Processing and Properties of Silver-Clad Ti-Ba-Ca-Cu-O Wires and Tapes*

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PROCESSING AND PROPERTIES OF SILVER-CLAD Tl-Ba-Ca-Cu-O WIRES AND TAPES

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ABSTRACT

TlBa₂Ca₂Cu₃O_x and Tl₂Ba₂Ca₂Cu₃O_x powders were synthesized, loaded into Ag tubes, and worked into wires and tapes by drawing and rolling. All processing outside of furnaces was in a dry-N₂ glovebox. All heat treatments were performed in O₂. The Ag-clad wires fabricated from these powders exhibited onset of superconductivity at ≈ 118 K and critical current densities at 77 K of 2×10^3 to 4×10^3 A/cm².

INTRODUCTION

Tl-based superconductors have the highest confirmed T_c values [1] and appear to have better resistance to flux creep than do the Bi-based superconductors [2-5]. In fact, the TlBa₂Ca₂Cu₃O_x (1223) compound has inherent flux-pinning characteristics superior to those of all high-temperature superconductors other than YBa₂Cu₃O_x [2]. It has proved to be very difficult to fabricate wires from YBa₂Cu₃O_x that do not suffer from weak-link problems [6,7]. It is hoped that the 1223 and Tl₂Ba₂Ca₂Cu₃O_x (2223) compounds will be easier to work into wires and tapes than is YBa₂Cu₃O_x. Encouraging preliminary results on the current-transport properties of Tl-Ba-Ca-Cu-O have been reported for both clad wires [4,8] and thick films [9].

The goals of this work were to fabricate 1223 and 2223 Ag-clad wires and to determine whether the superconducting properties were dominated by weak links, and if not, how the properties were dependent on composition and processing.

EXPERIMENTAL METHODS

The 1223 powder was synthesized from high-purity BaCO₃, CaCO₃, CuO, and Tl₂O₃. A Ba₂Ca₂Cu₃O_x powder was made first and then mechanically mixed with Tl₂O₃ [10]. The powders were screened through an 80-mesh sieve three times during the mixing. To minimize contact with CO₂ or H₂O, the mixing was performed within 15 min in a dry-N₂ glovebox. Approximately 15 g of the mixed powder was placed in a small Pt crucible that had a tight Ag lid and heated to 900°C, held for 0.1 h, cooled to 885°C and held for 12 h, and then cooled at about 3°C/min to room temperature. The short time at 900°C was designed to introduce a small amount of liquid phase so that the synthesis reaction kinetics could be accelerated [11]. The powder was crushed and given a second identical heat treatment. The final powders were removed from the furnace to the glovebox while still hot. The T_c onset of the powder was ≈ 120 K.

For the 2223 powder, the Ba₂Ca₂Cu₃O_x precursor powder was made from BaO, CaO, and CuO. The mixture was ground thoroughly and pressed into

pellets that were sintered at 930°C in flowing O₂ for 48 h. After the reaction was completed, Tl₂O₃ powder was added to form the nominal composition Tl_{1.5}Ba₂Ca₂Cu₃O_x. The mixture was pressed into pellets and heated in a sealed crucible filled with O₂ at 900°C for 10 h. To improve homogeneity, the heat treatment was repeated after an intermediate grinding. The final powder had a T_c onset of ≈120 K [12].

Ag-clad wires were fabricated by a powder-in-tube process [13]. The powders were loaded into closed-end tubes of 6.35 mm outer diameter and 4.35 mm inner diameter. The powder was vibrated and rammed to assist compaction. The tubes were evacuated, sealed, and drawn at ≈15% reduction per pass to a diameter of 1.8 mm. After every third drawing pass, the tubes were annealed at 260°C for 20 min to preserve the ductility of the Ag. In an attempt to produce favorable textures, some of the tubes were further reduced by flat rolling at 10% reduction per pass. The thicknesses of the resultant tapes were ≈450 μm.

The powders and wires and tapes were characterized by X-ray diffraction, scanning and transmission electron microscopy (SEM and TEM), and differential thermal analysis (DTA). The DTA was performed in flowing O₂, with a heating rate of 5°C/min. DTA was also performed on small amounts of the unreacted powders to monitor the synthesis reactions.

Several sintering schedules were used for the wires and tapes. Sintering was performed in the solid state or with partial melting. The 1223 and 2223 powders had onsets of melting in O₂ of 905 and 890°C, respectively. As shown in Fig. 1, however, the presence of the Ag sheath lowered the melting temperatures for each by about 45°C. Partial-melt heat treatments incorporated heating for 6–12 min at temperatures as high as 900°C for the 1223 and 885°C for the 2223. Higher temperatures or longer times at temperature resulted in perforation of the Ag.

A commercial SQUID magnetometer was used to measure T_c. Transport critical current density (J_c) values were obtained at 4.2 and 77 K. A standard four-probe method with a voltage criterion of 1 μV/cm was used. In addition, magnetic-hysteresis measurements were performed on a few samples with a commercial vibrating-specimen magnetometer containing a superconducting magnet in a gas-flow-type cryostat.

Fig. 1. DTA trace in O₂ of 1223 + Ag powder.

RESULTS AND DISCUSSION

The initial powders were greater than 90% phase pure. It has been reported that extensive substitution occurs on the Tl site in 2223 [14,15], and thus the Tl-deficient composition used was able to produce 2223 of good phase purity. Although some CaO and BaCuO₂ were observed in the powders, the phases were present in small isolated pockets. The total carbon contents of the Ba₂Ca₂Cu₃O_x powders were less than 0.02%. Carbon can have deleterious effects on the properties of bulk high-temperature superconductors, but 0.02% is the concentration quoted for (Bi,Pb)₂Sr₂Ca₂Cu₃O_x/Ag tapes with good electrical properties [16]. The process of adding the Tl to the Ba₂Ca₂Cu₃O_x was not expected to introduce appreciable carbon.

The superconducting properties of Ag-clad wires were dependent on heat treatment. Sintering schedules for the wires included either long heat treatments at 845°C for the 1223 and 830°C for the 2223, which occurred entirely in the solid state, or shorter-term heat treatments to temperatures of 870–900°C followed by an anneal in the solid state. For the partially melted wires and tapes, annealing at 830–845°C was necessary to raise the T_c onset to 118 K, although the transition was somewhat broad for most of the wires. In the absence of the 830–845°C anneal, the T_c values were 100–110 K and the transitions were very broad. No further attempts were made to optimize T_c by annealing at other temperatures or in other atmospheres [14]. For all of the better specimens, the J_c values ranged from 2 × 10³ – 4 × 10³ A/cm² at 77 K. These values increased to about 4 × 10³ – 10⁴ at 4.2 K. The partially melted specimens generally exhibited slightly higher J_c values, but as shown in Fig. 2, the J_c values decreased rapidly in an applied magnetic field. Thus, the properties of these wires and tapes were determined by weak links, not flux pinning.

The J_c values of the Tl-Ba-Ca-Cu-O/Ag wires and tapes were below those quoted for melt-textured materials or Ag-clad (Bi,Pb)₂Sr₂Ca₂Cu₃O_x tapes [7,16–18]. Relatively little fabrication work has been done to date, and properties are expected to improve.

Fig. 2. J_c versus applied field at 77 K for a 1223/Ag tape.

Representative magnetization data for 1223/Ag tapes are shown in Fig. 3. (J_c values were not calculated because of uncertainties in how to apply the Bean model.) Two important results emerged. First, the J_c would appear to have been higher with the applied magnetic perpendicular to the plane of the tape than parallel to it. Thus, the flat rolling procedures must have been ineffective in causing the grains to align favorably. Second, the fields at which the hysteresis loops collapsed were less than those reported for the irreversibility line in 1223 by Kim et al. [2]. It is unknown why this is so.

Fig. 3. Hysteresis data at (a) 40 K and (b) 77 K for 1223/Ag tapes that were sintered in O_2 at 890°C and then annealed at 845°C.

SEM and TEM examinations of the wires revealed very complex microstructures. CaO and BaCuO₂ phases were observed in all of the wires and tapes, but were much more prevalent in those that had been partially melted. These phases were all present as discrete grains; they did not coat grain boundaries (Fig. 4). No clear alignment of the grains was observed in either the wires or the tapes, which is in accordance with the magnetization measurements. Intergrowths were present in all of the superconductor grains examined. Given these poor microstructures, it was somewhat surprising that the J_c values were greater than 10^3 A/cm² at 77 K.

Fig. 4. TEM photomicrograph of 1223/Ag tape containing 1223 and CaO grains.

SUMMARY

Ag-clad wires and tapes made from 1223 and 2223 Tl-Ba-Ca-Cu-O powders had T_c values of ≈ 118 K and J_c values at 77 K of $2 \times 10^3 - 4 \times 10^3$ A/cm². All specimens exhibited weak-link behavior. The initial powders had good phase purities, but the final microstructures contained large concentrations of second phases. No favorable grain alignment was observed.

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