THE USE OF OXYGEN GRADIENTS AS A TEXTURING MECHANISM DURING ISOTHERMAL MELT PROCESSING OF Bi-2212 SUPERCONDUCTORS

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ISOTHERMAL MELT PROCESSING OF BI-2212 WIRES AND TAPES

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ABSTRACT

Isothermal melt processing has been used to produce high critical currents ($I_c$'s) and current densities ($J_c$'s) in Bi$_2$Sr$_2$CaCu$_2$O$_y$ round wires and flat tapes. $I_c$'s and $J_c$'s of 225 A and 80 kA/cm$^2$ have been obtained in short length, monocore wires. However, voids and other macroscopic defects have limited performance over longer lengths. Isothermally melt processed tapes have yielded $I_c$ and $J_c$ values up to 341 A and 245 kA/cm$^2$, although performance over longer lengths is somewhat reduced. A test coil made from 0.5 m of tape yielded $I_c$ and $J_c$ values of 208 A and 153 kA/cm$^2$, respectively.

INTRODUCTION

Isothermal melt processing (IMP) is a technique by which Bi$_2$Sr$_2$CaCu$_2$O$_y$ (Bi-2212) composite conductors are partially melted and solidified at the same temperature [1,2]. This technique is possible due to the dependence of the melting point of Bi-2212 on the oxygen partial pressure [3]. Bi-2212 can be partially melted at temperatures above 750°C in very low oxygen partial pressures or inert atmospheres. Under these conditions, the phases present in the partial melt are Bi$_2$Sr$_{3-x}$Ca$_x$O$_y$ (2:3 Cu-free), CaO, and liquid [4]. By simply increasing the oxygen
partial pressure after a given amount of time in the partial melt, the Bi-2212 phase is formed. IMP has been successfully applied to the processing of bulk bars, thick films, round wires, and flat tapes containing Bi-2212 [1,5,6]. In this paper, we present our most recent results with this technique as applied to the processing of Bi-2212 monocore round wires and multi-filament flat tape. High \( J_c \) values were obtained in both types of conductors although less variations in \( J_c \) over long lengths were obtained with the tapes.

**EXPERIMENTAL**

For the fabrication of the monocore round wire, powder of nominal composition Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_y\) was prepared from high-purity oxides and carbonates, calcined at 780°C, 800°C, and 825°C in air, and then splat-quenched in order to obtain a glassy precursor that is thoroughly mixed on the atomic scale. Details of this process are explained elsewhere [7]. The powder used in the current study had approximately 1.0 wt.% \( \text{Al}_2\text{O}_3 \) from reaction with the \( \text{Al}_2\text{O}_3 \) crucible during splat-quenching. Previous investigations on the effect of \( \text{Al}_2\text{O}_3 \) have shown that aluminum does not affect the superconducting properties of the Bi-2212 phase [4]. The glassy precursor was thoroughly ground and loaded into a silver or silver alloy tube with one end open. The silver alloy used was \( \text{Ag}_{0.97}\text{Cu}_{0.03}\text{Pb}_{0.004}\text{Al}_{0.001} \). A silver or silver alloy plug was then inserted into the opening and welded into place. The tubes were drawn as wire to an overall diameter of 1 mm. The Bi-2212 flat tape was manufactured at Oxford Instruments. Commercial Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_y\) powder was calcined and loaded into a silver tube. The silver tube was then drawn down as wire, bundled and repacked into another silver tube, and then drawn and rolled into a 55 filament tape of overall dimensions 3.85 mm x 0.35 mm.

All wires and tapes were processed by IMP. For the round wires, 4 cm or 15 cm long lengths were heated in an ultra-high purity argon atmosphere at 10°C/min from room temperature to between 770°C and 850°C and held for 90 minutes. After this step, the gas flow was switched to a mixture of 1%\( \text{O}_2 \), 10%\( \text{O}_2 \), 27%\( \text{O}_2 \), or 100% \( \text{O}_2 \) (balances Ar). Gas flows were set so as to change the equivalent furnace-tube volume seven times per hour. After a total of 25 hours at the processing temperature, the samples were cooled at 5°C/min to room temperature. Flat tapes 15 cm in length were also processed by IMP. In this case, the partial melt was created in vacuum prior to oxidation. During the vacuum-melt step, pressures less than 1 milli-Torr were maintained in the furnace. Melting times were from 0.5 to 2.6 hours. After the melting step was complete, the furnace was backfilled quickly (< 1 min) with either 10% \( \text{O}_2 / \text{Ar} \), 20% \( \text{O}_2 / \text{Ar} \), or pure oxygen. After a total of 15 hours, the tapes were cooled at 5°C/min to room temperature. Processing temperatures for the tapes ranged from 780°C to 865°C. One 0.5 m test coil was isothermally melt processed to characterize long lengths of Bi-2212 tape.

Sample characterization was performed by quantitative optical microscopy, backscattered electron imaging in the scanning electron microscope (SEM/BEI), SQUID magnetometry, and transport measurements at 4K (helium) and 75K (nitrogen). At the altitude of Los Alamos, the boiling point of nitrogen is 75 K. Samples were prepared for microscopy and quantitative analysis by mounting the samples in cross-section and polishing using standard metallographic techniques. Cross sections of the wires were measured by quantitative optical microscopy. The
critical current \( (I_c) \), critical current density \( (J_c) \), and engineering critical current density \( (J_e) \) were determined using an electric field criterion of 1.0 \( \mu \text{V/cm} \). For each wire or tape, three equal lengths from the middle of the sample were measured.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of \( J_c \) on the processing temperature and oxygen partial pressure used for oxidation during IMP of Bi-2212 wires. An oxidation mixture of 27% \( \text{O}_2/\text{Ar} \) consistently produced the highest \( I_c \) and \( J_c \) values. The \( I_c \) value of 130 A shown in Figure 1 corresponds to \( J_c \) and \( J_e \) values of 43 kA/cm² and

![Figure 1: Plot of \( I_c \) values for Bi-2212 wires as a function of the processing temperature and oxidation atmosphere.](image1)

Figure 2: Variation in \( I_c \) along a long length of Bi-2212 round wire processed by IMP at 810°C using 27%\( \text{O}_2/\text{Ar} \) as the oxidation atmosphere.

![Figure 2: Variation in \( I_c \) along a long length of Bi-2212 round wire processed by IMP at 810°C using 27%\( \text{O}_2/\text{Ar} \) as the oxidation atmosphere.](image2)
14 kA/cm², respectively. In all cases, the optimal processing temperature was between 800°C and 820°C. Note that these temperatures are significantly lower than those used in conventional melt processing of Bi-2212[8]. Shown in Figure 2 is the variation in $I_c$ along a 20 cm round wire that was processed at 810°C using 27%O₂/Ar for the oxidation step of IMP. These variations in $I_c$ along the length of long wires were common.

An attempt was made to minimize variations in the wires by using an Ag-Cu-Pb-Al alloy sheath. It was thought that an alloy would help with densification of the core during wire drawing and reduce any reactions between the silver and Bi-2212 during processing [9]. As shown in Figure 3, higher $I_c$ values were obtained with 1 mm diameter wire containing the alloy sheath. The $I_c$ value of 225 A translates into $J_c$ and $J_{sc}$ values of 80 kA/cm² and 28.3 kA/cm², respectively at 4 K and self field. In the case of the alloy-sheathed wire, a processing temperature of 780°C and oxidation atmosphere of 10%O₂/Ar was found to be optimal. However, long lengths of wire still showed large variations in $I_c$ in long wires. The decrease in optimal processing temperature may be related to the addition of lead to the alloy sheath which may react with the core to form a melt at lower temperatures.

Variations in $I_c$ were correlated with large amounts of porosity in fully processed wires. Figure 4a and b contain backscattered electron images (BEI) of as-drawn and fully processed silver-sheathed round wires. The as-drawn wire contains large cracks and significant porosity. The space represented by the cracks and porosity translates into regularly spaced voids in fully processed wires as shown in Figure 4b.

Figure 3: Current-voltage curves from a 1 mm diameter alloy-sheathed wire isothermally melt processed at 780°C using 10%O₂/Ar as the oxidizing atmosphere. The $I_c$ values of 225 A and 140 A in self-field and an applied field of 1 T translate into $J_c$ values of 80.4 kA/cm² and 50 kA/cm², respectively. The distance between voltage taps was 1.5 cm.
Other microstructural features in fully processed wires are dependent upon the processing temperature. Figures 5a and b contain short transverse sections of wires processed at 780°C and 850°C, respectively. The silver-sheathed wires processed around 780°C showed signs of insufficient melting prior to solidification. Grain sizes were small and the porosity was uniformly distributed throughout the core. This microstructure was correlated with low $J_c$ values. Note that with the alloy sheathed wires, the optimal processing temperature was shifted down to around 780°C. However, processing below 780°C also produced the microstructure resulting from insufficient partial melting. The wire processed at 850°C showed, in addition to the large pores, a large grain microstructure and grain-growth induced desintering. This microstructure also correlated with low $J_c$ values over short lengths as shown in Figure 1.

In contrast to the monocore round wire, significantly better results were obtained with multi-filament tape. This was attributed to the higher starting...
densities obtainable in rolled tapes compared to as-drawn wire. Results presented here suggest a much larger processing region exists for obtaining high \( J_c \) tapes depending on the oxidation atmosphere, time in the partial melt, and processing temperature. For example, tapes processed at 835°C with dwell times in the partial melt of 0.8 hours and oxidation atmospheres of 100%, 20%, and 10% \( O_2/Ar \) had \( J_c \) values of 108, 212, and 177 kA/cm², respectively. However, processing at 820°C using melt times of 1.2 hours and oxidation atmospheres of 20% and 10% \( O_2/Ar \) yielded \( J_c \) values of 158 and 245 kA/cm², respectively. Although the complete processing temperature, melt time, oxidation atmosphere relationships have not been worked out, several general trends appear in the data. As the processing temperatures are decreased, the oxygen partial pressure needs to be lowered to produce high \( J_c \) tapes. In addition, higher processing temperatures require shorter partial melt times in order to maximize \( J_c \).

The highest \( J_c \) values have been obtained at 820°C using 10% \( O_2/Ar \) as the oxidizing atmosphere. Shown in Figure 6 is a plot of the \( J_c \) values obtained in multifilament tapes as a function of time in the partial melt at 820°C. The highest \( I_c \), \( J_c \), and \( J_c \) values obtained across a three cm section of tape were 341 A, 245 kA/cm², and 25.6 kA/cm², respectively. The window for obtaining high \( J_c \) tapes is relatively wide. Melt times of 1 to 1.5 hours were found to give high \( J_c \) values. The standard deviations associated with the \( J_c \) values do not appear to correlate with the melt times or porosity. Hence it was assumed that the variations in \( J_c \) were due to local inhomogeneities in the starting tape. To test IMP on longer lengths of tape, a 0.5 m test coil was processed at 820°C using 10% \( O_2/Ar \) for oxidation. The time spent in the partial melt was 1.3 hours. The overall \( I_c \) and \( J_c \) of the coil was 213 A and 153 kA/cm². The coil values are consistent with the variations observed in the short lengths of tape.

Secondary phases were present in all fully processed tapes to various degrees.

[Figure 6: \( J_c \) values as a function of time spent in the partial melt for Bi-2212 tapes processed by IMP at 820°C using 10% \( O_2/Ar \) for oxidation. The best values are from 3 cm sections of long tapes. The average \( J_c \) and corresponding standard deviation represent all measurements from three sections of two or more tapes.]
Figure 7: Short transverse SEM/BEI image of a Bi-2212 processed by IMP at 820°C using 10% O$_2$/Ar for oxidation. Time spent in the partial melt was 1.3 hours. A region containing large secondary phases and some porosity is evident at the top of the micrograph.

Unlike the round wire, the tapes appeared to be dense and free of large pores. Shown in Figure 7 is a short transverse SEM/BEI image of a tape processed at 820°C for 1.3 hours and oxidized in 10% O$_2$/Ar. The $J_c$ value for this tape was 216 kA/cm$^2$ at 4 K and self-field. For the most part, the filament uniformity and phase purity were quite good although areas could be found where large secondary phases were concentrated. This random arrangement of the pockets of secondary phases is presumed to result from inhomogeneities in the starting tape. Further work is in progress to verify and minimize this problem.

The samples with low $J_c$ values in Figure 6 were found to have microstructures that resulted from either spending too little or too much time in the partial melt. Similar microstructures were encountered with the round wires. Figures 8a and b contain SEM/BEI images of tapes processed at 820°C where the times spent in the

Figure 8: Long transverse SEM/BEI images of Bi-2212 tapes processed by IMP at 820°C using 10% O$_2$/Ar for oxidation. The times spent in the partial melt were (a) 0.5 hours and (b) 2.6 hours.
partial melt were 0.5 and 2.6 hours, respectively. In Figure 8a, the tape that was partially melted for only 0.5 hours shows very good phase purity. This tape contained the fewest secondary phases of all of the tapes processed at 820°C. Unfortunately, the $I_c$ values were very low. With the short times in the partial melt, an insufficient amount of liquid is formed and the subsequent solidification step does not result in a well aligned, connected microstructure such as that shown in Figure 7. For the tape that spent 2.6 hours in the partial melt, a uniform distribution of large alkaline-earth cuprate needles was found throughout the sample. These large secondary phases were often found to span the entire thickness of the filaments as shown in Figure 8b.

One of the advantages of the IMP technique for Bi-2212 processing is that the filament uniformity can be maintained throughout the process. Figure 7 shows a high-$I_c$ tape where the Ag-Bi-2212 interface is smooth and well-defined with no grain growth into the silver. With conventional melt processing, maintaining filament uniformity is often a problem [10]. Peak temperatures in conventional melt processing can reach as high as 885°C to 920°C. At these temperatures, the silver sheath softens significantly and grain growth of Bi-2212 into the sheath material is often observed. Grain growth into the silver sheath was observed with IMP when processing temperatures of 850°C or greater were used. Shown in Figure 9 is a SEM/BEI image of a Bi-2212 tape processed by IMP at 865°C using 100% oxygen. Time spent in the partial melt was 0.9 hours and the $I_c$ value of the tape was 69.4 kA/cm². A common microstructural feature found in these latter tapes is the presence of grain colonies cutting across the filaments as shown in Figure 9. Filament cutting by misaligned colonies was not observed in tapes processed by IMP at temperatures below 850°C.

**SUMMARY**

Isothermal melt processing has been applied to the processing of Bi-2212 monocore round wires and multifilament tapes. IMP produced high $I_c$ values up to

![Figure 9: A long transverse SEM/BEI image of a Bi-2212 tape processed by IMP at 865°C using 100% oxygen. Time spent in the melt was 0.9 hours. The misaligned colony of grains seen cutting across the filament was a common feature in tapes processed above 850°C.](image-url)
80 kA/cm² at 4 K and self field in short lengths of round wires. However, large amounts of residual porosity caused significant variations in $I_c$ over long lengths. Such problems with the multifilamentary tapes were not encountered because of the higher starting density obtainable in rolled tapes. $J_c$ values in tapes processed by IMP were found to be dependent upon the processing temperature, time spent in the partial melt, and the oxidation atmosphere. The highest $J_c$ values were obtained in tapes processed by IMP at 820°C. $I_c$ and $J_c$ values of 341 A and 245 kA/cm² were obtained over short sections. A 0.5 m test coil processed under similar conditions was found to have $I_c$ and $J_c$ values of 213 A and 153 kA/cm², respectively. Variations in $I_c$ in the tapes were attributable to localized inhomogeneities in the starting material. It was found that filament uniformity was maintained in tapes processed by IMP when the processing temperature was kept below 850°C. Processing temperatures of 850°C or greater tended to produce misaligned colonies that cut across individual filaments.

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