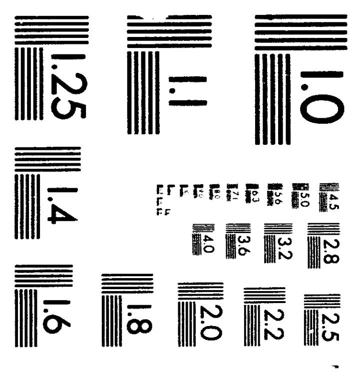

1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0

1 of 1

ANL/MSD/CP--81484

58916-00-105
49192-NO-105

Manuscript

November 1993

Conf-931009--15

The Effect of Processing on the Microstructure of Ag-Sheathed Bi-2223 Wires*

D.J. Miller, J.G. Hu, P. Kostic

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

U. Balachandran

Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439

P. Haldar

Intermagnetics General Corp., Guilderland, NY 12084

jmc

*Work at ANL and part of the work at IGC is supported by the U.S. Department of Energy, Divisions of Basic Energy Sciences-Materials Sciences and Energy Efficiency and Renewable Energy, as part of a program to develop electric power technology, under, contract #W-31-109-ENG-38.

Proceedings of the 1993 TMS Fall Meeting, Processing and Properties of Long Lengths of Superconductors, U. Balachandran, E. Collings, A. Goyal, eds., Pittsburgh, PA, October 17-21, 1993.

THE EFFECT OF PROCESSING ON THE MICROSTRUCTURE OF

Ag-SHEATHED Bi-2223 WIRES

D.J. Miller, J.G. Hu, P. Kostic
Materials Science Division,
Argonne National Laboratory
Argonne, Illinois 60439

U. Balachandran
Energy Technology Division
Argonne National Laboratory
Argonne, Illinois 60439

P. Haldar
Intermagnetics General Corp.
Guilderland, New York 12084

Abstract

The effect of processing on the microstructure of long-length $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) wires has been evaluated using scanning and transmission electron microscopy. In particular, these studies have focused on the effect of the final heat treatment conditions on the microstructure of the wires and the corresponding variations in critical currents (I_c). It is found that variations in I_c for segments cut from various points along the length of a wire can be correlated with variations in the volume fraction and nature of second phases. Similar variations are observed between wires processed under different final annealing conditions. A common feature found in all of the wire segments with lower I_c values was the presence of the $Pb_3Sr_2Ca_2CuO_x$ phase (Pb-3221). Microchemical analysis suggests that the formation of this phase leads to variations in the composition of the Bi-2223 grains. As a result, the wires which exhibit the Pb-3221 phase consist of an assemblage of grains with a range of transition temperatures based on composition. Thus, in these segments, the current carrying capacity of individual grains at 77K varies from very good to poor, and a significant reduction in the overall I_c of the segment is observed.

Research at ANL and part of the work at IGC is supported by the U.S. Department of Energy, Divisions of Basic Energy Sciences-Materials Sciences, and Energy Efficiency and Renewable Energy, as part of a program to develop electric power technology, under Contract W-31-109-Eng-38.

Introduction

The development of reliable, long-length conductors based on $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Bi-2223) superconductors has been pursued by a large number of investigators as a key to commercial development of these materials [1]. The oxide-powder-in-tube technique (OPIT) is an efficient method by which to produce such lengths of conductors. However, although sufficiently high critical currents (I_c) and critical current densities (J_c) have been attained in short length samples [2,3], it has been more difficult to achieve similar properties over long lengths [4-7]. At the current stage of development, it appears that variations from point to point along the length of these wires play a crucial role in limiting the development of these wires for practical applications. Thus, it is desirable to identify the features which limit current densities in long length wires.

The basic mechanism of current transport in wires is still not clearly understood, but it is clear that a high degree of texture is required for most of the proposed transport mechanisms [8,9], and this has been confirmed by experiment [10]. Some macroscopic features which disrupt aligned growth have been identified as factors which may lead to variations in critical currents in long lengths. For example, severe variations in core thickness ("sausaging") have been observed in rolled samples [11,12]. Such sausaging creates a constriction for current flow, frequently destroys the alignment of the superconducting grains, and introduces a further difficulty in defining the appropriate cross-sectional area used for calculation of J_c. In addition, the presence of second phases has been reported to disrupt aligned growth, leading to decreased critical currents [11], although some investigators have reported a trend towards less disruptive effects due to alignment of second phase particles as a function of processing conditions [13]. In addition to these somewhat more macroscopic features, microscopic features may also influence critical currents. For example, the presence of a few layers of Bi-2212 along [001] twist grain boundaries has been correlated with reduced J_c in Bi-2223 wires [14]. The purpose of this work has been to correlate the microstructure with measured properties for segments cut from long wires in order to identify the macroscopic and microscopic features which limit current densities in long length wires.

Experiment

Long-length (≈70 meter) wires of the Bi-2223 superconductor were prepared using conventional OPIT processing techniques. Partially reacted precursor powders of a lead-added Bi-2223 composition were loaded into Ag tubes, drawn and rolled with an intermediate heat treatment, and then given a final anneal in air for ≈ 50 hours. The two wires examined in this work were processed under identical conditions except that one wire was given a final anneal at 835°C (wire A) while the other was annealed at 840°C (wire B). In addition, a number of short segments of as-rolled wires were annealed at various temperatures to study phase development. The critical current at 77 K and zero field was measured for several sections of each wire which were cut from various points along the length of the wires. Microstructural characterization was then carried out by scanning electron microscopy (SEM) on each measured segment for both wires. The wires were prepared for SEM studies by standard metallographic techniques using alcohol- or oil-based slurries to avoid contact with water. Microstructural characterization by transmission electron microscopy (TEM) was also performed on some of the samples. These studies were carried out on the segments of each wire which exhibited the highest and lowest I_c values. Samples were prepared by standard cross-section techniques including ion milling at liquid nitrogen temperature. Microscopy was performed in a Philips CM-30 microscope equipped with an EDAX thin-window detector for energy dispersive spectroscopy (EDS). Compositional analysis based on EDS spectra was performed using semi-quantitative routines.

Results and Discussion

Figure 1 shows a plot of I_c measured for each segment as a function of arbitrary distance along the wire. For reference, an *average* I_c was determined for each wire from the I_c values of the various segments, although this value has no physical significance since the properties of a long length are expected to be dominated by the segment with the lowest I_c. Two features are of particular interest in this plot. Firstly, there is a significant variation in I_c from point to point within a given wire. In comparison with the average value, it is seen that for each wire there are a number of segments which fall below or near the average value and a few segments which lie significantly above the average. Thus, these segments can be grouped into two categories: one of "typical" samples, most closely associated with I_c values expected across a long length of wire, and "exceptional" samples which exhibit significantly higher I_c values. Secondly, there is a distinct difference in the average I_c. Even neglecting the "exceptional" segments, the "typical" I_c values for wire A are significantly better than for wire B. The microstructural work performed in this study was aimed at understanding the basis for these variations from point to point within a given wire as well as the differences between the wires.

The differences in I_c from point to point within a given wire can be explained in part on the basis of differences in the relative volume fractions of second phase and Bi-2223. For example, Fig. 2 shows backscattered SEM images from two segments of wire B, one with an I_c value of $\approx$16 A, the other with an exceptionally high I_c near 20 A. Although lower magnification imaging revealed some variations in core thickness, no sign of severe sausaging was observed in any of these wires. However, there are distinct differences in the volume fraction of second phases, most of which appear dark in these images. In particular, the segment with the lower I_c exhibits a few large particles which appear to limit the cross-sectional area of superconductor available to carry current, similar to the type of variation reported previously [15]. It is likely that these variations result from subtle inhomogeneities in composition during initial packing of the tube. Variations in core thickness have been linked with packing density [16], so it is not unreasonable to assume similar factors could lead to

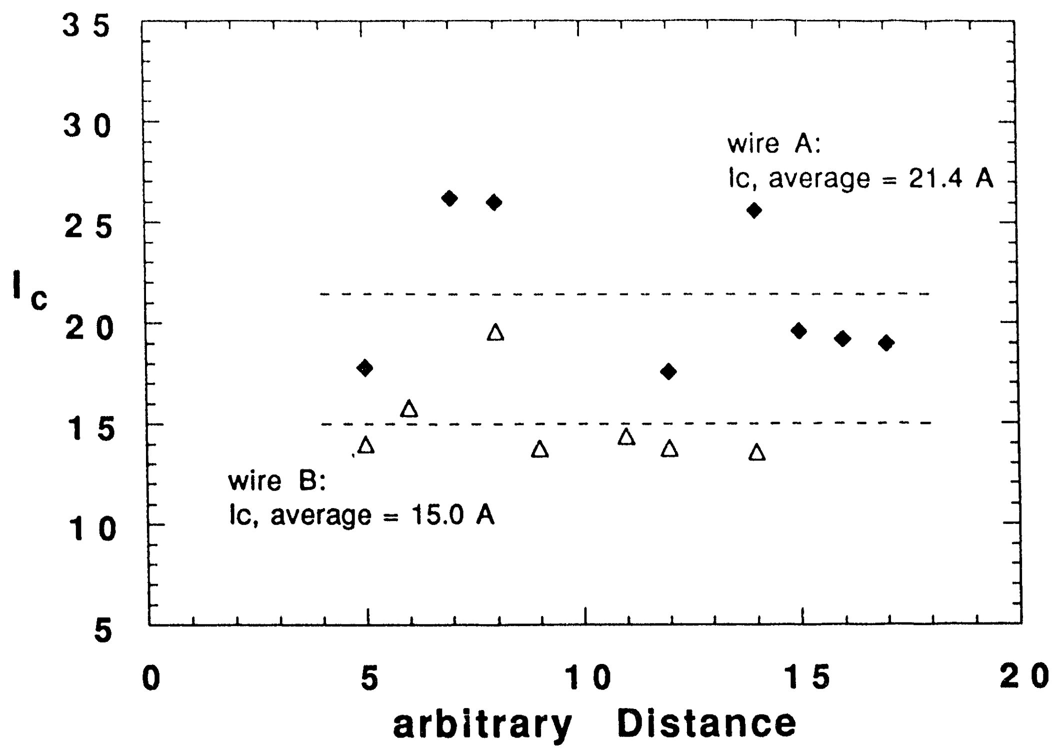
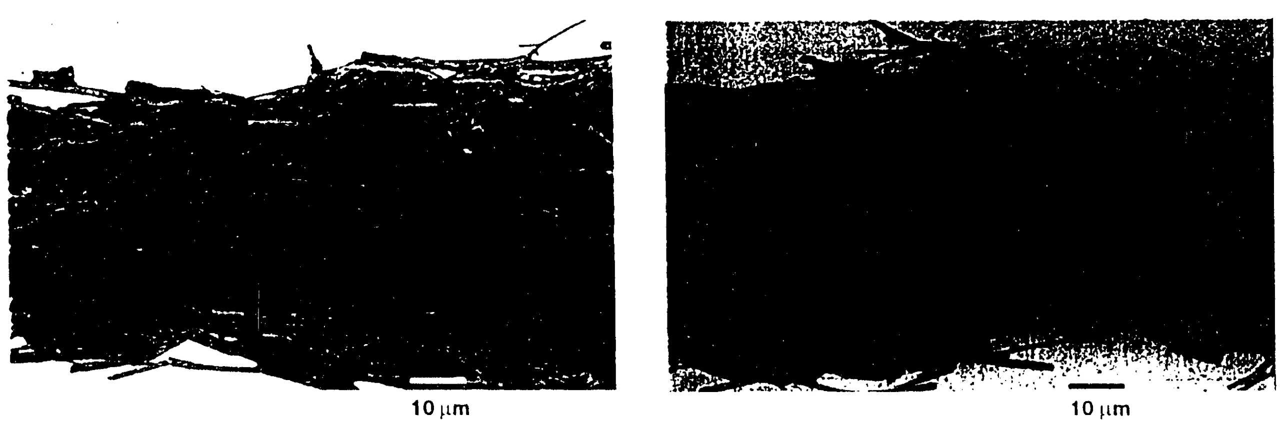


Figure 1: Plot of I_c (77 K, zero field) measured for segments cut from Bi-2223 wires as a function of arbitrary distance along the wire.

compositional variations. These inhomogeneities may become more distinct and exaggerated by mechanical working. For example, most of the second phases observed in these images are CuO, CaO, $(Ca,Sr)_{14}Cu_{24}O_{41}$ (14-24 phase), and Ca_2CuO_3. Since none of the second phases observed are rich in Bi, it is clear that the composition in the portion of the wire seen in Fig. 2a contains relatively less Bi than the region seen in 2b. In wire A, differences in second phase fraction from segment to segment were more difficult to correlate with I_c values and, as will be described in more detail below, the formation of a $Pb_3Sr_2Ca_2CuO_x$ phase (Pb-3221) seems to play a key role.

The subtle differences in phase assemblage leading to variations in I_c from point to point in



(a) (b)

Figure 2 Backscattered electron SEM micrographs of two segments from wire B with $I_{c,segment}$ of (a) ≈16 A and (b) ≈20 A wire A were similar to the differences observed between segments from wire A and wire B. The most striking difference in microstructure between wire A and wire B was the presence of regions of material which appeared to have decomposed. This is illustrated in Fig. 3 in which the microstructure of the segment of vire A with the highest I_c is compared to that of the lowest I_c segment of wire B. As seen in the micrographs, the segment from wire B exhibits a large fraction of these decomposed regions while the segment of wire A shows few if any of these regions. In comparisons between the two wires as well as from point to point within a given wire, it was found that the "exceptional" segments of wire A showed very few of these decomposed regions, the more typical segments from wire A and the exceptional segment from wire B showed some of these regions, and the typical segments from wire B exhibited large fractions of these regions. Thus, a correlation can be made with the presence of these decomposed regions and I_c.

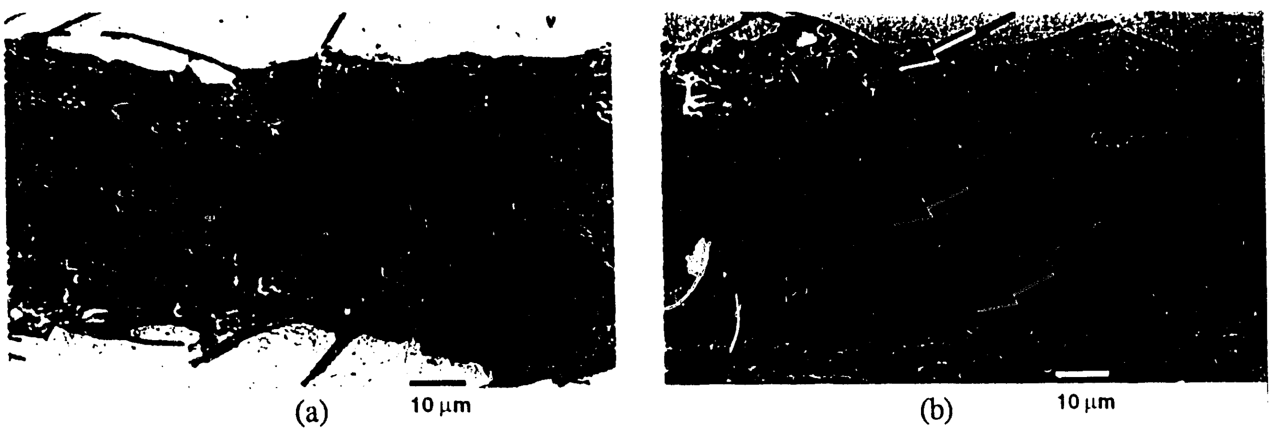


Figure 3 Secondary electron SEM micrographs of segments from (a) wire A with $I_{c,\ segment} \approx 26$ A and of (b) wire B with $I_{c,\ segment} \approx 14$ A. Some of the regions which appear to have undergone some decomposition are indicated by arrows in (b).

In order to more fully understand the nature of the decomposed regions, TEM was employed to examine the best and worst segments from each wire. Each wire was observed to consist of colonies of Bi-2223 grains with second phase particles interspersed between them. A typical colony structure is shown in Fig. 4 for a segment from wire A with the highest I_c. These TEM samples also served to confirm the effect of second phase volume fraction on I_c. As an artifact of TEM sample preparation, preferential ion milling of second phases tended to yield an enhanced view of the superconducting portions of the core. In the exceptional wires with little second phase, broad, continuous colonies were frequently observed. In contrast, for the wires with higher fractions of second phase, fewer, narrower colonies were observed. In general, the presence of second phase particles was not observed to have severely disrupted colony growth.

Examination of the wires by TEM did allow the presence of a Pb-3221 phase to be established. The Pb-3221 phase has been identified as a hexagonal crystal with a = 0.9919 nm, b = 0.3471 nm and a reported composition of $Pb_{3.4}Bi_{0.33}Sr_{2.6}Ca_{2.3}Cu_{1.0}$ [17]. An example of this phase is seen in Fig. 5 in which a large particle is present between two colonies. The identity of this

Figure 4 TEM bright-field micrograph of a typical colony structure observed in all of the wire segments.

phase was established by selected area electron diffraction patterns which can be indexed consistently according to this phase, as seen in Fig. 6, and by compositional analysis based on EDS. The location of the Pb-3221 phase did not suggest a significant role in limiting I_c. For example, there was no sign that this phase segregated to grain boundaries or resulted in an accumulation of impurities in those locations. While the Pb-3221 phase was frequently observed to grow into Bi-2223 grains from adjacent Ca_2PbO_4 grains, most of the samples exhibited many small, discrete particles. It is believed that the decomposed regions observed in SEM are associated with the presence of the Pb-3221 phase. For example, Fig. 7 shows a particularly large Pb-3221 grain which is clearly associated with the surrounding decomposed regions. In addition, TEM suggested a correlation between the volume fraction of Pb-3221 and I_c. The lowest I_c segment showed the highest volume fraction of Pb-3221 while the best segment showed virtually none of this phase. This is the same correlation with I_c noted for the fraction of decomposed regions observed by SEM. Based on TEM observations, it is not clear what mechanism leads to the appearance of the decomposed regions. As noted above, although TEM generally revealed many small Pb-3221 particles, there was no evidence of any severe decomposition reaction associated with these particles, as is clear from Fig. 5. It is believed that the appearance of the decomposed regions in SEM samples is due to a reaction during polishing. However, it is concluded that the reaction that leads to formation of the Pb-3221 phase indicates the onset of decomposition since this phase was most commonly observed in the wire annealed at 840°C while significantly less was found in the wire annealed at 835°C. The significant impact of these differences based on only slight variations in processing

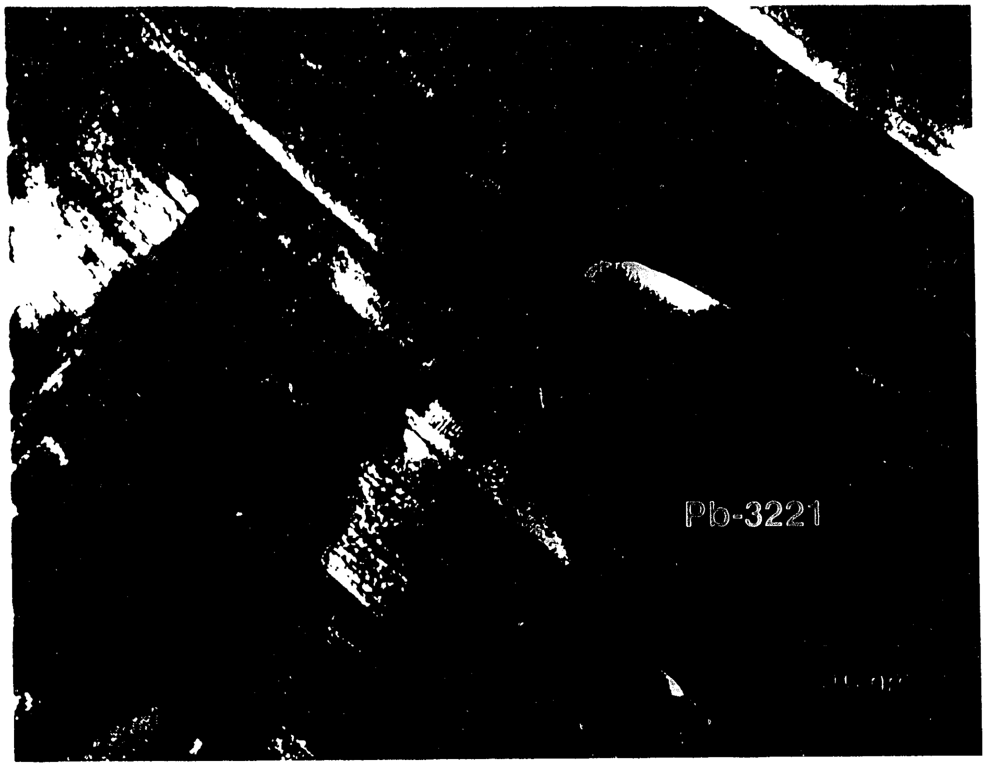
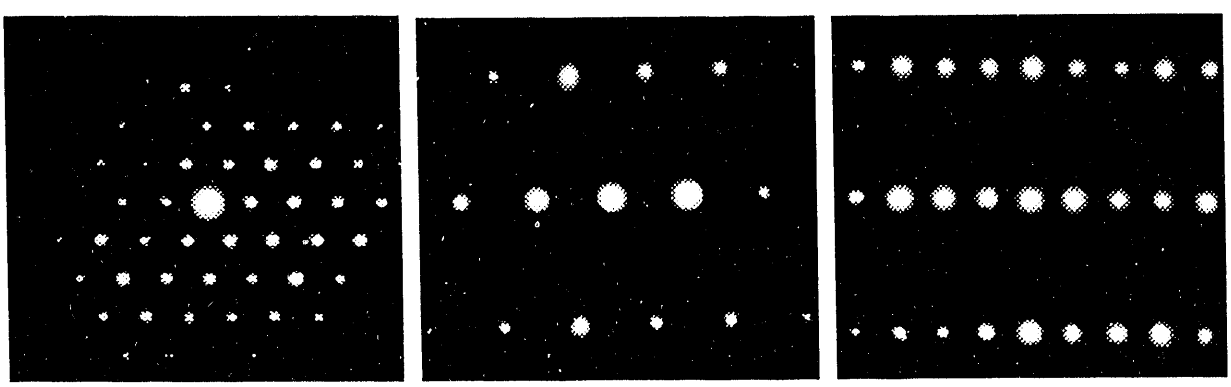


Figure 5 TEM bright-field micrograph showing a Pb-3221 particle within a Bi-2223 colony.

temperature underscores the importance of precise control of processing parameters during processing. This is a particularly critical issue for long length wires which pose a more difficult control problem due to the larger size of these samples.

The formation of the Pb-3221 phase did have an effect on the composition of the superconducting grains. EDS measurements were performed on approximately ten Bi-2223 grains from each sample examined by TEM in order to measure their composition. The grains were selected at random without regard to their proximity to Pb-3221 particles. The results of these measurements are summarized in Table 1 in which it can be seen that the average composition of the Bi-2223 grains in the best segment examined is significantly different from that measured for the other segments which showed progressively more of the Pb-3221 phase.



[0001] [1013] [1216]

Figure 6 Selected area electron diffraction patterns from the Pb-3221 phase, indexed as indicated.

Figure 7 Secondary electron SEM image of a segment from wire A. A large grain of the Pb-3221 phase surrounded by decomposed material is visible near the center.

It is expected that a larger sample size would lead to differences in average composition between the other three wires as well. The variations in composition of the Bi-2223 grains between the segments are expected to lead to some differences in superconducting behavior from grain to grain. For example, changes in cation content in Bi-2212 have been shown to lead to significant differences in transition temperature.[18,19] In order to explore the potential effect of these compositional variations, resistance and magnetization measurements were performed as a function of temperature on the samples from each wire with the highest and lowest I_c values. The resistance data is shown in Fig. 8. The general behavior is that samples with lower I_c values show a broadened transition with a correspondingly lower $T_{c,\ R=0}$. However, the resistance data only yields information for the very best conduction path based on the measurement current. During an I_c measurements, a sample must carry the optimum current in *all* possible conduction paths to maximize the total current. The magnetization data provides a measure of the superconducting behavior of all the grains in the sample and thus gives a measure of the bulk behavior. Shown in Fig. 9, the magnetization data reflects an increasingly broadened transition as a function of decreasing I_c. The implications of such a broadened transition on I_c are significant in that it suggests that there is a wide variation in the

Table 1 Cation stoichiometry for the Bi-2223 grains in the highest and lowest I_c segments from wire A and wire B.

wire	$I_{c,\ segment}$	Bi	Pb	Sr	Ca	Cu
A	26.2	2.2	0.4	2.2	1.5	2.7
A	17.6	1.8	0.3	1.9	1.9	2.9
B	19.6	1.8	0.3	2.0	1.9	2.9
B	13.6	1.8	0.3	1.9	1.9	3.0

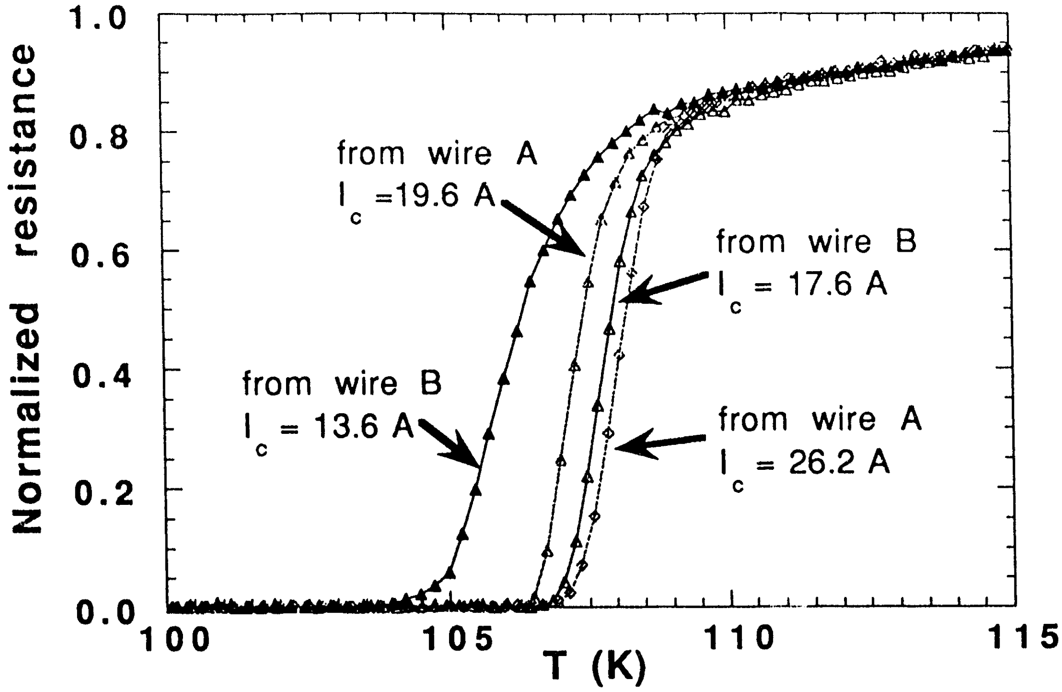


Figure 8 Normalized resistance versus temperature for the highest and lowest I_C segments from wire A and wire B.

conduction capacity of individual grains at a given temperature since the J_C of a sample tends to be proportional to the difference between the transition temperature and the measurement temperature. For example, in the sample from wire B with an I_C of 13.6 A, it is seen that there are a large fraction of grains which are not superconducting at the measurement temperature of 77 K and thus can carry no superconducting current. Similarly, there is a large number of grains which have transition temperatures only slightly above the measurement temperature and will carry a correspondingly lower current compared to other grains with transition temperatures which are much higher. In contrast a large fraction of grains will be far below T_C for the best segment of wire A during measurement at 77 K. It should be noted that these measurements have not been normalized based on the volume of the sample and therefore do not reflect the absolute volume of superconducting material, only the relative fraction of the total superconducting volume. Thus, differences in superconducting volume may also play a role and can be used to account for the smaller variations in I_C between wires which show an intermediate transition.

The relationship between the volume fraction and composition of secondary phases which lead to changes in the Bi-2223 grains suggests a change in phase equilibrium as a function of processing conditions. Variations in these features likely result from the interrelated effects of composition and annealing temperature. As noted previously, small variations in composition can be seen from point to point along the length of a wire. It is expected that changes in phase relations may result from these variations alone but such an effect may be enhanced at higher processing temperatures for which the compositional range of the superconducting phase tends

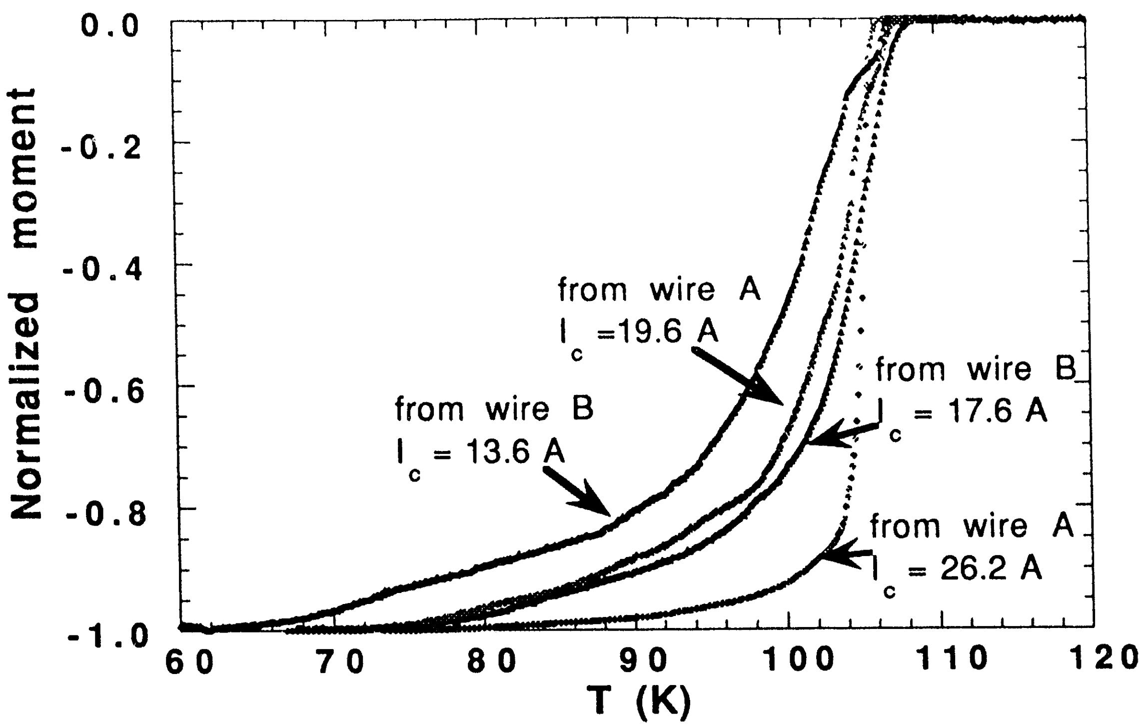


Figure 9 Normalized magnetic moment versus temperature for the highest and lowest I_c segments from wire A and wire B.

to decrease. Thus, all the segments of wire B, processed at 840°C, were found to contain the Pb-3221 phase, although the volume fraction of that phase varied from segment to segment, similar to the variations observed in the fraction of alkaline earth cuprates. In contrast, only the low I_c segments from wire A, processed at 835°C, showed a significant fraction of this phase. At this lower processing temperature, only the more extreme compositional fluctuations may have led to the formation of Pb-3221, leaving most of the segments relatively devoid of this phase.

Conclusions

One microstructural basis for variations in I_c from point to point along the length of lead-doped Bi-2223 wires has been found to be related to the volume fraction of second phases as well as the specific reactions which lead to the formation of those impurities. Specifically, the presence of a Pb-3221 phase has been found to be a key marker which indicates a shift in equilibrium. The reaction which results in the formation of the Pb-3221 phase also produces a change in composition of the Bi-2223 grains which results in degraded superconducting properties of these grains and therefore limits I_c in the segment. The significant variations noted in microstructure and properties as a result of only small differences in processing temperature between the various samples examined in this work underscores the importance of precise control of processing conditions, particularly for long length wires.

References

1 see, for example, *IEEE Trans. Appl. Superconductivity* 3 (1) Part II: Superconducting Materials (1993).
2 Q. Li, et al., "Thermomechanical processes of Ag-sheathed Bi-2223 tapes" (Paper H12.26 presented at the 1992 Fall MRS meeting, Boston, MA, 3 December 1992).
3 K. Sato, et al., *IEEE Trans.* MAG-27 (1991) 1231.
4 G. Riley, Jr., W.L. Carter, *Am. Cer. Soc. Bull.* 72 [7] (1993) 91.
5 E.E. Hellstrom, *MRS Bulletin* 17 (8) 45 (1992).
6 T. Kitamura, T. Hasegawa, H. Ogiwara, *IEEE Trans. Appl. Superconductivity* 3 (1) (1993) 939.
7 H. Mukai, et al., "Multifilamentary Bismuth (2223) Multilayer-wound Conductors for Power Transmission Lines" (Paper presented at the 1992 Spring MRS meeting, San Francisco, CA, April 27-May1, 1992).
8 B. Hensel, et al. *Physica C 205* (1993) 329.
9 L.N. Bulaevskii, et al., *Phys. Rev. B* 45 [5] (1992) 2545.
10 N. Enomoto, et al., *Jpn. J. Appl. Phys.* 29 (1990) L447.
11 Y. Feng, et al., *Physica C* 192 (1992) 293.
12 L.R. Motowidlo, et al. *Appl. Phys. Lett.* 59 [6] (1991) 736.
13 J.S. Luo, et al., manuscript submitted to *J. Mat. Res.* (1993).
14 A. Umezawa, et al., *Physica C* 198 (1992) 261.
15 T. Kato, et al., *MRS Bulletin* 17 [8] (1992) 52.
16 Y. Yamada, B. Obst, R. Flükiger, *Supercond. Sci. Tech.* 4 (1991) 165.
17 S.X. Dou, et al., *Supercond. Sci. Tech.* 4 (1991) 203.
18 T.G. Holesinger, et al., *Physica C* 202 (1992) 109.
19 P. Majewski, H-L. Su, B. Hettich, *Advanced Materials* .

DATE FILMED

1 / 31 / 94

END