FABRICATION, PROPERTIES, AND MICROSTRUCTURES OF HIGH-T_c TAPES AND COILS MADE FROM Ag-CLAD Bi-2223 SUPERCONDUCTORS*

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ABSTRACT

Bi-2223 precursor powders were prepared via a solid-state reaction using carbonates and oxides of Bi, Pb, Sr, Ca, and Cu. Our results indicate that an in-situ reaction between constituent phases with the formation of a transient liquid that is consumed during final heat treatment, is essential to obtain increased density with greater connectivity between the 2223 grains. Relative amounts of the constituent phases were adjusted in the powder by varying the calcination conditions, and the powder was then used to fabricate Ag-clad tapes by a powder-in-tube technique. By improving process conditions, transport critical current density (J_c) values greater than 4×10^4 A/cm^2 at 77 K and 2×10^5 A/cm^2 at 4.2 and 27 K have

been obtained in short tape samples. Long tapes were cut into lengths upto 10 m long and used in parallel to fabricate small superconducting pancake coils. The coils were characterized at 77, 27 and 4.2 K and the results are discussed in this paper.

INTRODUCTION

Several studies on obtaining single phase and phase identification [1-3] have been made in the system Bi-Sr-Ca-Cu-O (BSCCO) since the discovery of 110 K (2223) superconductor by Maeda et al. [4]. The kinetics of 2223 phase formation are very slow. Lead addition was shown to increase the fraction of 2223 phase [2]. The critical current densities (J_cs) of conventionally consolidated and sintered 2223 samples are very low at 77 K. The powder-in-tube (PIT) method represents a very favorable technique to make long lengths of flexible superconductors. Much effort has been expended in the last few years to improve the properties of Ag-clad 2223 tapes fabricated by the PIT process [5-9]. The main advantages of fabricating tapes by the PIT approach is that grain alignment ("texture") can be achieved by a sequence of thermomechanical processes; texture appears to be a key parameter in improving transport critical current density (J_c).

Work in the 2223 system using the PIT process has progressed rapidly toward the production of long, practical high-T_c superconductors [7,10,11]. Several groups have successfully demonstrated high Jcs in short tape samples with values >4 x 10^4 A/cm^2 at 77 K in zero applied field [5-9, 12,13]. Control of the thermomechanical process makes it possible to achieve a high J_c over long lengths of composite tapes. Little has been reported on the optimum processing schedules and it is well known that

BSCCO superconductors are highly sensitive to preparative conditions. In this paper we discuss the effect of calcination temperature and time on the relative phase content of the BSCCO powder. We also report the fabrication procedures to produce high J_c Ag-clad tapes, together with some aspects of fabricating long-length conductors.

EXPERIMENTAL PROCEDURE

Appropriate amounts of high-purity Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO were weighed, mixed, and calcined at various temperatures in the range of 750-850°C for 50-100 h with intermittent grinding. The synthesized powders were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), and SQUID magnetometer. The calcined powders were then packed by mechanical agitation into Ag tubes. The packed tubes were lightly swaged and drawn through a series of dies, and then rolled to a final thickness of ≈0.1 mm. It is important to keep the reduction ratios during drawing below 15% per pass to achieve optimal properties. A slightly irregular superconductor/Ag sheath interface is formed when high reduction ratios (≈50%/pass) are used during initial stages of the drawing process. Tapes of ≈100 m length have been produced by this technique. Short lengths of tapes were cut and heat treated at temperatures between 830 and 860°C in air with intermittent uniaxial pressing. Long lengths of Ag-clad tapes were tested by winding them into pancake coils. One to six tapes were cowound in parallel on alumina mandrels with insulation (used to separate each turn) and heat treated by the "wind-and-react" approach. Transport J_cs were measured by the standard four-probe technique with a 1 μV/cm criterion.

RESULTS AND DISCUSSION

Nearly phase-pure 2223 powders, as determined by XRD, were obtained by calcining at ≈850°C for 100 h. The phase-pure powders were compacted into pellets and sintered in air at 840–860°C. Sintered pellets were porous (density ≈4.4 g/cm^3) and exhibited J_c of ≈50 A/cm^2. The superconducting transition temperature, as determined by magnetization measurement, was ≈110 K. Heating the powders at temperatures of less than 850°C or for shorter times at ≈850°C resulted in powders with 2223, 2212 (85 K phase), and other nonsuperconducting phases such as the alkaline-earth cuprates and calcium plumbate. The DTA trace exhibited two endotherms with onset temperatures of ≈835°C and ≈850°C. The mixed-phase powders were compacted into pellets and sintered for ≈100 h at temperatures in the region bounded by the two endotherms. Transient-liquid phase sintering was observed in pellets (density ≈5 g/cm^3) made with the mixed-phase powders. The J_c of sintered pellets were ≈250 A/cm^2. These pellets were found by XRD to be single-phase 2223. These results indicate that a transient liquid that is fully consumed by an in-situ reaction during sintering is essential to obtain increased density. The relative amounts of the constituent phases were adjusted in the powder by varying the calcination conditions, and the powders were then used to fabricate Ag-clad tapes. The liquid phase formed during the heat treatment may help to heal the cracks formed during the mechanical working, resulting in superior properties. In contrast, when completely reacted powders consisting of phase-pure 2223 were used, the powders tend to decompose and sustain mechanical damage when subjected to heat treatment and cold working.

High J_c values for short tapes have been achieved by a combination of uniaxial pressing and heat treatments. Samples of ≈4 cm in length were cut from the rolled tapes and subjected to a series of thermal and mechanical treatments. The short length tapes were heat treated at ≈850°C for ≈50 h, cooled, uniaxially pressed at ≈1 GPa and again heated for additional 100 h. The cooled samples were characterized by J_c measurement, scanning electron microscopy (SEM), and XRD and subjected to further pressing and heat treatment cycles.

Polished SEM micrographs of the Ag-clad 2223 tapes are shown in Fig. 1 (a) and 1(b). As-fabricated tape [Fig. 1(a)] shows no texturing. SEveral secondary phases up to 10 μm in size can also be seen to be distributed throughout the matrix. Uniaxial pressing followed by thermal treatment facilitates the texturing of the 2223 grains, as seen in Fig. 1(b). The secondary phases are fragemented and consumed during the thermomechanical processing. The sample in Fig. 1(b) had a critical current (Ic) of ≈30 A and a J_c ≈3×10^4 A/cm^2 at 77 K, zero applied field. This sample was subjected to a total heat treatment time of ≈250 h at ≈850°C in air with two intermittent pressing. Continuation of thermomechanical processing increased the J_c to $>4 \times 10^4$ A/cm^2 at 77 K.

Figure 2 illustrates the transformation of partially reacted powders into nearly phase-pure 2223 by the thermomechanical treatment. The XRD pattern in Fig. 2, curve A, is an example of a tape sample that received a single pressing and heat treatment routine. The XRD patterns were taken by peeling off a Ag layer with the bulk of the superconductor core remaining intact. A large fraction of the core consists of the 2212 phase, and some 2223 is evident. When the sample was pressed and reheated, the core was converted to >95% well-aligned grains of 2223, as displayed in Fig. 2, curve B. The repeated mechanical deformation and heat treatment thus assists the formation, growth alignment, and joining of the 2223 grains that enable it to carry high currents. However, when the thermomechanical cycles were repeated over a certain limit (this limit depends up on the precursor powder, heat treatment temperature, atmosphere, etc.), the samples start decomposing. Figure 2, curve C shows the XRD of a sample that was subjected to a total heat treatment time of ≈450 h with four intermittent pressing. This figure displays the presence of both the 2212 and 2223 phase. SEM observation revealed that texturing is also deminished considerably in this sample. The J_c of this sample is significantly lower (≈1.5×10^4 A/cm^2) than those measured in samples heat treated for ≈250 h with two uniaxial pressing.

To determine the uniformity and consistency of J_cs along the length of a long conductor, several short samples were sectioned from an as-rolled length at final thickness. These were given a range of specific heat treatments. Similar studies were performed on uniaxially pressed samples; the results are plotted and compared in Fig. 3. As can be seen, the uniaxially pressed samples usually performed much better than the rolled and heat treated samples. This is attributed to additional densification provided by uniform deformation during uniaxial pressing. Repeated rolling (unlike pressing) introduces cracks and reduces J_c. However, as seen from Fig. 3, a large spread in J_c is still observed in both the pressed and rolled samples, due in large part to nonuniformities in the core of the superconducting composite.

The J_c values of short samples fabricated by uniaxial pressing and heat treatment procedure as a function of applied field at liquid nitrogen (77 K) and pumped liquid nitrogen (64 K) temperatures have been measured. There is a considerable increase in J_c ($\approx 4 \times 10^3$ A/cm^2) at a field of 1 T (H//c) at 64 K compared to the values at 77 K. J_c values as high as 2×10^4 A/cm^2 were achieved at 64 K in a field of 1 T applied parallel to the a-b plane. These results show that practical devices can be made with 2223 tapes operated at temperatures obtainable by pumping liquid nitrogen.

Although the Bi-2223 tapes do not exhibit high J_c in large applied fields at 77 K, at lower temperatures (<40 K) they outperform the NbTi and Nb_3Sn superconductors in very high fields (≥15 T) [8,14,15]. Figure 4 shows J_c measurements taken at liquid helium (4.2 K) and liquid neon (27 K) temperatures in applied magnetic fields up to 20 T. The J_c data were taken for short, pressed, and heat-treated tape samples with the field applied parallel (H // ab) to the flat direction of the tape and also in the perpendicular (H // c) direction. At 4.2 K, field-independent behavior is observed for both directions in applied fields up to 20 T. At 27 K, however, applied fields in the perpendicular direction tend to drive the conductor to the normal state in fields >15 T. As seen in Fig. 4, the samples carry $\approx 10^5$ A/cm^2 in low fields at 4.2 and 27 K. Similar samples were measured over a range of temperatures (from 4.2 to 90 K) as a function of applied field and the results were reported earlier [16]. At 40 K and above, the J_c was seen to drop drastically when magnetic fields are applied in the perpendicular direction.

In order to fabricate long-length tapes successfully, a practical approach such as rolling (without uniaxial pressing) is needed. Using a two-step rolling with an intermediate and final heat treatment, we have fabricated Ag-clad 2223 tapes that are more than 30 m long and ≈0.1 mm thick. These long conductors were spirally wound on a ≈20 cm diameter alumina mandrel and tested. The 33 m long conductor carried a I_c of 16 A at 77 K in self field (corresponding to $J_c > 10^4$ A/cm^2). Long lengths of rolled Bi-2223 conductors were also tested by winding them into pancake coils.

We have fabricated a pancake coil that was wound from three lengths of 10-m-long conductor tapes onto a 2.5-cm-diameter mandrel, resulting in a coil with 7.65 cm outside diameter. The total number of turns in this coil is 57. With a 1 μV/cm criterion, the critical current for this coil was determined to be ≈22 A at 77 K and ≈280 A at 4.2 K. The coil exhibited ≈1250 ampere-turns at 77 K and ≈16,000 ampere-turns at 4.2 K. The generated fields were 330 G (77 K) and 4200 G (4.2 K). Recently we fabricated six such pancake coils, each containing three 10-m lengths of rolled Bi-2223 tapes [17]. These six pancake coils were stacked together, connected in series, and tested at 4.2 and 27 K as a function of applied magnetic fields up to 14.5 T. The total length of rolled conductor tapes in this stack of coils was 180 m. At 4.2 K, the stack carried a maximum I_c of 190 A and a minimum of 109 A in self-field, and 100 A (maximum) and 60 A (minimum), in a field of 14.5 T. A maximum generated field of 1.25 T was measured in zero applied field. At 27 K, the maximum and minimum I_cs were 125 A and 78 A in zero applied field and 69 A and 42 A in an applied field of 14.5 T [17].

SUMMARY

We have outlined some of the parameters affecting the resulting superconducting properties of Ag-sheathed Bi-2223 tapes fabricated by the powder-in-tube process. The mechanical deformation operation had important implications for the integrity of the conductor tapes. By improving processing conditions, we have been able to enhance the J_cs of the conductors made by the powder–in–tube (PIT) process. Long lengths (total length 180 m) have also been processed and fabricated into pancake coils with properties approaching practical levels. Although some parameters have been optimized, it should be noted that better control of the variables is still needed in order to obtain the properties reproducibly in long lengths of tapes.

ACKNOWLEDGMENTS

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REFERENCES

1. M. Takano, J. Takada, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda, Y. Tomii, and H. Mazaki, High-Tc phase promoted and stabilized in the Bi,Pb-Sr-Ca-Cu-O system, Jpn. J. Appl. Phys. 27, L1041 (1988).

2. K. Togano, H. Kumakura, H. Maeda, E. Yanagisawa, and K. Takashashi, Properties of Pb-doped Bi-Sr-Ca-Cu-O superconductors, Appl. Phys. Lett. 53, 1329 (1988).

3. J. M. Tarascon, Y. Le Page, P. Barboux, B. G. Bagley, L. H. Greene, W. R. McKinnon, G. w. Hull, M. Giroud, and D. M. Hwang, Crystal structure and physical properties of the superconducting phase $Bi_4(Sr,Ca)_6Cu_4O_{16+x}$, Phys. Rev. B37, 9382 (1988).

4. H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, A new high-T_c oxide superconductor without a rare earth element, Jpn. J. Appl. Phys. 27, L209 (1988).

5. K. Sato, T. Hikata, H. Mukai, M. Ueyama, H. Shibuta, T. Kato, T. Masuda, M. Magata, K. Iwata, and T. Mitsui, High-T_c silver-sheathed Bi-based superconducting wires, IEEE Trans. Mag. 27, 1231 (1991).

6. Y. Yamada, B. Obst, and R. Flukiger, Microstructural study of Bi(2223)/Ag tapes with J_c (77 K, O T) values of up to 3.3×10^4 A/cm^2, Supercond. Sci. Technol. 4, 165 (1991).

7. K. H. Sandhage, G. N. Riley, Jr., W. L. Carter, Critical issues in the OPIT processing of high-J_c BSCCO superconductors, J. Metals. 43, 21 (1991).

8. P. Haldar, J. G. Hoehn, Jr., J. A. Rice, M. S. Walker, and L. R. Motowidlo, Transport critical current densities of silver clad Bi-Pb-Sr-Ca-Cu-O tapes at liquid helium and hydrogen temperatures, Appl. Phys. Lett. 61, 604 (1992).

9. U. Balachandran, A. N. Iyer, P. Haldar, and L. R. Motowidlo, Processing and properties of commercially viable high-T_c Bi-2223 tapes and coils fabricated by the powder-in-tube technique, J. Metals. September, 1993 (in press).

10. L. R. Motowidlo, E. Gregory, P. Haldar, J. A. Rice, and R. D. Blaugher, Critical currents and processing of wound coils of Ag-sheathed Bi-2223 high T_c tape: Microstructural and pinning effects, Appl. Phys. Lett. 59, 736 (1991).

11. P. Haldar, J. G. Hoehn, Jr., J. A. Rice, and L. R. Motowidlo, Enhancement in critical current density of Bi-Pb-Sr-Ca-Cu-O tapes by thermomechanical processing: Cold rolling versus uniaxial pressing, Appl. Phys. Lett. 60, 495 (1992).

12. D. Y. Kaufman, M. T. Lanagan, S. E. Dorris, J. T. Dawley, I. D. Bloom, M. C. Hash, N. Chen, M. R. DeGuire, and R. B. Poeppel,

Thermomechanical processing of reactively sintered Ag-clad $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ tapes, Appl. Supercond. 1, 81 (1993).

13. R. Flukiger, B. Hensel, A. Jeremie, M. Decroux, H. Kupfer, W. Jahn, E. Seibt, W. Goldacker, Y. Yamada, and J. Q. Xu, High critical current densities in Bi(2223)/Ag tapes, Supercond. Sci. Technol. 5, 561 (1992).

14. P. Haldar, J. G. Hoehn, Jr., U. Balachandran, and L. R. Motowidlo, Processing and transport properties of high-J_c silver-clad Bi-2223 tapes and coils, J. Electronic Materials, 1993 (in press).

15. K. Sato, M. Shibuta, T. Hikata, T. Kato, and Y. Iwasa, Critical currents of silver-sheathed bismuth-based tapes at 20 K: Small coils and field orientation anisotropy in external fields up to 20 T, Appl. Phys. Lett. 61, 714 (1992).

16. P. Haldar and L. R. Motowidlo, Processing high critical current density Bi-2223 wires and tapes, J. Metals. 44, 54 (1992).

17. P. Haldar, J. G. Hoehn, Jr., L. R. Motowidlo, U. Balachandran, and Y. Iwasa, Fabrication and characteristics of small pancake coils from HTS Bi-2223 Ag-clad tapes, Advances in Cryogenic Engg. 40, 1993 (in press).

FIGURE CAPTIONS

Figure 1: Polished SEM micrographs of the Ag-clad 2223 tape (a) as-fabricated, and (b) after ≈250 h at ≈850°C and two uniaxial pressing.

Figure 2: X-ray diffraction patterns of 2223 tapes after (curve A) a single uniaxial pressing and heat treatment cycle, (curve B) an additional pressing and heat treatment cycle, and (curve C) a total heat treatment time of ≈450 h with four intermittent uniaxial pressing.

Figure 3: J_c at 77 K and O T vs. total heat treatment time, comparing samples that were rolled and heat treated to those that were uniaxially pressed and heat treated.

Figure 4: J_c vs. applied magnetic field for short tape samples at liquid helium (4.2 K) and liquid neon (27 K) temperatures.

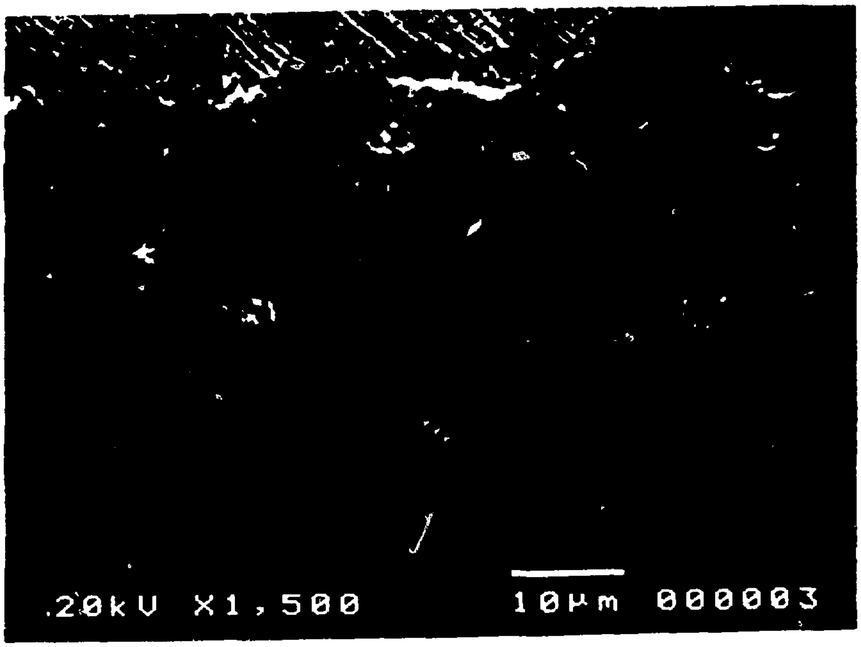


Figure 1 (a)

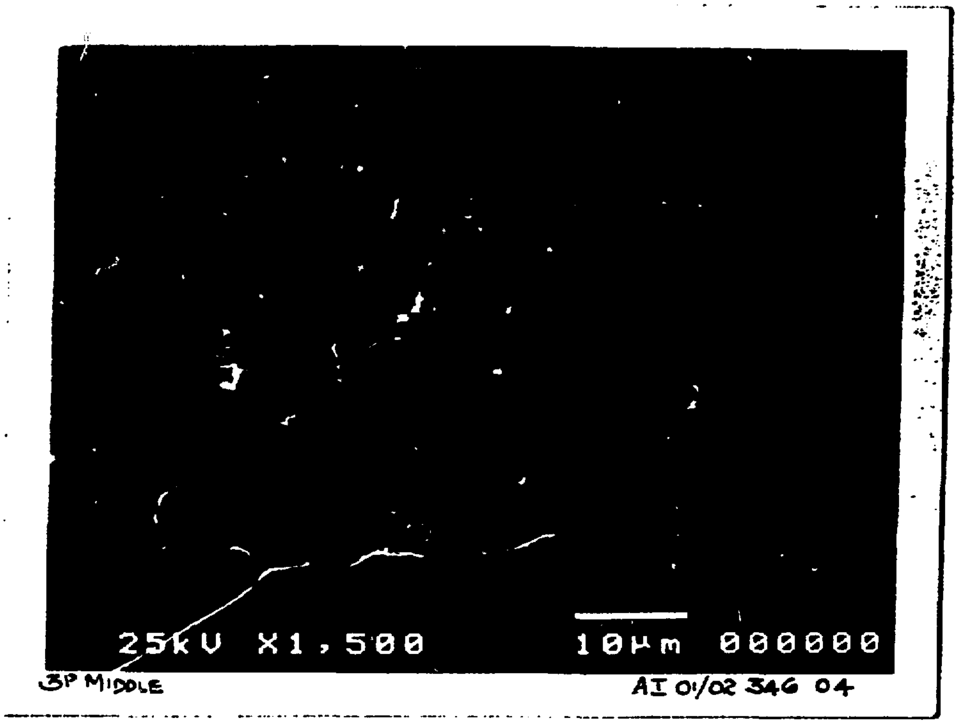


Figure 1(b)

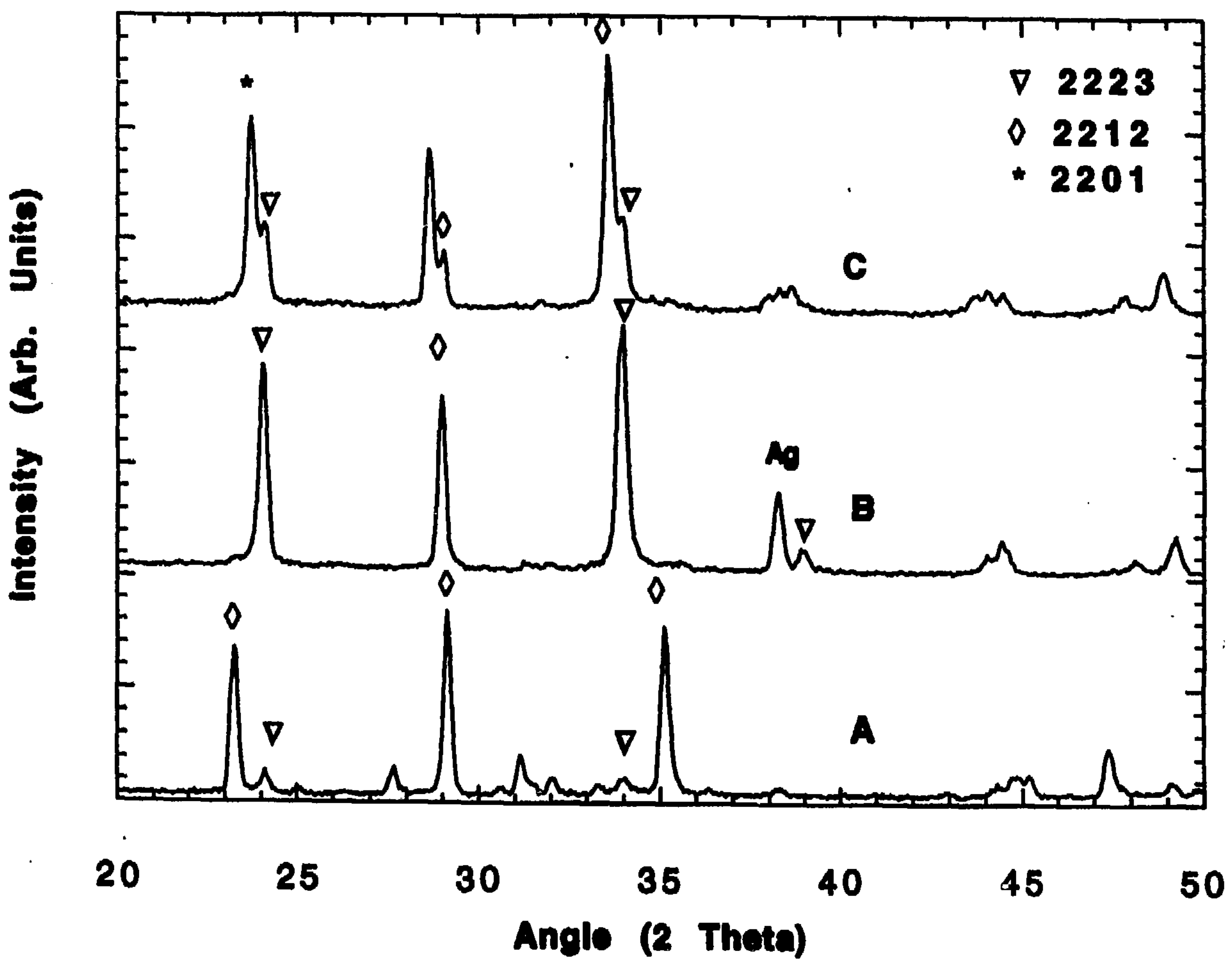
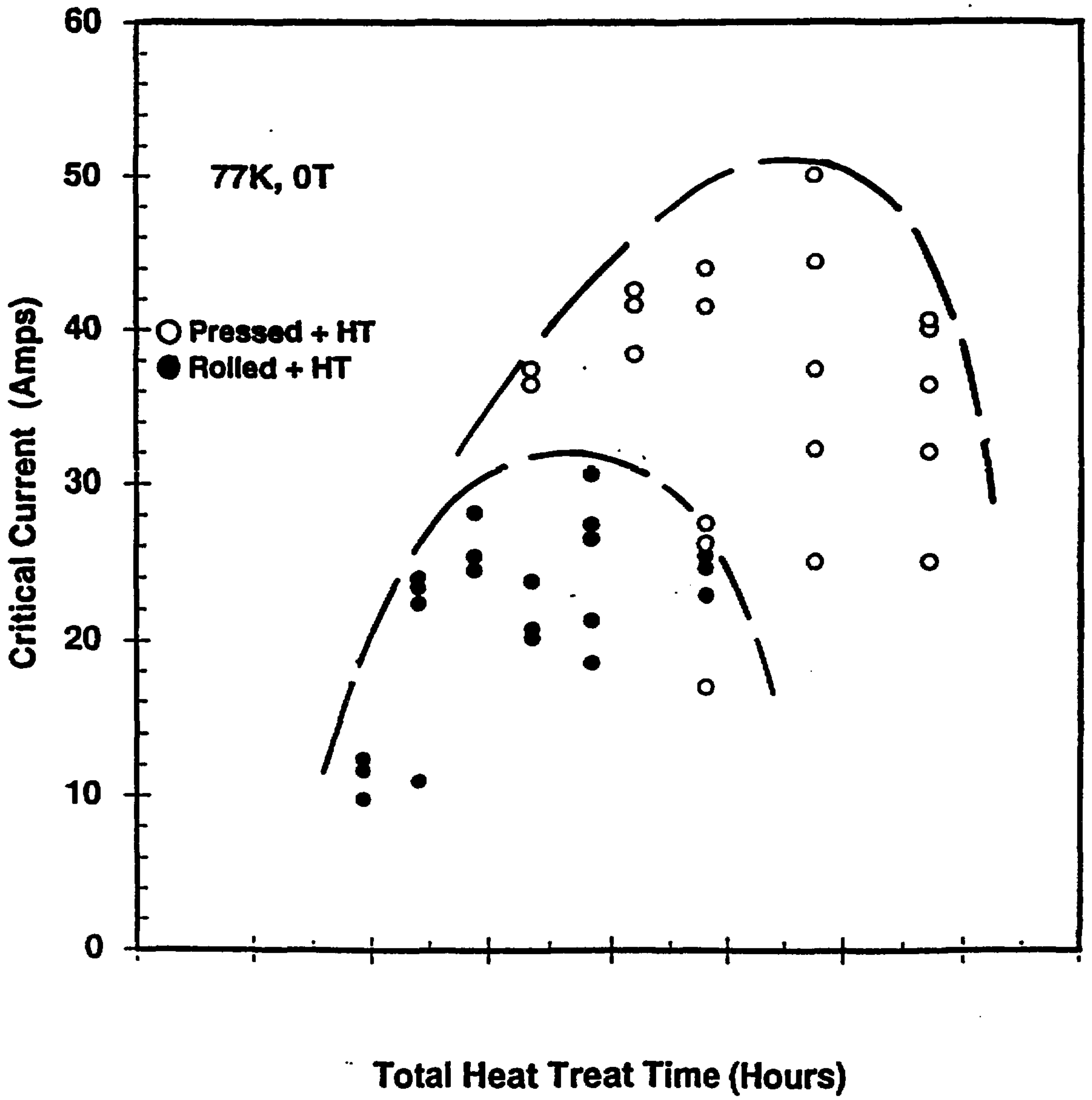
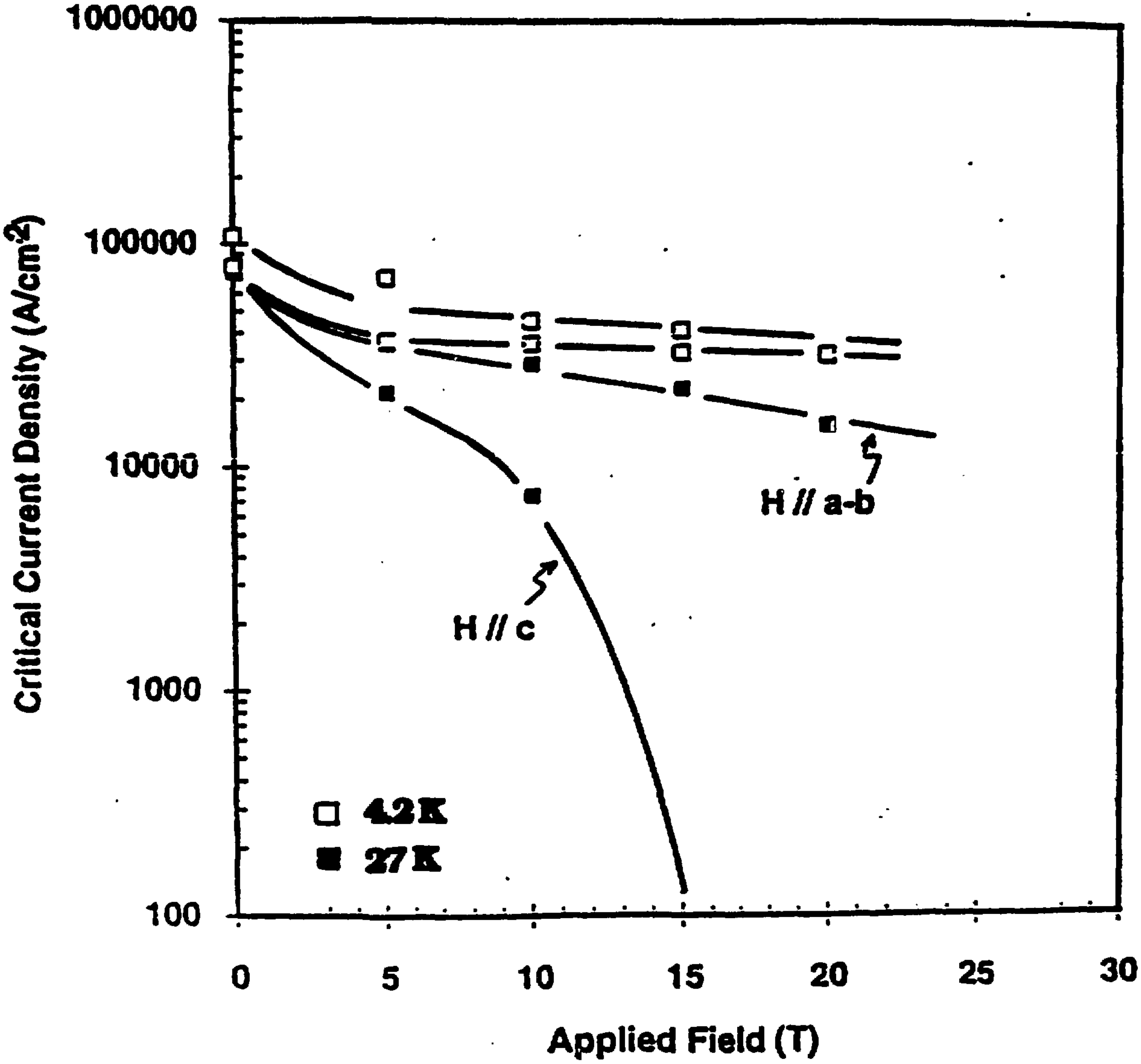

▽ 2223
◊ 2212
* 2201
C
B
A
Ag
Intensity (Arb. Units)
20
25
30
35
40
45
50
Angle (2 Theta)

Figure 2



60
50
40
30
20
10
0
77K, 0T
Pressed + HT
Rolled + HT
Critical Current (Amps)
Total Heat Treat Time (Hours)

Figure 3



1000000
100000
10000
1000
100
Critical Current Density (A/cm2)
0
5
10
15
20
25
30
Applied Field (T)
H // a-b
H // c
4.2K
27K

Figure 4