Cooling Rate Effects on the Microstructure, Critical Current Density, and T_c Transition of One- and Two-Powder BSCCO-2223 Ag-Sheathed Tapes

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***Abstract*—An important variable controlling the critical current density (J_c) of Ag-sheathed BSCCO-2223 tapes is the degree of phase purity of the reacted tapes. Most correlations between J_c and microstructure show that it is highly desirable to reduce the amount of non-superconducting second phases to as low a level as practical. In recent studies of the influence of cooling rate after the final reaction, we find contradictions to this general rule. The J_c (77 K, 0 T) of so-called "one-powder" tapes can be raised by as much as 50% (from ~8,000 A/cm^2 to 12,000 A/cm^2) by slow cooling in 7.5%O_2 at 0.05°C/min, even though large 2212 grains are usually seen in the slowly cooled microstructure. However, the higher J_c of the slow-cooled state does correlate with a sharper T_c transition. Experiments with "two-powder" tapes have produced similar results. These apparently anomalous results emphasize the important role played by the connectivity of the polycrystalline core in determining J_c.**

I. INTRODUCTION

Many parameters must be controlled and optimized during the fabrication and thermomechanical processing of Ag-clad $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (hereafter referred to as BSCCO-2223, or 2223) tapes. The effects of powder composition, mechanical deformation, and heat treatment temperature, time, and atmosphere on the J_c of 2223 tapes have been studied extensively. One aspect that has received less attention in the literature is what occurs during the cool-down after the 2223 formation reactions. Lay [1] found that cooling at 1°C/min in air resulted in a ~15% J_c (77 K, 0 T) increase over tapes cooled at ~3°C/min, and reported that holding below the 2223 reaction temperature of ~830°C in 2-5%O_2 after processing in air could in some cases increase the J_c by a factor of two. Other groups have reported that the T_c transition of bulk 2223 samples can be sharpened by post-annealing above 700°C for ~10 hours in 6-10%O_2 [2,3].

We have found, as have others [4,5], that processing tapes in 7.5%O_2 is more favorable for 2223 formation than processing in air. Here we summarize several cooling rate experiments on 2223 tapes which have been reacted *and* cooled in 7.5%O_2, and discuss the effect of cooling rate on the superconducting properties and microstructure.

Many advances in the J_c of Ag-clad BSCCO-2223 tapes have come from improving the degree of 2223 phase purity. Microstructures containing a large volume fraction of non-superconducting "second phase" particles are not desirable because these particles are typically many μm in size, and thus disturb the local alignment of the plate-like 2223 grains [6] and decrease the superconducting fraction of the conductor cross section. The importance of the 2223 phase purity extends to an even finer scale; it has been shown that intergrowths of even one or a few half-unit-cells of residual BSCCO-2212 within 2223 grains can be detrimental to J_c [7,8]. Thus, since many experiments to improve J_c have the goal of producing a more homogenous 2223 microstructure, it was interesting to find a contradiction to this general rule. It was found that cooling at rates sufficiently slow as to allow some decomposition of the 2223 phase often resulted in better superconducting properties, even though the 2223 phase purity was evidently degraded on a scale of μm.

Manuscript received October 16, 1994.
The Wisconsin work was supported by ARPA (N00014-90 J-4115) and EPRI (RP8009-05), and the ANL work by the U.S. Department of Energy, Energy Efficiency and Renewable Energy Office, as part of a program to develop electric power technology, under contract W-31-109-Eng-38.

II. EXPERIMENTAL PROCEDURE

Ag-clad tapes about 3 mm wide and 0.2 mm thick were made by rolling round wires produced by standard oxide-powder-in-tube methods. Tapes were fabricated with a standard "one-powder" uncontrolled phase balance powder of nominal composition $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_{2.0}Cu_{3.0}O_x$ and with "two-powder" controlled phase assemblage powders ($Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{1.0}Cu_{2.0}O_x$ and $CaCuO_2$ powders were mixed to give an overall composition of $Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{2.0}Cu_{3.0}O_x$) [9,10]. The tapes were then thermomechanically processed as described below. All heat treatments and cool-downs were given in a 7.5% O_2/balance N_2 atmosphere, and tapes were uniaxially pressed at ~1 GPa between heat treatments.

A. One-powder tape processing

The one-powder tapes were given three heat treatments of 72 hours each at 818°C. The cooling rate to 730°C from the reaction temperature after the third reaction heat treatment was either 4°C/min or 0.05°C/min. After reaching 730°C, the samples were furnace cooled at ~20°C/min.

B. Two-powder tape processing

Two separate experiments were performed with the two-powder tapes. In the first experiment, only one heat treatment was given (and thus the conversion to 2223 was incomplete), and the cooling rate after this single heat treatment was varied. The second experiment was similar to the one-powder tape experiment described above, in that the cooling rate after the final heat treatment was varied.

1) Cooling rate varied after the first heat treatment: A sample was given a 30 hour heat treatment at 825°C, and cooled to 725°C at 5°C/min. After this short heat treatment the conversion of the precursor powder to BSCCO-2223 was not complete. A second sample was given the same 30 hour reaction heat treatment, and then cooled to 725°C at 0.05°C/min. Because the length of the cool-down of this sample was comparable to the length of the 30 hour reaction heat treatment (during cool-down the sample was between 825°C and 725°C for ~33 hours), a third sample was given a 63 hour reaction heat treatment at 825°C, and was cooled at 5°C/min to 725°C.

2) Cooling rate varied after three heat treatments: Two-powder tapes were given a 50 hour first heat treatment at 825°C, followed by 100 hour second and third heat treatments. After the third heat treatment and subsequent cool-down (at 4°C/min), the samples were quickly (~15°C/min) re-heated to 825°C in the 7.5%O_2 atmosphere (with no intermediate pressing), held for 1 hour at 825°C, and then cooled to 725°C at four different rates: 5, 0.5, 0.16, and 0.05°C/min.

The transport critical current values (1 μV/cm) were converted to J_c by dividing by the average of two or three cross-sections measured by image analysis. All critical currents were measured at 77 K, 0 T. The temperature dependence of the zero-field-cooled AC susceptibility of many of the samples was measured at 1 and 20 G, at 125 Hz, with the field applied normal to the rolling plane of the tape (i.e. nominally parallel to the c-direction of the aligned 2223 grains). A scanning electron microscope (SEM) operated at 15 kV was used to examine the microstructures of the tapes. X-ray diffraction (XRD) using Cu-Kα radiation was also used to examine the phase purity of some samples.

III. Results

A. Fully processed one-powder tape experiments

Fig. 1 is a plot of the AC susceptibility of the fast (4°C/min) and slow (0.05°C/min) cooled samples as a function of temperature. The inset in Fig. 1 shows J_c as a function of heat treatment time for the fully processed one-powder tapes. Slow cooling at 0.05°C/min to 730°C in 7.5%O_2 increased the J_c by almost 50% to ~12,000 A/cm^2 compared to the tape that was fast cooled at 4°C/min. The slow cooled sample has a sharper T_c transition than the fast cooled sample, and no T' kink indicative of BSCCO-2212 intergrowths [7,8] is visible, whereas a kink in the transition is apparent for the fast cooled sample.

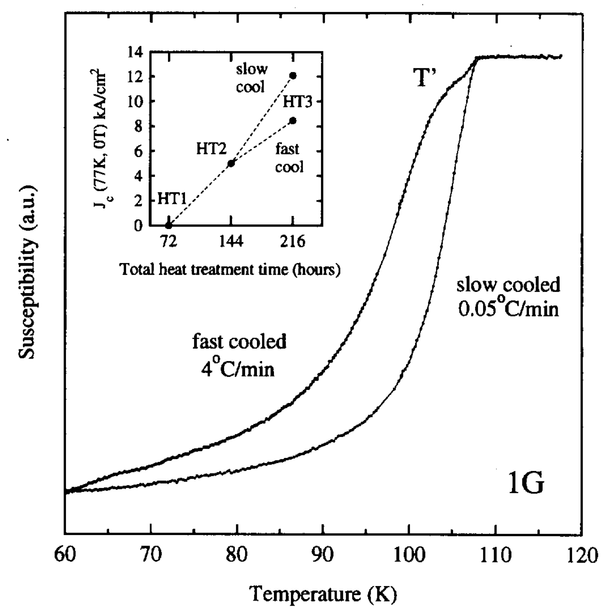
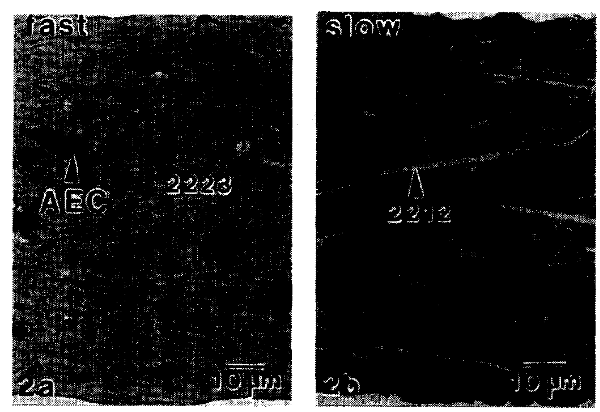


Fig. 1. Normalized AC susceptibility (1 G) of the fast cooled (4°C/min) and slow cooled (0.05°C/min) fully processed (3 heat treatments) one-powder samples. The inset shows critical current density (77 K, 0 T) as a function of heat treatment time and number.



Figs. 2a and 2b. SEM backscatter micrographs of typical fast (4°C/min) and slow (0.05°C/min) cooled fully processed one-powder samples, respectively. Large BSCCO-2212 grains (light gray needles) are dispersed throughout the thickness of the slow cooled core.

Figs. 2a and 2b are SEM backscatter micrographs of typical fast cooled (4°C/min) and slow cooled (0.05°C/min) one-powder tape microstructures, respectively. Many large BSCCO-2212 grains (light gray "needles") are visible throughout the thickness of the slow cooled sample (Fig.

2b). These 2212 grains were seldom seen in the second heat treatment or in the fast cooled (4°C/min) third heat treatment samples (Fig. 2a), which suggests that slow cooling at 0.05°C/min to 730°C caused the regular formation of these 2212 grains. Presumably these 2212 grains formed as a result of 2223 decomposition, since 2223 is reported to be unstable below ~790°C in 7.5%O_2, decomposing to 2212, $(Ca,Sr)_2PbO_4$, and other non-superconducting phases [5,11].

In summary, cooling fully processed one-powder tapes at 0.05°C/min to 730°C in 7.5%O_2 resulted in a sharper T_c transition and a 50% higher J_c than tapes cooled more quickly at 4°C/min. The superconducting properties improved, despite many large 2212 grains in the sample.

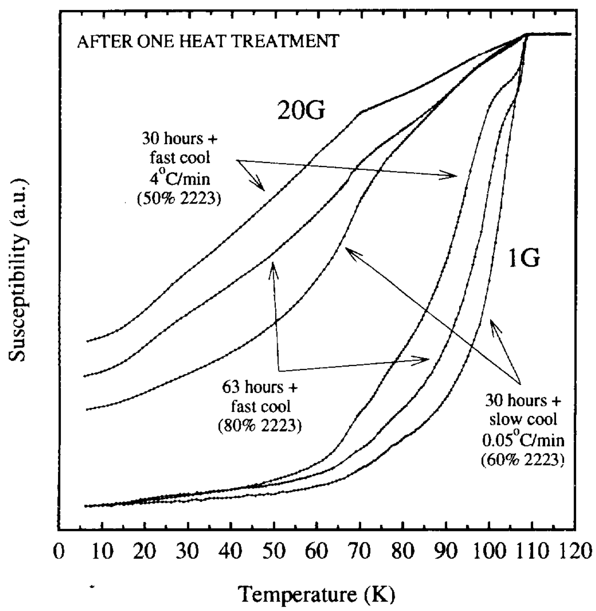


Fig 3. AC susceptibility (normalized to 1 G signal) of the partially reacted two-powder samples. The slowly cooled sample has a sharper transition than the more extensively converted sample (the 63 hour heat treated sample).

B. Two-powder tape experiments

1) Cooling rate varied after the first heat treatment: It was found that the cooling rate has an effect on the critical current density and T_c transition of two-powder tapes after the first heat treatment, when the 2223 conversion is far from complete. The sample that was heat treated for 30 hours and cooled at 5°C/min contained ~50% 2223 (by XRD) and had a J_c of 1,100 A/cm^2, compared to the sample given a 30 hour heat treatment and cooled at 0.05°C/min, which was ~60% converted and had a J_c of 2,800 A/cm^2. This slowly cooled sample had a J_c value greater than that of the sample given the longer 63 hour heat treatment (J_c = 2,300 A/cm^2), even though this more completely reacted sample contained ~80% 2223. AC susceptibility results for these three partially reacted samples, shown in Fig. 3, show that the T_c transition was substantially sharpened by slow cooling at 0.05°C/min, as was also found in the fully processed one-powder tapes. Note that the slowly cooled sample (containing 60% 2223) has a sharper transition than the sample that was 80% converted to 2223 (the 63 hour heat treated sample), and that at 20 G the slowly cooled sample exhibited a greater fraction of its 1 G signal than did the fast cooled tapes.

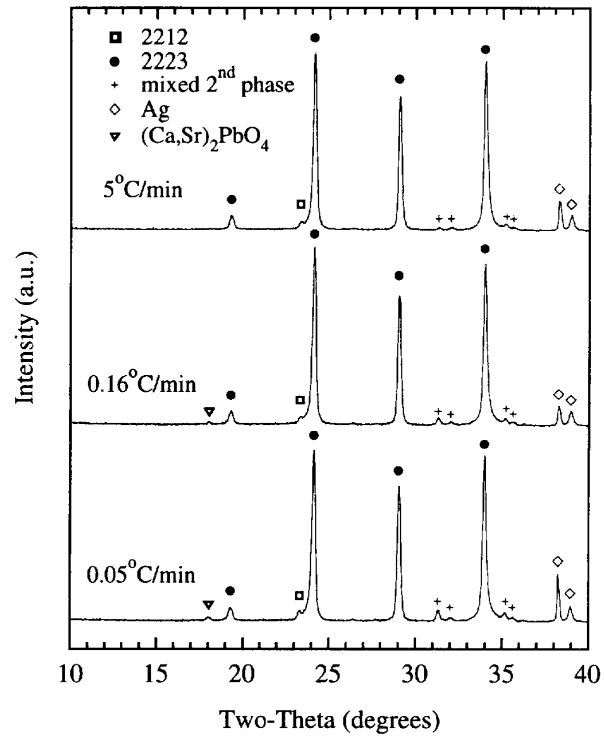


Fig. 4. XRD spectra for the fully processed two-powder tapes that were cooled from 825°C to 725°C at 5, 0.16, and 0.05°C/min in 7.5%O_2. The fraction of impurity phases increases with decreasing cooling rate.

2) Cooling rate varied after three heat treatments: Fig. 4 shows XRD patterns for the samples that were cooled to 725°C at 5, 0.16, and 0.05°C/min. Note that as the cooling rate was decreased, the diffraction peak heights for $(Ca,Sr)_2PbO_4$ and other second phases (mainly alkaline earth cuprates) increased, presumably because of 2223 phase decomposition. However, unlike what was observed for the one-powder tapes (Fig. 2b), the relative amount of 2212 did not noticeably increase (as determined by SEM and XRD).

Fig. 5 shows J_c as a function of cooling rate for the two-powder samples that received three heat treatments, were re-heated to 825°C, and then cooled at different rates in 7.5% O_2. The J_c increased as the cooling rate was decreased, reached a maximum value at a rate of 0.16°C/min, and then decreased at still slower rates. Thus, as was found for the one-powder samples, slow cooling can increase the J_c of fully processed two-powder tapes, even though the 2223 phase homogeneity was reduced. However, the fractional J_c increase (~20%) was less than for one-powder tapes.

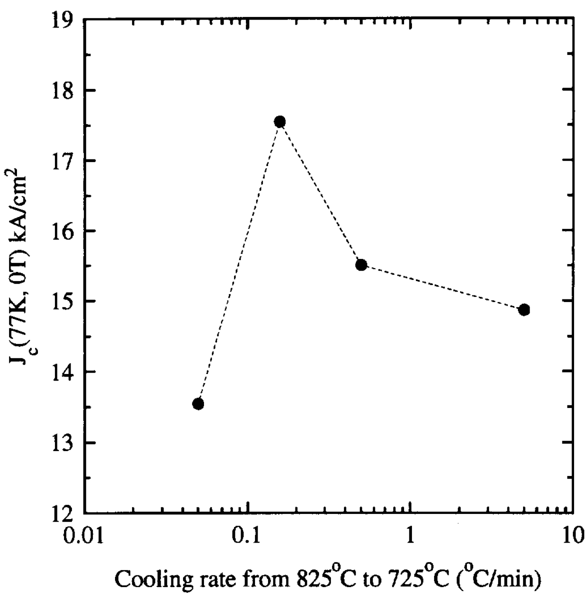


Fig. 5. Critical current density as a function of cooling rate from 825°C to 725°C for the fully processed two-powder tapes.

IV. Discussion

In principle, the J_c of 2223 tapes can be determined either by flux pinning or by the connectivity of the 3-D grain network. We are not aware of any work that has explicitly proved that it is possible to vary the flux pinning of the 2223 phase by varying the processing conditions. Indeed, the small composition range of the phase field [12], and the small sensitivity of T_c to O doping makes the opportunities for flux pinning by composition control small. We thus conclude that the observed changes in properties are more likely to be the result of changes in the connectivity of the samples than in their flux pinning properties.

Whether or not the current path in BSCCO tapes is dominated by "brick wall" [13] or "railway switch" [14] linkages, the dominant experimental evidence until now is that there is a strong positive correlation between a higher J_c(0 T, 77 K) and a higher or absent kink in the AC or DC susceptibility trace [7,8]. The source of the kink is 2212 intergrowths, one to a few half-unit-cells thick, remaining from the unconverted precursor powder. In the present case, the 2212 is on a much larger scale, μm rather than nm, and is formed by decomposition of the 2223 phase. It is possible to rationalize both sets of data by postulating that the 2212 formed by decomposition has a very different morphology than that of residual 2212. Whereas residual 2212 was found in almost all 2223 grains [7,8] and thus exerted a large effect on the current path, the 2212 formed by decomposition of the 2223 phase is larger (Fig. 2b) and seems to form discrete grains. Testing of this hypothesis by transmission electron microscopy is desirable in order to make clear the reason for the unexpected results reported here.

V. Conclusions

Although in general it is desirable to achieve a phase-pure 2223 microstructure to maximize J_c in BSCCO-2223 tapes, an exception to this rule is found for tapes that are cooled slowly after reaction heat treatment. J_c increases of 20-50% and marked sharpening of the T_c transition were observed for both one- and two-powder tapes when samples were cooled at a rate of ~0.15-0.05°C/min in 7.5%O_2. These improvements in superconducting properties were observed despite a reduced microstructure phase purity caused by 2223 decomposition. However, once the decomposition of the 2223 phase to 2212 and other non-superconducting phases became too extensive, the J_c decreased. We attribute this behavior to changes in the connectivity of the polycrystalline core as the cooling state is varied.

Acknowledgment

We would like to thank Y.S. Sung and R.D. Parrella for the X-ray diffraction traces.

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