been achieved by a combination of uniaxial pressing and heat treatment. Critical current values above 40 A were typically attained at 77 K, the highest of which was 51 A. Table 1 summarizes the transport properties of both short and long mono- and multifilament conductors at 77 K. The superconductor fraction of the monofilament samples ranged from 20 to 27%, whereas that of the multifilament conductor was ~24-32%. The $I_c$ of a 114-m-long monofilament conductor was ~20 A, corresponding to a $J_c$ of 12,000 A/cm² at 77 K. A consistent $J_c$ of 1.2 x 10⁴ A/cm² has also been achieved in 850-m-long and, recently in 1260-m-long, 37-filament tapes at 77 K in self fields, as shown in figure 1.

Table 1
Table 1. Summary of transport current properties of short and long mono- and multifilament Ag-clad BSCCO conductors.

<table>
<thead>
<tr>
<th>Conductor Type</th>
<th>Length (m)</th>
<th>$I_c$ (A)</th>
<th>Core $J_c$ (A/cm²)</th>
<th>Overall $J_c$ (A/cm²)</th>
<th>Fill Factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monofilament</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short Pressed</td>
<td>0.03</td>
<td>51</td>
<td>45,000</td>
<td>9,000</td>
<td>20</td>
</tr>
<tr>
<td>Short Rolled</td>
<td>0.03</td>
<td>51</td>
<td>29,000</td>
<td>7,800</td>
<td>27</td>
</tr>
<tr>
<td>Long Length</td>
<td>70</td>
<td>23</td>
<td>15,000</td>
<td>3,500</td>
<td>24</td>
</tr>
<tr>
<td>Long Length</td>
<td>114</td>
<td>20</td>
<td>12,000</td>
<td>3,200</td>
<td>27</td>
</tr>
<tr>
<td>Multifilament</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Long Length</td>
<td>20</td>
<td>42</td>
<td>21,000</td>
<td>6,800</td>
<td>32</td>
</tr>
<tr>
<td>Long Length</td>
<td>90</td>
<td>35</td>
<td>17,500</td>
<td>5,600</td>
<td>32</td>
</tr>
<tr>
<td>Long Length</td>
<td>850</td>
<td>16</td>
<td>10,500</td>
<td>2,500</td>
<td>24</td>
</tr>
<tr>
<td>Long Length</td>
<td>1,260</td>
<td>18</td>
<td>12,000</td>
<td>3,500</td>
<td>30</td>
</tr>
</tbody>
</table>

These results indicate steady progress in the fabrication of Ag-clad BSCCO conductors with consistent transport properties by the PIT technique. Such long-length conductors were co-wound in parallel to form pancake coils and racetrack-shaped solenoids. High-$T_c$ test magnets were fabricated by stacking the coils and connecting them in series. A test magnet (Fig. 2) fabricated by stacking 20 pancake coils generated a record high field of $\approx 3.2$ T at 4.2 K and zero applied field. Total length of the conductor in the magnet was 2400 m. The outer and inner winding diameters of the coil were 0.203 and 0.04 m, respectively; ampere turns at 4.2 K were $>250,000$. Another test magnet, fabricated with eight double-pancake coils, each containing three 16-m lengths of BSCCO conductors co-wound together, generated a field of 1 T at 4.2 K and 0.6 T at 27 K, in a background field of 20 T. Total length of the conductor in the magnet was 770 m. Such HTS magnets can be used as inserts to form hybrid magnets with low-$T_c$ magnetic coils, which are already in commercial use, to generate higher fields. This opens up the possibility of using high-$T_c$ magnets for sensing applications, e.g., in magnetic resonance imaging. The racetrack-wound solenoid was used to develop a 0.25 kVA high-$T_c$...
Fig. 2. Test magnet that generated field of \( \approx 3.2 \) T at 4.2 K and zero applied field.

Fig. 3. Photograph of 0.25 kVA HTS transformer, shown with its iron core superconducting transformer (Fig. 3) that has an iron core and can operate at liquid nitrogen temperature. The primary end of the transformer was made of \( \approx 85 \) m of high-\( T_c \) conductor and the secondary end, of \( 31 \) m. Turns in the primary and secondary winding were 140 and 40, respectively.
Superconducting Joints

Joint Fabrication

Although long-length conductors have been employed in the fabrication of prototype coils and high-\(\text{T}_c\) magnets, resistive interconnections were used to join conductors for coil winding and for interconnecting various parts of the superconducting magnets. Because the resultant joule heating is undesirable, it is efficacious to replace such connections with true superconducting joints. In addition, customizing conductor length for specific applications may not be economical and it might be more advantageous to form loss-less joints between high-quality short- or medium-length conductors, which are relatively easy to process. To date, very few techniques have been reported in the literature for joining superconducting materials.\(^{10}\) Tkaczyk et al. reported that superconducting joints could be formed by mechanically peeling away the Ag sheath of BSCCO tapes and then joining the tapes by overlapping the exposed cores.\(^{14}\) Rather than using mechanical methods to remove the Ag sheath, with the associated risk of damage to the superconductive core, we employed a novel chemical etching technique to form joints between Ag-clad BSCCO tapes.

To fabricate joints, we used short (\(\approx 50\)-mm) lengths of Ag-clad BSCCO tape. Keeping the surface of the tape to be etched unprotected, we carefully masked the remainder of the tape with a Teflon sheath. Ag from the unmasked side of the tape was then chemically etched to expose the underlying superconductor core. Of the various etchants that were tried, a combination of \(\text{HNO}_3/\text{H}_2\text{O}\) and \(\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}\) proved the most successful.\(^{10}\) After etching, the Teflon sheath was peeled away. Butt joints were then formed by carefully aligning and pressing the two tapes together, and heat treating for \(\approx 50\) h. The joined tapes were then subjected to a series of thermomechanical treatments that consisted of uniaxial pressing and heat treatment. Liquid phase that is formed in the reacting precursor powder mixture during heat treatment aids in healing the joint region. Detailed microstructural analysis and current transport characterization of the joints have been carried out. For qualitative comparison, transport properties of the joined tapes were compared with those of a regular tape subjected to the same thermomechanical treatment. Figure 4a is a schematic representation of the joint configuration. A modified etching technique was employed in the case of multifilament tapes to ensure maximum connectivity between the superconducting cores. Scanning electron microscopy shows that the joint (fig. 4b) is well healed after 250 hr of thermomechanical treatment.

Electrical Characterization

Critical current as a function of heat treatment time for a butt joint is shown in fig. 5. Typical \(I_c\) through the joint was >70% of the \(I_c\) carried by the unjoined part of the tape. This is in contrast to 30% current transport through the lap joint configuration we used previously.\(^{10}\) The \(I_c\) carried by joints in multifilament tapes is \(\approx 60\)% of the \(I_c\) in the unjoined portion of the tape. Currently, effort is underway to improve these figures by exploring different processing techniques and configurations. Preliminary studies of the strain tolerance of tapes with joints shows behavior identical to that of tapes without joints, which indicates that the joints are robust.

Strain Tolerance of Ag-clad BSCCO tapes

Most applications of Ag-clad BSCCO tapes require winding the tape into some form of a coil. During the fabrication of coils and magnets, the tapes are subjected to both tensile and
bending stresses. In addition, during operation, they are subjected to large electromagnetic hoop stresses that develop because of Lorentz forces. At times, these stresses could even reach the ultimate strength of the material. Because high-$T_c$ superconductors are ceramic compounds, and because silver, which is widely used as the sheath material in the PIT process, is a soft metal, Ag-clad BSCCO tapes are susceptible to damage under such stresses. Cracks induced in the superconducting core because of these stresses could lead to degradation.

Fig. 4. (a) Schematic representation of the joint before pressing and heat treatment; (b) microstructure of joint region after 250 h of heat treatment.
Fig. 5. Critical current as a function of heat treatment time

of the current transport properties of the tapes. Therefore, the importance of understanding the
strain tolerance of these tapes as a function of their transport properties cannot be
overstated.2,4,8,13,15-18

Bend strain characterization

Axial strain tolerance of mono- and 61-filament conductors, reported previously, 6 was
evaluated by subjecting the tapes to an in-situ tensile test. Retention of Ic as a function of
applied strain was measured at 77 K and in applied fields of 0 and 0.5 T. Most of the bend
strain characterization techniques reported to date are not performed in-situ, inasmuch as they
involve bending of the test tapes around formers of predetermined radii at room temperature,
followed by electrical characterization at cryogenic temperatures. Such techniques suffer from
the obvious disadvantage of errors introduced by repeated handling and thermal cycling of the
tapes. Some electrical characterization techniques make use of pressure contacts, which could
add to the error in evaluation of strain tolerance. To circumvent these problems, we obtained
the bend characteristics of the conductors in-situ, with a custom-designed test fixture. The test
tape was fixed between two movable arms mounted on lead screws. The tapes were bent in a
bath of liquid nitrogen by moving the arms toward each other with a crank-shaft. The
correlation between the number of turns of the crank shaft and the radius of curvature to which
the tapes were bent was preestablished at ambient temperature. The bend strain (ε) was
determined from the relationship

\[ \varepsilon = \frac{t}{2R}, \] (1)

where t is the total thickness of the tape and R is the radius of curvature.16 The irreversible
strain limit (\( \varepsilon_{irr} \)) is defined as that strain beyond which a decrease in Ic is irreversible. Bend
tests were conducted on both mono- and 61-filament conductors at 77 K and zero applied field.
Figure 6 shows normalized Ic as a function of bend strain for mono- and multifilament tapes.

Strain tolerance of Ag-clad BSCCO tapes can be improved by using Ag addition;
alternative sheath materials, such as AgMgNi, AgMg, Ag-10 at.% Cu, or Ag-\( \text{Al}_2\text{O}_3 \); or
multifilament conductors. As illustrated in fig. 6, the mechanical properties of multifilament conductors are better, when compared with monofilament conductors. Singh et al. showed that the strain tolerance of tapes can be improved without much loss in $J_C$ by adding Ag to the superconductor powder. Clearly, Ag appears to have a positive influence on the strain tolerance of these tapes, although some degradation in $J_C$ has been observed with increasing Ag content. To better understand the role of Ag, we fabricated a series of tapes with various superconductor/Ag (sheath) ratios (superconductor fill factor). As expected, the strain tolerance of the tapes increased with increasing Ag content (decreasing fill factor).

![Graph](image)

Fig. 6. Degradation of $I_C$ in mono- and multifilament tapes with decreasing bend radius

**Multilayer tapes**

When a tape is subjected to bending, the strain on the tape has two components: tensile strain on the outer side of the bent tape and compressive strain on the inner side of the bend. Because it is well known that ceramics withstand much higher compressive strains than tensile strains, cracks would be initiated on the tensile side of the bend, eventually propagate through the thickness of the core, and impede the flow of current. However, if Ag reinforcement is included in the core to isolate the cracks in the tensile side of the bent tape, current can still flow unimpeded through the part that is under compression. In addition, as reported by several researchers, the interfacial region between the BSCCO core and the Ag sheath with well-aligned BSCCO grains is believed to be responsible for high $J_C$. Thus, the added Ag should not only enhance the $\varepsilon_{irr}$, but the increased Ag-BSCCO interfacial area should also increase the $J_C$.

Employing the etching technique described previously for joint fabrication, we have fabricated tapes with a multilayer structure that incorporates Ag foil or 25-μm wires. The Ag sheath from one side of a pair of tapes was etched while the other side was kept intact. The exposed cores were then aligned and joined with either a single filament of 25-μm-thick Ag foil (fig. 7) or 25-μm-thick Ag wires (fig. 8) sandwiched in between. The joined tapes were pressed and subjected to the same thermomechanical treatment that was used for regular tapes. It was expected that the continuous reinforcement provided by the Ag between the two joined tapes would arrest crack propagation when the multilayer tape is bent. The increased interfacial area in multilayer tapes should also improve electrical properties.
Fig. 7. Multilayer tape showing 25-μm-thick Ag foil sandwiched between two tapes with exposed cores.

Fig. 8. Multilayer tape showing 25-μm Ag wires sandwiched between two tapes with exposed cores.
Preliminary observations of such tapes indicate enhanced strain tolerance, as shown in the plot of fig. 9. A multilayer tape with a fill factor of 40\% exhibited higher strain tolerance than monofilament conductors with fill factors of 23, 30, and 38\%; and it retained 90\% of its initial \( I_c \) at a bend strain of 1\%. Work is in progress to understand the influence of the geometry and processing of the sandwiched Ag layer on the electrical and mechanical properties of multilayer tapes.

![Plot of fig. 9](image)

**Fig. 9.** Strain tolerance of Ag-clad BSCCO mono- and multilayer (foil) tapes with various superconductor fill-factors (in paranthesis)

**Summary**

Long-length mono- and multifilament Ag-clad BSCCO-2223 tapes with a consistent \( I_c \) of 12000 A/cm\(^2\) at 77K have been fabricated. High-\( T_c \) magnets and a prototype 0.25 kVA transformer have been constructed from such long-length tapes. Superconducting joints that transport 70\% of the \( I_c \) carried by normal tapes have been developed by employing a chemical etching technique. In-situ strain tolerance tests were conducted with a custom-made test fixture. Multilayer Ag/BSCCO composite tapes were fabricated by sandwiching Ag foil/wires between the cores of two tapes. Continuous reinforcement provided by the sandwiched Ag appears to enhance the strain tolerance of such tapes in spite of increased superconductor/Ag ratio.

**References**


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