Near-Net-Shape Fabrication of Continuous Ag-Clad Bi-Based Superconductors*

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Abstract—We have developed a near-net-shape process for Ag-clad Bi-2212 superconductors. This alternative to the powder-in-tube process offers the advantages of nearly continuous processing, minimization of processing steps, reasonable ability to control the Bi-2212/Ag ratio, and early development of favorable texture of the Bi-2212 grains. The powder is rolled into an Ag channel, a cap is applied, and the assembly is lightly rolled. To minimize distortion during heat treatment, it is especially important that the Bi-2212 powder be nearly free of volatile species such as carbon. A vacuum-calcination process was developed to control CO₂ evolution during heating. Superconducting properties are discussed.

I. INTRODUCTION

Most high-temperature superconducting wires and tapes are fabricated by the powder-in-tube (PIT) technique in which Ag/superconductor composites are produced. The PIT process is currently the most common technique for manufacturing superconductor wire and tape with enhanced electrical and mechanical properties. Critical current density (J_c) for PIT-processed YBa₂Cu₃O_y (Y-123) has been shown to be three times higher than that for conventionally sintered YBCO [1]. Bi-based superconductor tapes with J_c values $>10^5$ A/cm² have been recently produced by the PIT method [2], [3]. In addition, Bi-based superconductors with Ag-alloy sheaths have been produced by the PIT method, and have been shown to have excellent strain and stress tolerance [4].

PIT processing begins with a well-characterized powder blend that is muzzle-loaded into Ag or Ag-alloy tubes, which are then sealed and mechanically worked by processes such as drawing or rolling [5]. The purpose of the mechanical

working is to increase the core texture and density before heat treatment [6]. The superconductor core microstructure is significantly affected by rolling parameters such as total deformation, reduction-per-pass, and the volume fraction of Ag in the composite. The stress state of the Ag/superconductor composite is complicated because of the difference in mechanical properties between the superconductor core and the Ag sheath [7]. For the PIT process, many reduction steps are required to achieve the final monocoil or multifilament wire or tape.

Several variations of the PIT fabrication process are used to manufacture Ag-clad tapes. Multilayer Bi-2212-based tapes can be made by slurry coating an Ag foil, stacking the foil, and rolling the composite to form a sandwich structure [3], [8]. Round wire has been manufactured by forming a tube from Ag foil [9]; superconductor powder is continuously loaded into the tube, which is subsequently drawn and rolled. In this paper, we discuss a modification of the PIT process that produces a textured core with high density and significantly reduces the number of mechanical deformation steps. This process is virtually continuous and can be used to produce clad tapes from nearly any high-temperature superconductor or metallic sheath. We have focused primarily on Ag/Bi-2212, but have also studied the use of YBa₂Cu₃O_x (Y-123) because it is substantially more difficult to heat treat than Bi-2212 [1], [2].

II. EXPERIMENTAL DETAILS

We have modified the conventional PIT process to reduce the number of mechanical deformation steps. Our process begins with an Ag sheet or plate that is formed into an open, flat-bottomed channel [10]. Superconductor powder is then continuously loaded and rolled into the Ag channel.

A. Powder Preparation

Precursor powders consisting of carbonates and oxides were mixed in stoichiometric amounts and vacuum-calcined in flowing oxygen [11]. The calcination furnace was

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equipped with a rotary vane pump and an infrared CO₂ monitor. Oxygen flow through the furnace was ≈ 4 L/min, and total pressure was maintained between 250 and 1500 Pa. The total CO₂ in the furnace was controlled by a feedback loop between the CO₂ monitor and the furnace controller that adjusted the temperature ramp according to the threshold CO₂ value. Resultant powder phase purity was characterized by X-ray diffraction.

B. Wire Fabrication

The tape fabrication process is shown in Fig. 1. The process begins with shaping an Ag sheath into a trough measuring ≈ 0.30 mm high and 3 mm wide. Powder is then poured into the trough and rolled to compact the core. A cap is then continuously welded on top of the compacted core by a high-energy source, such as a laser. A 1-m length of tape was made and its thickness was reduced by rolling. The Ag-clad/Bi-2212 was heat treated by incongruently melting and slow cooling below the peritectic melt temperature [12].

III. RESULTS AND DISCUSSION

The calcination process was optimized to enhance phase-formation kinetics and reduce the total amount of retained carbon in the powder. Balachandran et al. showed that for optimal Y-123 phase formation, the total CO₂ content should be maintained below 2% [11]. For Y-123, the CO₂ production during calcination can be described by

The CO₂ produced during calcination of a 1946.9 g batch is shown in Fig. 2a. The CO₂ level oscillated because the control loop was a simple on-off function. The oscillation could be avoided if a proportional controller was used. In Fig. 2a, the copper carbonate and barium carbonate decompose at 240 and 750°C, respectively. The total CO₂ produced was calculated by integrating the CO₂ curve in Fig. 1 and multiplying by the O₂ flow in the furnace. A total of 8.16 moles of CO₂ were measured, close to the total of 8.11 moles of CO₂ calculated from Eq. 1. A similar calcination process was carried out for Bi-2212 (Fig. 1b). In this case, the calcium and strontium carbonates decompose between 600 and 800°C. Total carbon content for vacuum-calcined Bi-based superconductors is typically <0.02 mol%, much lower than has been shown to be detrimental to electrical properties and phase formation [13].

The calcined powder was poured into the Ag trough and compacted by rolling. Mechanical deformation of the powder significantly enhances the texture over a randomly oriented powder, as can be seen by the enhanced (001) peaks

Fig. 1. Fabrication sequence for Ag/Bi-2212 tapes. (a) Continuous Ag channel is fabricated; (b) powder is added by a vibratory feed system; (c) BSCCO powder is roll compacted; (d) an Ag cap is laser welded to the Ag channel; and (e) Ag-clad Bi-2212 is flat rolled.

Fig. 2. CO_2 evolution during powder calcination: (a) $\text{YBa}_2\text{Cu}_3\text{O}_y$ formation from yttrium oxide, barium carbonate; and copper carbonate (b) $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ formation from bismuth oxide, strontium carbonate, calcium carbonate, and copper oxide.

in the X-ray diffraction data (Fig. 3). In addition, the density of the rolled core was calculated to be nearly 6.4 g/cm^3 , which is close to full density and is significantly higher than that of powder packed for PIT tubes ($\approx 2 \text{ g/cm}^3$).

An Ag cap was joined to the silver trough by a continuous laser weld to form a tape that was $\approx 500 \text{ } \mu\text{m}$ thick (Fig. 4). The rectangular cross section was rolled in stages to a final thickness of $150 \text{ } \mu\text{m}$. Specimens were cut at incremental thickness reductions and J_c was measured as the thickness was reduced. In general, the tape J_c increased as the tape cross section was reduced by rolling, which is consistent with work by Osamura et al. [14]. The maximum J_c at 4.2 K of $23,000 \text{ A/cm}^2$ was measured for a $200 \text{ } \mu\text{m}$ tape. Total fill factor for this tape was 50%, substantially more than the 25 to 30% typically reported for conventional PIT processing [15]. This has the advantage of small reduction and high engineering J_c . The transport J_c values produced thus far have been quite modest. We have produced only a

Fig. 3. X-ray diffraction data showing texture development of BSCCO core after roll compacting the powder in the silver trough: (a) untextured loose powder; Bi-2212 (b) roll-textured core. Δ indicates (001) peaks.

few tapes to date and have not optimized the powder or heat-treatment schedules. We believe that the relative simplicity of the process described, its limited number of steps, and the resultant configuration of the tapes militates for further development effort.

IV. SUMMARY

Most Bi-based superconducting wires and tapes are fabricated by a PIT technique in which a powder blend or preconsolidated slugs are muzzle-loaded into Ag or Ag-alloy tubes. We have developed a modification of this process in which Ag sheet or plate is formed into an open, flat-bottomed channel, Bi-2212 powder is rolled into the channel, an Ag lid is attached, and the sealed channel is given a final flat rolling. This near-net-shape process offers many advantages over the conventional PIT technique, including nearly continuous processing, minimization of processing steps, reasonable ability to control the Bi-2212/Ag ratio, and early development of favorable texture of the Bi-2212 grains. An additional advantage is that alloy plate is more readily available in foil form than in tube form, which will facilitate development of alternative sheath materials. This process could also be adapted to Tl-based superconductors that originate with a Ba-Ca-Cu-layer core. The reactants could be rolled in separately in this process and then reacted for form Tl-1223 based superconductors [16].

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Fig. 4. Optical photomicrograph of polished Ag-clad Bi-2212 tape after welding the Ag cap.

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