

**Processing and Microstructural Development of
Ag-Clad Bi-Sr-Ca-Cu-O Tapes***

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PROCESSING AND MICROSTRUCTURAL DEVELOPMENT OF Ag-CLAD Bi-Sr-Ca-Cu-O TAPES

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ABSTRACT

Ag-clad $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212) and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223) tapes were fabricated by drawing and rolling. Highly textured microstructures and high critical current density values were obtained for each system. However, the heat treatments and phase evolutions for 2212 and 2223 were different. For 2212, nearly phase-pure powder was used, and the heat treatments consisted of partial melting followed by solid-state sintering. For 2223, several compositions, initial phases, and sintering schedules were used. The results are discussed in terms of microstructural evolution as observed by X-ray diffraction and scanning and transmission electron microscopy.

INTRODUCTION

Powder-in-tube methods have produced textured bulk superconductors with high transport critical current density (J_c) values.¹⁻⁵ In this paper, recent results⁵⁻⁸ from Ag-clad tapes made from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212) and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223) are presented.

EXPERIMENTAL METHODS

Basic powder-in-tube techniques were common to all tapes.^{5,8} Powder was loaded by vibrating and ramming into closed-end Ag tubes of 6.35-mm outer diameter and 1 mm wall thickness. Each tube was heated in air, sealed, and formed into a wire by drawing. The tubes were drawn with ≈ 10 –15% reduction in diameter per pass to final diameters of 1–2 mm. Annealing was performed at 250–475°C for 10–20 min for every ≈ 30 % reduction in diameter. After drawing, the wires were flat-rolled into tapes by a two-high rolling mill. Many of the tapes went through an intermediate heat treatment, after which they were rerolled or pressed and given an additional heat treatment.

For the 2212, $\text{Bi}_2\text{Sr}_{1.7}\text{CaCu}_2\text{O}_x$ powder was synthesized by solid-state reaction of reagent-grade Bi_2O_3 , SrCO_3 , CaCO_3 , and CuO .^{5,9} Studies of homogeneous, quenched Bi-Sr-Ca-Cu-O crystallized glasses have indicated that this composition is within the range of the single-phase 2212 compound.^{10,11} X-ray diffraction indicated that the powder consisted of 2212 and a trace amount of $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ (2201). Differential thermal analysis in air revealed a broad endotherm with an onset at $\approx 870^\circ\text{C}$, confirming the existence of some impurity phase because this composition of 2212 should exhibit an onset of significant melting at $\approx 885^\circ\text{C}$.⁹ All of the better 2212 tapes were given an intermediate heat treatment in air at 890°C for 0.5 h. A relatively slow

cooling rate from 890°C of 10°C/h and a 10-h hold at $\approx 860^\circ\text{C}$ were best for obtaining high J_c values. After the first heat treatment, the samples were rolled at $\approx 10\%$ reduction per pass to a thickness of 0.12 mm. All of these tapes were then heated for 100 h at 840°C and cooled to room temperature at 180°C/h. Some tapes were quenched into water from various temperatures to examine microstructural evolution.

Ag-clad tapes of 2223 BSCCO were fabricated from multiphase powders that sintered reactively in situ to form 2223. In some tapes, 20 wt.% Ag flake was added to the powder charge. Reactive sintering of multiphase tapes was very sensitive to annealing temperature and had to be optimized to allow maximum transformation to the 2223 phase. Continued intermittent pressing, after initial grain-growth annealing, was necessary to advance the reaction, allow maximum consumption of alkaline-earth-cuprate phases, and promote texturing. In one part of the work with 2223, a $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ mixture was prepared from Bi_2O_3 , PbO , SrCO_3 , CaCO_3 , and CuO powders. Heat treatment yielded products that contained varying proportions of phases.⁸ For example, one powder consisted primarily of 2212, 2201, and 2223; another powder contained much less 2201 and 2212. In another part of the 2223 work,¹² mixtures of $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_y$ and $\text{Sr}_x\text{Ca}_{1-x}\text{CuO}_z$ were processed. The overall composition was $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ and the x values were 0.0, 0.25, 0.50, 0.75, and 1.0. Samples were cut from the tapes and heat treated in air or 8% O_2 . In air, the temperature range was 835–845°C. In 8% O_2 , the temperature range was 815–825°C. These ranges were based on differential thermal analysis (DTA) results. Thermomechanical processing of the tapes included a 50-h anneal at the chosen heat treatment temperature, after which the tapes were uniaxially cold pressed at ≈ 2 GPa. Following pressing, the tapes were annealed for an additional 100 h at the selected temperature. In some cases, the process of pressing and annealing was repeated. Maximum total heat treatment time was 350 h.

The microstructures of the final tapes and wires were examined by optical microscopy and scanning and transmission electron microscopy (SEM and TEM). Phase formation and qualitative grain alignment were examined by X-ray diffraction. $\text{Cu K}\alpha$ radiation, with voltage of 30 kV and current of 15 mA, was used. Critical temperature (T_c) was measured by either a dual-coil, mutual-inductance, eddy-current technique or a commercial SQUID magnetometer. J_c was measured in liquid He or liquid N_2 by a four-probe method with a 1 $\mu\text{V}/\text{cm}$ criterion. Electrical contacts to the samples were made with Woods metal solder.

RESULTS AND DISCUSSION

The 2212 tapes were heat treated by partial melting and subsequent annealing to re-form the 2212 phase. The 2223 tapes were heat treated by reactive sintering that incorporated a transient liquid. The results from each are discussed separately.

2212 Tapes

Optimal heat treatment, which included cooling from 890 to $\approx 860^\circ\text{C}$, resulted in large, highly textured 2212 grains and some alkaline-earth cuprates.⁵ Cooling to 855°C resulted in large grains that exhibited significant favorable texture near the Ag sheath, but not in the center of the core. For all tapes, alignment was strongest at the Ag interfaces.^{5,12-14} Solidification of the 2212 phase appears to have occurred heterogeneously. Cooling to the lowest temperature of 855°C allowed coarsening of the alkaline-earth cuprates that formed during the partial melting at 890°C. Examination of the quenched tapes revealed that partial melting caused formation of primarily $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_x$ (14/24) and $(\text{Sr,Ca})_2\text{CuO}_3$ (2/1). The 14/24 phase persisted at all temperatures and became very coarse during cooling. The 2/1 phase was smaller and was consumed at lower temperatures by the 2212 phase. These results suggest that heating and cooling schedules should be modified so that the coarseness of 14/24 is minimized. More rapid cooling from 880 to 860°C may accomplish this (Fig. 1). The type and size of the alkaline-earth cuprates that form are

dependent on composition.^{5,12-14} Solid-state sintering at 840°C after final rolling did not change the microstructures significantly, although textures improved slightly.

The highest transport J_c obtained at 4.2 K was 1.0×10^5 A/cm². Reductions of 10% or less per pass during rolling led to higher J_c values. Quantitative X-ray diffraction analysis indicated a strong correlation between J_c and texture.¹⁵ The 2212 grains formed a colony structure.¹³ Within each colony, the c-axis alignment was very good, but the angles between colonies were generally ≈ 10 – 30° . The key to optimal processing was an appropriate partial-melting heat treatment. Alkaline-earth cuprates formed during the partial melting; it was impossible to eliminate them entirely. In tapes with high J_c values, the cuprates were flattened and textured and thus had little deleterious effect on J_c .



Fig. 1. SEM photomicrographs of (a) 2212 quenched from 890°C, showing large 14/24 and smaller 2/1 needles; (b) 2212 held 1 h at 870°C during cooling, showing very large needles; and (c) 2212 held 1 h at 860°C during cooling, showing smaller 14/24 than in figure (b).

2223 Tapes

X-ray diffraction data indicated that the 2223 phase was formed within a fairly narrow temperature range. The range varied with the phases present. In general, the optimal range in air was 841–845°C.^{8,12} SEM indicated that the alkaline-earth cuprates increased in size during annealing at $\approx 843^\circ\text{C}$. In addition, a Cu-deficient phase closely related to the $\text{Bi}_9(\text{Sr,Ca})_{16}\text{O}_x$ phase was detected.^{8,12} A temperature higher than 845°C hindered 2223 formation; the microstructures consisted of 2212, large grains of 14/24, and smaller grains of 2/1. The microstructural development was reflected in the J_c data. After 150 h in air at 845°C, the phase mixtures that reacted to form 2223 had the highest J_c values.

The 2223 work was extended into a study of the effects of small amounts of liquid phase on powder-in-tube processing. The liquid phase was thought to benefit powder-in-tube processing by facilitating grain growth and texturing, and by healing damage incurred during mechanical processing.^{12,16} The total amount of liquid that formed during processing of 2223 was manipulated by compositional adjustments. The largest DTA endotherm in air for $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_y$, presumed to result from partial melting, increased from $\approx 830^\circ\text{C}$ for $x = 1.0$ to $\approx 865^\circ\text{C}$ for $x = 0.0$. The DTA traces of $\text{Sr}_x\text{Ca}_{1-x}\text{CuO}_z$ also varied significantly, but not monotonically, with x . The DTA traces of the powder mixtures, however, varied only slightly with x . This possibility was supported by SEM, which indicated very little second phase

in the $x = 0.0$ mixture after only 50 h at 820°C in 8% O_2 . Very large regions of second phase were observed in the $x = 1.0$ mixture under the same conditions, but the size of the second phase decreased dramatically after a total heat treatment time of 150 h. As shown in Fig. 2, annealing at $\approx 843^\circ\text{C}$ in air or at $\approx 820^\circ\text{C}$ in 8% O_2 for extended periods caused the mixture of 2212 and alkaline-earth cuprates to react to form the 2223 phase.

The highest J_c at 77 K, $3 \times 10^4 \text{ A/cm}^2$, calculated from the cross-sectional area of the superconductor core, was obtained with the $x = 0.0$ mixture after heating in 8% O_2 at 820°C for 350 h. This tape contained a 20 vol.% Ag addition. J_c values for the other samples under the same conditions ranged down to $0.8 \times 10^4 \text{ A/cm}^2$ for the $x = 1.0$ sample. The highest J_c for samples processed in air, $1.3 \times 10^4 \text{ A/cm}^2$, was also obtained with the $x = 0.0$ sample. It was found that Ag additions helped to distribute the liquid during heat treatment of 2223 BSCCO.

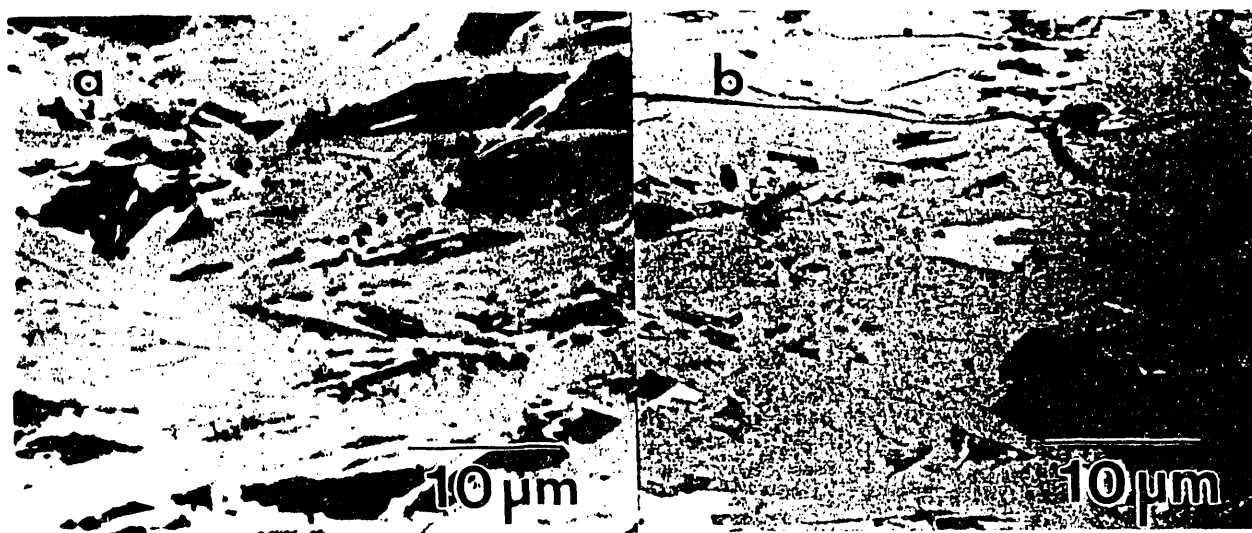


Fig. 2. SEM photomicrographs of 2223 tapes annealed in air at 845°C, (a) low- J_c tape containing large alkaline-earth cuprates and (b) high- J_c tape containing fewer large alkaline-earth cuprates.

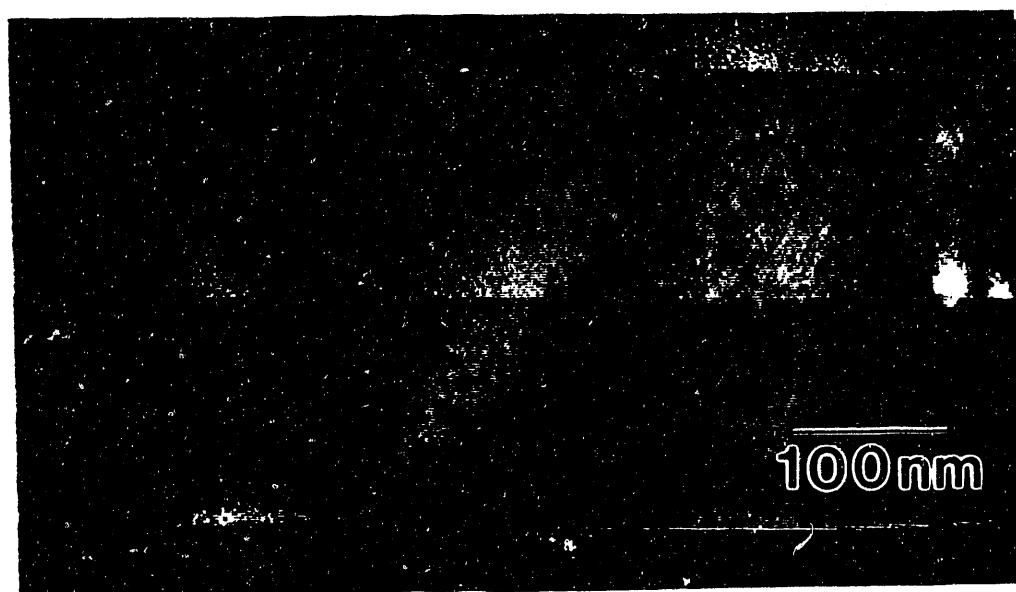


Fig. 3. TEM photomicrograph of 2223 tape annealed in air at 845°C, showing oriented grains.

SUMMARY

Ag-clad tapes were fabricated from 2212 and 2223 Bi-Sr-Ca-Cu-O. A liquid phase was present during heat treatment of both types of tape. As a consequence, alkaline-earth cuprates were always present in the final conductor. In the tapes with the highest J_c values, the cuprates tended to be relatively small and to be aligned with the rolling direction.

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