Microstructure and J_C Improvements in Overpressure Processed Ag-Sheathed Bi-2223 Tapes

Y. Yuan, J. Jiang, X. Y. Cai, S. Patnaik, A. A. Polyanskii, E. E. Hellstrom, D. C. Larbalestier, R. K. Williams, and Y. Huang

***Abstract*—Overpressure (OP) processing influences the microstructure and critical current density (J_c) of Ag sheathed Bi-2223 tapes. SEM and mass density measurements show higher core density and fewer micro-cracks in OP tape than in 1 atm tape. The self-field critical current density, J_c (0 T, 77 K) in multifilamentary tapes was increased from 33.5 kA/cm^2 with 1 atm processing (1 atm IR) to 48 kA/cm^2 with OP processing (OP pressure $=$ 148 atm) after the first heat treatment (OP HT1), and to 58.7 kA/cm^2 with OP processing after intermediate rolling (OP IR). The corresponding values for J_c (0.1 T, 77 K) are 12.3 kA/cm^2 (1 atm IR) to 18.2 kA/cm^2 for OP HT1 and to 22.4 kA/cm^2 for OP IR.**

***Index Terms*—Bi-2223, critical current density, overpressure processing, porosity.**

I. INTRODUCTION

THE HIGH temperature superconductor that is used for large scale applications is Ag-sheathed (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (Bi-2223) tape. The self-field critical current density at liquid nitrogen temperature, J_c (0 T, 77 K), of long-length commercially available Bi-2223 tape is as high as $\sim$40 kA/cm^2, which is lower than the desired J_c (0 T, 77 K) of at least 100 kA/cm^2. The major goal of Bi-2223 research is to improve J_c. Bi-2223 tapes are currently fabricated from a mixture of 2212 and other phases by the oxide-powder-in-tube (OPIT) method. These OPIT tapes are typically processed using a two-step thermomechanical cycle, consisting of a first heat treatment (HT1), intermediate rolling (IR), and a second heat treatment (HT2), which may be followed by post annealing. Intermediate rolling increases the core density [1], [2] but it also breaks many of the grains forming large numbers of cracks that can not be fully healed in HT2. Furthermore, the filaments can dedensify when 2223 forms in HT2. It has been observed that even the best multifilamentary tapes still contain 10–30% porosity [3]. The pores and unhealed deformation damage from IR, which are inherent defects in the currently practiced conventional 2223 processing, destroy the integrity of grain connectivity, limiting supercurrent flow in the filaments.

Overpressure (OP) processing is designed to increase J_c by overcoming the problems associated with the conventional Bi-2223 processing. OP processing is a low-pressure variant of hot isostatic processing [4], [5] that uses a mixture of Ar and O$_2$ with a total pressure (P_{total}) up to 200 atm to isostatically compress the tapes. The Ar applies the isostatic pressure that compresses the tape. The O$_2$, which can diffuse through the Ag sheath surrounding the ceramic filaments, sets the pO$_2$ needed to form 2223. Heat treating under external isostatic pressure squeezes the tape, which can remove pores, heal cracks, and align growing 2223 grains. Thus OP processing can increase J_c by densifying the ceramic superconducting core, and improving grain alignment and connectivity.

In this study, we investigated OP processing of multifilament and monocore Bi-2223 tapes. We demonstrate that OP processing significantly improves the microstructure and J_c of Bi-2223 tapes compared to tapes processed using the identical 1 atm processing.

II. EXPERIMENTAL PROCEDURES

The OP processing was performed in a flowing gas OP system [5]. The pressure is supplied by a commercial Ar/O$_2$ gas mixture (Matheson Gas) in a high pressure tank (400 atm) that can be used until the tank pressure equals the desired P_{total} in the OP system. The design pO$_2$ in the mixture was 0.077 atm for $P_{total} = 148$ atm. All OP studies reported here were done with $P_{total} = 148$ atm. In the flow system, P_{total} and pO$_2$ remain constant during a run because the gas mixture inside the OP furnace is continuously being replaced during a run. Any gas lost from small leaks or O$_2$ consumed by oxidizing the Inconel tube in the OP furnace is replaced by the incoming gas.

The Bi-2223 multifilamentary and monocore tapes used in this study were produced at American Superconductor Corp. The tape specimens were from various points in the conventional 1 atm heat treatment: after the initial rolling (green tape—GT), after the first heat treatment (HT1), and after intermediate rolling (IR). Samples were cut 3-cm in length and hermetically sealed in a Ag foil envelope with a crimping tool (Team Company, Inc.). The Ag envelope was sealed so it contained an O$_2$ atmosphere.

Two heat treatment schedules were used in the OP processing. The first, called simple heat treatment (SHT), had only one annealing step, which was varied between 804 and 824 °C for 36 hours. SHT was used with GT samples to help determine $T_{\max}$ for the second OP heat treatment schedule.

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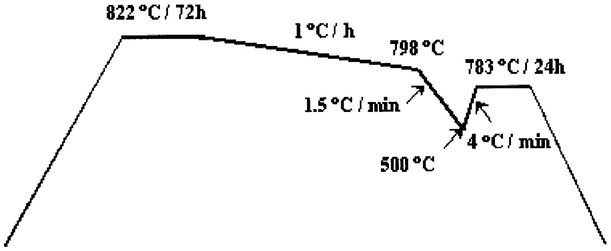


Fig. 1. Final heat treatment (FHT) schedule used for 1 atm and 148 atm OP processing.

TABLE I
LIST OF SAMPLES AND CORRESPONDING PROCESSING CONDITIONS

Sample	Heat treatment and pressure conditions
1 atm GT	FHT of GT @ 1 atm
1 atm HT1	HT1 @ 1 atm + FHT @ 1 atm
1 atm IR	HT1 @ 1 atm + IR + FHT @ 1 atm
OP GT	FHT of GT @ 148 atm
OP HT1	HT1 @ 1 atm + FHT @ 148 atm
OP IR	HT1 @ 1 atm + IR + FHT @ 148 atm

The second heat treatment we used, called final heat treatment (FHT), is shown in Fig. 1. It is a simplified version of the multi-step 1 atm heat treatment developed by Jiang *et al.* [6] that uses a higher $T_{\max}$ than that used for HT1. We used the FHT schedule shown in Fig. 1 to 1 atm and OP process GT, HT1, and IR multifilamentary and monocore samples. The 1 atm processing was done in a normal tube furnace with flowing Ar/O_2 gas. The 1 atm experiments were done to compare J_c in 1 atm and OP samples that had received identical FHT processing, except for the difference in total pressure. The 1 atm processing was also done to study the effects of varying pO_2, explained below. Each FHT OP and 1 atm run contained monocore and multifilament GT, HT1, and IR samples. The sample designations for the various heat treatments are summarized in Table I.

The as-received 400 atm OP gas mixture had a very low O_2 content, 520 ppm, to set the desired $pO_2 = 0.077$ atm at $P_{total} = 148$ atm. It is difficult for the gas supplier to control precisely the O_2 content at such low values. We measured the O_2 content using a zirconia oxygen sensor and determined that the O_2 content in the tank corresponded to pO_2 between 0.075 and 0.10 atm at 148 atm. To investigate how the J_c is affected by changes in pO_2 over this range, we carried out FHT on GT, HT1, and IR samples at 1 atm with $pO_2 = 0.075$, 0.09, and 0.105 atm.

The voltage–current measurements were made with a standard four-probe method in liquid nitrogen in magnetic fields up to 1 T. The magnetic field H was applied perpendicular to the broad tape surface ($H \| c$). I_c was extracted from the V–I curves using a 1 μV/cm criterion, and J_c is defined as I_c/A, where A is the average cross sectional area of the Bi-2223 core. The mass density of the filament in monocore Bi-2223 was calculated from the mass, length, and cross sectional area of the superconducting filaments. The cross sectional area of the superconducting filaments was measured using image analysis of three polished cross sections. The mass was measured by weighing the core after etching off the Ag. The microstructure was examined using JEOL 6100 and LEO1530 scanning electron microscopes. X-ray diffraction was done using a STOE diffractometer with Cu radiation.

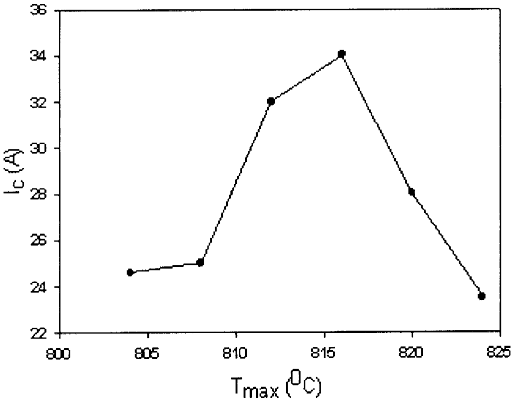


Fig. 2. I_c of multifilamentary Bi-2223 GT sample as a function of $T_{\max}$ for SHT (148 atm).

III. RESULTS

Fig. 2 shows that I_c of multifilamentary Bi-2223 GT samples OP processed using SHT at 148 atm for 36 hours varies with $T_{\max}$. The maximum I_c is at 816 °C. SEM images of these samples' microstructures show that the sample processed at 816 °C has the best phase assemblage. The microstructures of samples processed at lower $T_{\max}$ contain more 2212 because the 2212 to 2223 conversion reaction is slower at lower temperature. Samples processed at higher $T_{\max}$ contain more 2201 due to the more transient liquid in the sample at $T_{\max}$ that converts to 2201 during cooling.

When we OP processed HT1 and IR samples with FHT (Fig. 1), we found that the optimum $T_{\max}$ for FHT was 822 °C, which is higher than $T_{\max}$ found in SHT for the GT samples. We used $T_{\max} = 822°$C for the FHT for all samples (multifilamentary and monocore GT, HT1, and IR samples) even though there is microstructural evidence that a different $T_{\max}$ may be needed to achieve higher J_c for some of the samples.

Fig. 3 presents the I_c of 1 atm GT, HT1 and IR samples at $pO_2 = 0.075$, 0.09, and 0.105 atm. For the 1 atm HT1 and IR samples, I_c is essentially constant over this pO_2 range. For the 1 atm GT samples, I_c decreases with increasing pO_2, with the highest I_c for 0.075 atm. This is consistent with reported results that the optimum pO_2 for 2223 formation is around 0.075 atm [7], [8].

Fig. 4 shows the microstructures of 1 atm IR and OP IR samples. In the 1 atm IR sample, large, well-aligned 2223 grains are only present in a thin layer near the Ag/Bi-2223 interface. The centers of the filaments are partially filled with poorly connected 2223 grains that are separated by large amounts of porosity and cracks. The cracks formed by IR are not effectively removed by FHT at 1 atm, and the porosity may have even increased in the IR sample during FHT at 1 atm. The OP IR sample appears to have much higher density compared to the 1 atm IR sample

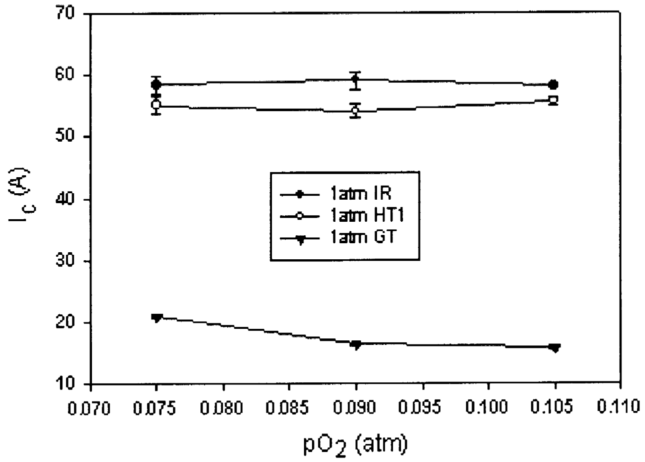
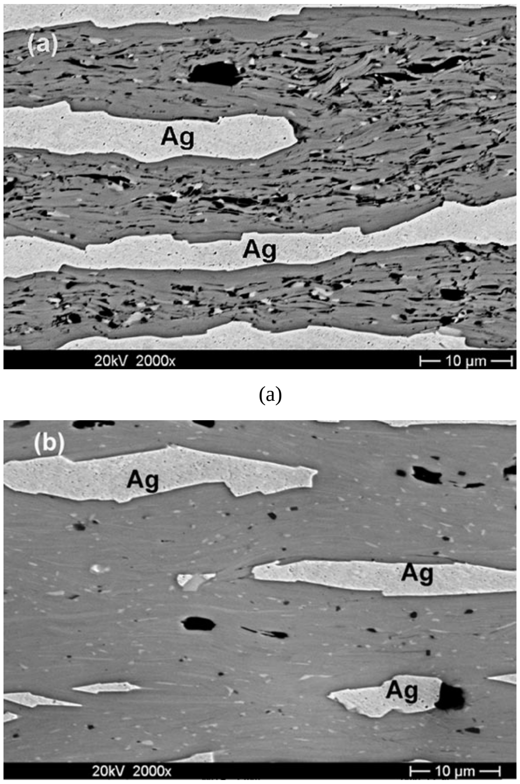


Fig. 3. I_c of multifilamentary Bi-2223 samples as a function of pO$_2$ with 1 atm FHT processing.



(a)

(b)

Fig. 4. Backscattered electron micrographs of multifilamentary Bi-2223 samples (a) 1 atm IR and (b) OP IR. The gray regions are Bi-2223. Large black particles are alkaline earth cuprates (AEC) or CuO. Small, white particles are Pb-rich phases. White line-like particles are Bi-2212/2201. The tiny irregular and line-like black regions are pores and cracks, respectively.

and the 2223 grains appear to be well connected throughout the filament. OP processing significantly reduced the porosity and healed the cracks. The small white particles dispersed through the microstructure in both the 1 atm IR and OP IR samples are the Pb-rich phase (Pb-3221), which formed during the last annealing step in FHT [5], [6].

Fig. 5 displays the Bi-2223 cross sectional areas of 1 atm and OP processed multifilamentary samples. Compared to the 1 atm IR sample, the cross sectional areas of OP HT1 and OP IR samples were reduced by 11% and 16%, respectively. Density measurements on monocore OP IR samples showed the core was up to 97% dense.

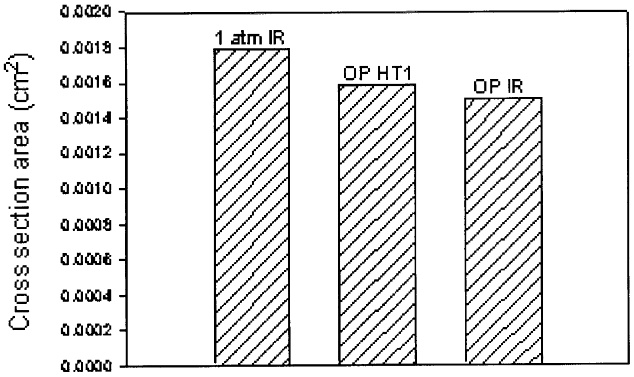


Fig. 5. Total cross sectional area of Bi-2223 filaments in samples processed using FHT at 1 atm and 148 atm.

TABLE II
J_C OF 1 ATM AND OP PROCESSED (148 ATM) MULTIFILAMENTARY SAMPLES

Sample	I_c(0T,77K) A	J_c(0T,77K) kA/cm^2	I_c(0.1T,77K) A	J_c(0.1T,77K) kA/cm^2
		1 atm		
1 atm GT	21	12	-	-
1 atm HT1	56	31	-	-
1 atm IR	60	33.5	22.1	12.3
		OP at 148 atm		
OP GT	55	31	-	-
OP HT1	76	48	28.7	18.2
OP IR	88	58.7	33.6	22.4

Table II lists I_c and J_c of 1 atm and OP processed samples. It shows that OP processing significantly increases J_c compared to identical 1 atm processing. The self-field J_c (0 T, 77 K) of the OP GT sample is $\sim$2.5 times greater than the 1 atm GT sample; J_c (0 T, 77 K) of the OP HT1 sample is 55% greater than the 1 atm HT1 sample; and J_c (0 T, 77 K) of the OP IR sample is 75% greater than the 1 atm IR sample. J_c (0 T, 77 K) for the OP IR sample is 58.7 kA/cm^2. J_c (0.1 T, 77 K) of the OP IR sample is 82% greater than the 1 atm IR sample, having reached 22.4 kA/cm^2, which is the highest 0.1 T, 77 K value reported so far for Bi-2223 sample.

IV. DISCUSSION

The OP heat treatment schedule we used (FHT in Fig. 1) was not fully optimized. We adopted a simplified version of the 1 atm processing schedule Jiang *et al.* [6] developed. In spite of not being completely optimized, Table II shows the OP processing reported here dramatically increased J_c relative to identical 1 atm processing.

We found that $T_{\max}$ was 822 °C when using FHT for OP HT1 and OP IR samples, which was slightly higher than for the OP SHT of GT samples (816 °C). As Jiang *et al.* explain [6],

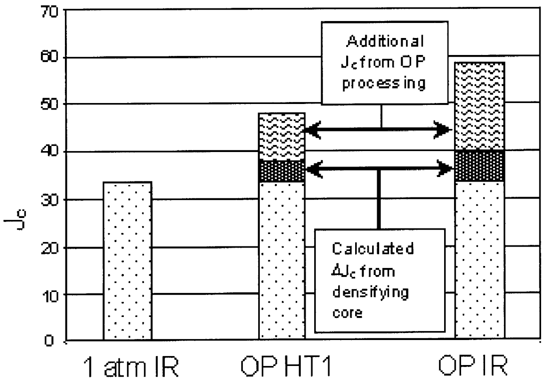


Fig. 6. Calculated portion of the J_c increase between 1 atm and OP processing that is due to densifying the core.

this higher temperature is needed because both the HT1 and IR samples have undergone HT1, in which ~80% of the 2212 in the sample is converted to 2223. At higher temperatures during HT2, more transient liquid forms in the HT1 and IR samples that may help heal cracks and enhance densification. We expect the same phenomena occur during OP processing.

The data in Fig. 3 for the 1 atm FHT experiments show that I_c is essentially independent of pO_2 from 0.075 to 0.105 atm for 1 atm HT1 and IR tapes. Although we do not know the exact pO_2 in the OP system at 148 atm, our measurements have bracketed it in the range 0.075 to 0.100 atm (for this tank of gas). Extrapolating from the results for the 1 atm samples, we assume I_c for the OP HT1 and OP IR samples would be essentially constant for any pO_2 between 0.075 and 0.105 atm.

The microstructure in Fig. 4, measurement of the cross sectional area of the core (Fig. 5), and measurement of filament density show that OP processing densified the 2223 core. If I_c is constant and the core is densified, J_c increases. Thus one can ask how much of the J_c increase that occurs in OP samples is due to densification and how much is caused by other factors. Fig. 6 shows the portion of the increase in J_c in OP HT1 and OP IR samples that can be attributed to densification. For the OP HT1 sample, OP increased J_c (0 T, 77 K) by 14.5 kA/cm^2 over the 1 atm IR sample and densification can only account for 4.2 kA/cm^2 of this increase. For the OP IR sample, OP increased J_c (0 T, 77 K) by 25.2 kA/cm^2 over the 1 atm IR sample and densification can only account for 6.4 kA/cm^2 of this increase. For this calculation, the base line was sample 1 atm IR whose J_c (0 T, 77 K) was 33.5 kA/cm^2. This shows that OP increases J_c by doing more than just densifying the core.

Patnaik *et al.* [9] have used current reconstruction [10] of magneto-optical images to visualize and quantify J_c in 1 atm IR and OP IR samples. They reconstructed the current in longitudinal sections of monocore tape. In the 1 atm IR tape, most of the current was concentrated in a thin layer near the Ag/Bi-2223 interface. In contrast, the current in the OP IR tape was distributed more uniformly throughout the entire core, the average J_c was higher throughout the core, the highest J_c observed in localized regions in the core was ~300 kA/cm^2 compared with ~200 kA/cm^2 in the 1 atm IR tape, and most important, OP processing improved the connectivity throughout the core.

Huang *et al.* [11] have used SQUID measurements of the magnetic moment of Bi-2223 tapes to determine the amount of 2212 in the tape. They measured 1 atm IR and OP IR samples from our study and found that the OP IR samples contain less 2212 than the 1 atm IR samples. X-ray diffraction studies also show less 2212 in the OP samples. Umezawa *et al.* [12] and Huang *et al.* observed that decreasing the 2212 content correlates with increasing J_c. At present we do not know how OP processing decreases the 2212 content. We speculate that the local regions in the OP sample with the highest J_c may contain the fewest 2212 intergrowths.

A practical goal of OP processing is to achieve high J_c without the IR step. To date, our highest J_c is for OP IR samples, and the largest increase between 1 atm and OP samples is for IR samples. The 2223 (and 2212) grains are fractured during IR. We expect that fewer 2223 and 2212 grains are broken by the isostatic compression the OP HT1 samples experience compared to the shear deformation that occurs during IR. In 1 atm processing, the cracks that form in IR do not completely heal during FHT and thus they limit J_c. However, grain fracture that occurs during IR also exposes and mixes unreacted material, which is similar to what occurs during intermediate grinding when doing solid state reactions. This may allow more 2223 to form during the final heat treatment. Thus an IR sample, which has more grain fracture than an HT1 sample, may form more 2223 than the HT1 during OP FHT processing.

Fig. 4(b) shows the OP IR sample still contains nonsuperconducting phases, micropores and microcracks, suggesting there is room for OP processing to improve the microstructure and further increase J_c.

V. SUMMARY

OP processed Bi-2223 tapes have higher core density, less porosity, more uniform J_c distribution, higher local J_c, and better connectivity than tapes that received identical 1 atm processing. With our partially optimized OP processing schedule, we have increased J_c (0 T, 77 K) of IR tape by 75% from 33.5 kA/cm^2 (1 atm IR) to 58.7 kA/cm^2 (OP IR). The J_c (0.1 T, 77 K) data for the OP IR tape is 22.4 kA/cm^2, which is the highest value reported to date. We believe that further understanding and optimizing the OP processing will significantly improve J_c in Bi-2223 tape.

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