

CONF-960850--9 AN4ET/CP--88996

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August 1996

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Abstract submitted to Applied Superconductivity Conference, Pittsburgh, PA, August 25-30, 1996.

*Work supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, as part of a DOE program to develop electric power technology, under Contract W-31-109-Eng-38.

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Fabrication and Characterization of (Bi,Pb)-Sr-Ca-Cu-O (2223) Bars*

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Abstract—Bulk bars for current lead applications were fabricated from (Bi,Pb)-Sr-Ca-Cu-O (Bi-2223) for low thermal conductivity and high critical current. Bars measuring 17.8 cm in length were made by uniaxially pressing Bi-2223 powder of controlled (1.7/0.34)223 and (1.8/0.4)223 phase composition. The bulk bars were densified by subjecting them to a schedule of alternate liquid-phase sintering and cold isostatic pressing. Liquid-phase sintering temperatures were optimized from differential thermal analysis and microstructure morphology. Phase purity and microstructure were evaluated by X-ray diffraction and scanning electron microscopy. Low-resistance silver contacts were applied to the bars by hot-pressing at 820°C and 3 MPa. Critical current densities ≈ 1000 A/cm² (critical currents of 750 A at 77 K in self-field conditions) were achieved.

I. INTRODUCTION

Current leads require bulk superconductor bars with high current-carrying capacity and low thermal conductivity [1]. Bulk (Bi/Pb)SrCaCuO (BPSCCO) bars of controlled (1.7/0.34)223 and (1.8/0.4)223 stoichiometries are candidate materials for this application. Previous work on powder-in-tube (PIT) tapes has shown that a liquid phase is necessary to increase reaction kinetics and critical current density [2]. A similar reactive-liquid sintering approach was used in this study; however, processing temperatures were higher for bulk BPSCCO than for PIT tapes due to the absence of silver, which lowers the melting temperature of BPSCCO [3].

II. EXPERIMENTAL METHODS

A. Powder Processing

The nominal 2223 stoichiometric phase was formed by the two-powder process, which consists of reacting 2212 and CaCuO₂ powders [4]. Precursor powders Bi_{1.7}Pb_{0.34}Sr_{2.0}Ca_{1.0}Cu_{2.0}O₈ and CaCuO₂ were obtained from Seattle Specialty Ceramics Inc., and the Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{1.0}Cu_{2.0}O₈ precursor powder was obtained from Superconductive Components Inc.

The 2212 powders were calcined at reduced pressures of 3.5 torr in 100% flowing O₂ at 740°C for 6 hr to reduce residual carbonates. The calcination temperature was then

*Work supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, as part of a DOE program to develop electric power technology, under Contract W-31-109-Eng-38.

raised to 840°C for 24 hr in flowing CO₂-free air at ambient pressure to oxidize the precursor powders to the single 2212 phase. Powder phase purity was monitored by X-ray diffraction. Stoichiometry was verified by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Phase-pure 2212 and CaCuO₂ powders were batched stoichiometrically into 2223 and vibratory-milled for 4 hr in isopropyl alcohol to homogenize the powder. The 2223 two-powder mixture was pan-dried under constant stirring to prohibit particle segregation, then oven-dried for 24 hr, and finally sieved through a 50-mesh screen.

B. Bar Fabrication and Processing

Bar fabrication commenced with uniaxially pressing of the stoichiometric two-powder mixture in a 17.8 x 1.27 cm rectangular steel die at 16.5 MPa. Cross-sectional areas of the pressed bars averaged 1.0 cm². Green-state density values for the pressed bars were near 54% of theoretical density.

The bars underwent thermomechanical processing by subjecting them to an alternating liquid-phase sinter/cold isostatic pressing (CIP) schedule to achieve phase-pure 2223 and final densities approaching 80% of theoretical. Liquid-phase sintering parameters were characterized by differential thermal analysis (DTA). Post-processing cross-sectional areas averaged 0.75 cm².

Both stoichiometries of 2223 bars were sintered at 852 to 866°C for 50 hr in air, followed by a CIP at 138 MPa. This schedule was completed twice, followed by a final sintering for a total sintering time of 150 hr. Ag contacts were diffusion-bonded to the bars via hot pressing for 2 hr at 820°C in air at 3 MPa. The contacts showed excellent mechanical strength and contact resistivities as low as 300 nΩ-cm² at 77 K [5].

Transport critical current densities, J_c, were measured by the four-probe method with a 1000-A pulsed (300 ms pulse width) current source at 77 K in self-field conditions.

III. RESULTS AND DISCUSSION

A. Temperature Effects

Measurements of critical current density between 852 and 866°C (Fig. 1) show that the optimal processing temperature for both the (1.7/0.34)223 and (1.8/0.4)223 bars is 861°C. Average J_c for the (1.7/0.34)223 bars peaked at 960 A/cm², while the (1.8/0.4)223 bars peaked near 880 A/cm². More than 20 bars at peak J_c have been produced for prototype current leads [6].

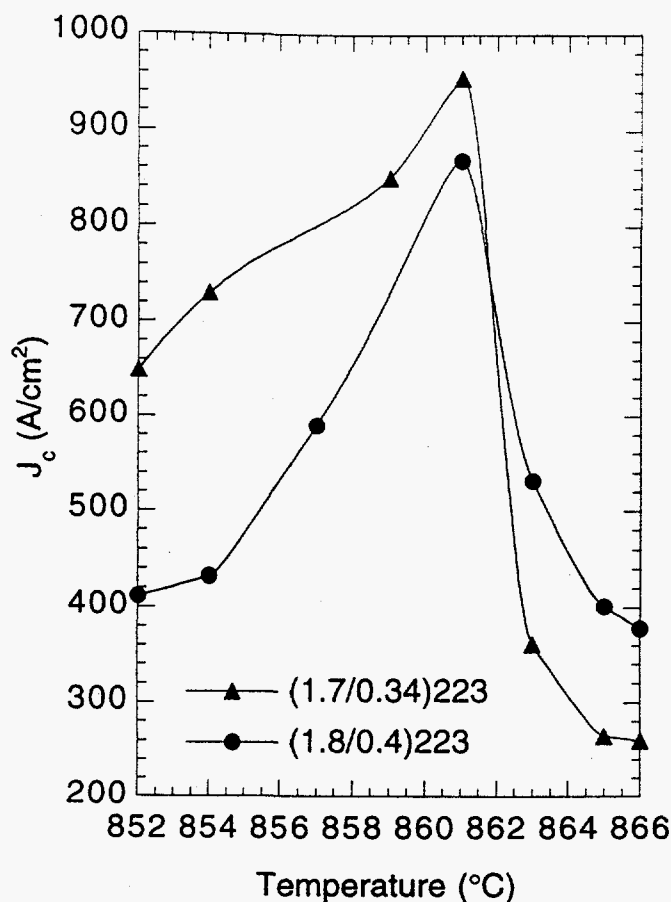


Fig. 1. Critical current density (J_c) vs. sintering temperature ($^{\circ}\text{C}$) for (1.7/0.34)223 and (1.8/0.4)223 bars.

The optimized heat treatment temperature was compared with the melting onset temperature via DTA (Fig. 2). Figure 2 shows the change in melt behavior during conversion of the two-powder mixtures to phase-pure 2223. The 861 $^{\circ}\text{C}$ sintering temperature is well within the liquid-phase region of the two-powder mixture during the first 50 hr of sintering, and this temperature is greater than the onset of melting for longer sintering times.

The melting points (defined as the endotherm trough) of (1.7/0.34)223 and (1.8/0.4)223 are $\approx 876^{\circ}\text{C}$ and $\approx 882^{\circ}\text{C}$, respectively. Stoichiometries rich in Bi and Pb tend to lower the melting temperatures [7]. For heat treatment times >50 hr, the melting onset temperature ($\approx 850^{\circ}\text{C}$) is roughly the same for both stoichiometries. Processing temperatures just above the melt-onset temperature produce the best J_c , which is independent of BPSCCO stoichiometry.

The shape of the curve for J_c versus processing temperature ($^{\circ}\text{C}$) (Fig. 1) provides insight into the rate of reaction and reaction products. At temperatures $<861^{\circ}\text{C}$, phase conversion and grain growth kinetics are slow because of the lack of liquid phase. Similar results have been found in PIT tapes at lower temperatures [8]. Liquid-phase sintering is accomplished through a transient, reactive Pb-rich liquid. Both the (1.7/0.34)223 and the (1.8/0.4)223 contain Pb contents slightly greater than the lead solubility limits for

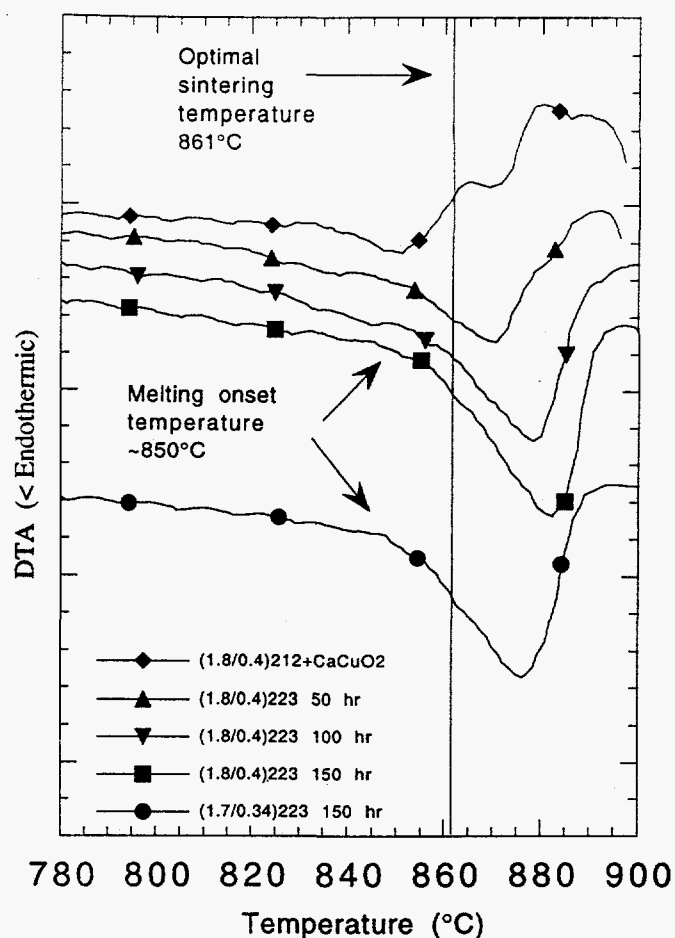


Fig. 2. Differential thermal analysis (DTA) for (1.7/0.34)223 and (1.8/0.4)223 bars.

2223 given by Majewski [7]; this allows for a Pb-rich liquid to act as a sintering aid. The lead content for the (1.7/0.34)223 bars is 0.037 in the 2223, phase whereas that for the (1.8/0.4)223 bars is 0.043. Pb-rich liquids help to heal the damage caused by cold isostatic pressing [2] which is vital because it improves densification and aids sintering kinetics by bringing the grains in contact with each other to increase diffusional necking and grain boundary diffusion [9].

Figure 3 shows the density progression of the (1.7/0.34)223 bars fired at 861 $^{\circ}\text{C}$ and is typical of bars fired between 852 $^{\circ}\text{C}$ and 866 $^{\circ}\text{C}$. Bars of the (1.8/0.4)223 stoichiometry shows identical behavior. The sharp initial increase in density after 50 hr of sintering from the green state is due to the large amount of liquid present, as evident from figure 2, which allows for particle rearrangement and capillary forces to draw particles together [9]. The intermediate CIP'ing offsets retrograde densification from 50 to 150 hr of sintering and allows final density values near 80% of theoretical.

At temperatures $<861^{\circ}\text{C}$, the amount of liquid aiding the reaction is prohibitively low and does not allow complete conversion from 2212 to 2223 within 150 hr, and grain growth is minimal. Figure 4 is a back-scattered electron (BEI) photomicrograph of a (1.7/0.34)223 sample processed

at 852°C for 150 hr. The large number of black phases indicate considerable unreacted Ca_2CuO_3 and CuO [7], [10]. Grain development is retarded by the lack of sufficient liquid phase during sintering and lacks the platelike grain structure typical of 2223. The (1.8/0.4)223 bars processed at 852°C show identical traits.

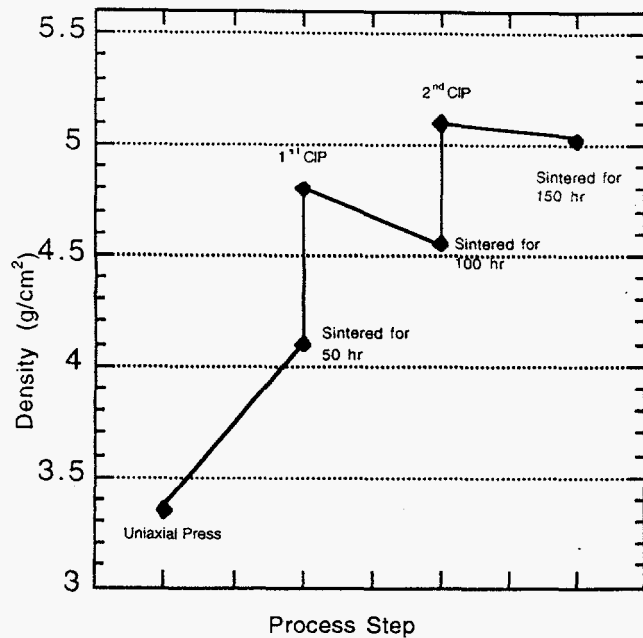


Fig. 3. Density progression for the (1.7/0.34)223 bars sintered at 861°C.

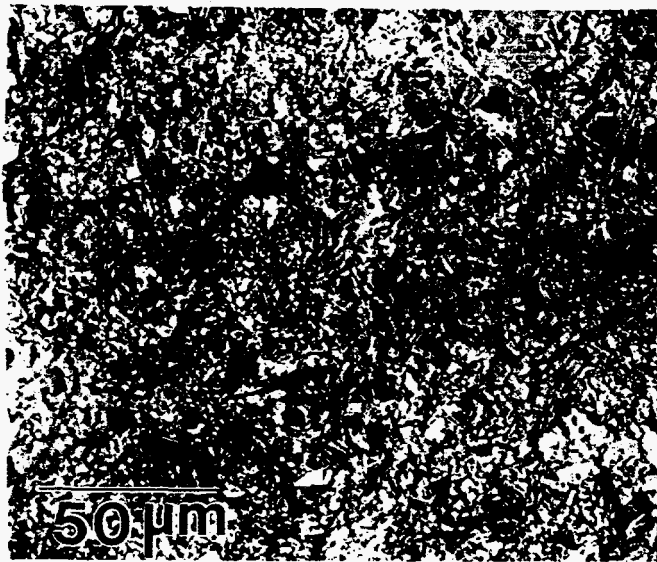


Fig. 4. BEI photomicrograph of (1.7/0.34)223 bar fired at 852°C for 150 hr.

Figures 5 and 6 shows the microstructures of the (1.7/0.34)223 and (1.8/0.4)223, respectively, at the optimal processing temperature of 861°C. Both microstructures show well-developed 2223 platelike grains and minimal second phases.



Fig. 5. BEI photomicrograph of (1.7/0.34)223 bar fired at 861°C for 150 hr.



Fig. 6. BEI photomicrograph of (1.8/0.4)223 bar fired at 861°C for 150 hr.

The sharp drop-off in critical current density at temperatures $>861^\circ\text{C}$ was coincident with a significant microstructural change. This region suggests the decomposition of the sample [7] and the subsequent formation of a large degree of $(\text{Sr,Ca})_x\text{Cu}_y\text{O}_z$ and Pb-rich phases that are nonsuperconductive [10], [11]. These second phases reduce J_c by their reduced volume fraction of 2223. Scanning electron microscopy studies validate this decomposition. Figure 7 is a BEI photomicrograph of a (1.7/0.34)223 bar fired at 865°C for 150 hr, showing a large number of white regions containing Pb-rich second phases [7]. Results were similar for the (1.8/0.4)223 stoichiometry.

IV. SUMMARY

Critical current densities of $\approx 1000 \text{ A/cm}^2$ (750 A at 77 K in self-field conditions) were achieved in the (1.7/0.34)223 composition at 861°C after 150 hr. (1.8/0.4)223 bars peaked at 880 A/cm^2 (660 A) under the same processing and testing conditions. In the case of the (1.7/0.34)223 bars, the liquid phase is transient and Pb solubility levels suggest that most of this liquid is absorbed into the matrix material as the phase conversion from 2212 and CaCuO_2 proceeds to phase-pure 2223. (1.8/0.4)223 has a higher Pb content, and less of the transient liquid is incorporated into the 2223 matrix in the conversion from 2212, leading to higher residual Pb-rich liquid levels. J_c measurements and microstructural morphology suggest that reducing the amount of residual liquid phase in the final microstructure leads to higher J_c levels.

DTA results show similar liquid onset temperatures of $\approx 850^\circ\text{C}$ for the (1.7/0.34)223 and the (1.8/0.4)223 despite their different stoichiometries. Identical maxima in the J_c vs. processing temperature curves at 861°C reinforce the DTA results, suggesting that subtle differences in stoichiometries do not play as large a role in determining optimal processing temperatures as does the liquid onset temperature.

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Fig. 7. BEI photomicrograph off (1.7/0.34)223 bar fired at 865°C for 150 hr.

B. Stoichiometric Effects

The lead solubility limit of 2212 at 861°C is ≈ 0.059 (Pb/Bi+Pb+Sr+Ca+Cu), as given by Majewski [7]; the value for 2223 decreases to ≈ 0.034 . This drop in Pb solubility limit in the phase conversion from 2212 to 2223 results in the exuding of Pb-rich liquid from the matrix. Any excess Pb-rich liquid not incorporated into the 2223 combines with calcium to form a nonsuperconducting phase of CaPbO_4 and aids in the formation of other nonsuperconducting second phases, all of which result in a corresponding decrease in J_c [11].

Explanations for the higher J_c in the (1.7/0.34)223 bars may be found in the lead solubility limits for the two stoichiometries. The lead content of the (1.7/0.34)223 bars (0.037) is nearly at the solubility limit given by Majewski (0.034) at 861°C [7] and therefore should contain less residual Pb-rich liquid in the final microstructure than the (1.8/0.4)223 bars (0.043) and in turn should exhibit a higher J_c . The difference in the amount of Pb between the stoichiometries maybe subtle enough that the difference in residual Pb-rich liquid phase between the final microstructures is beyond the resolution of our micrographs. This would be especially true if the Pb-rich liquid phase is present as a thin amorphous phase coating the 2223 platelike grains.