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Recent Processing Advances For Increased J_c in $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ Tapes

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Methods to increase the critical current density J_c in Ag-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223) tape by eliminating current limiting mechanisms of porosity, cracks, and the $Bi_2Sr_2CaCu_2O_x$ (2212) phase are presented. J_c increased in samples that had undergone a low temperature post annealing step following the final heat treatment. A Pb-rich phase $(Bi,Pb)_3Sr_2Ca_2CuO_x$ (3221) was present in samples that had undergone the post annealing and had increased J_c. The post annealing also decreased the amount of 2212 as measured by a newly developed analysis of SQUID magnetometry data. Overpressure (OP) processing using a total pressure of 148 bar decreased the pores and cracks in the samples. OP processing fully processed 2223 tapes using a heat treatment schedule that included post annealing decreased the porosity, cracks, and 2212 content, leading to J_c(0.1T,77K) to 30.8 kA/cm^2, which is the highest value reported to date.

Key words: $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ 2223, overpressure processing, post annealing, critical current density

1. INTRODUCTION

Ag-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223) tape is currently the only high temperature superconductor available in kilometer lengths that already has industry-scale electrical demonstration applications. Processing 2223 tapes using the oxide-powder-in-tube process[1,2] consists of synthesizing precursor powder, packing the powder into a Ag tube, drawing and rolling the tube into a tape, then heat treating the tape using a thermomechanical cycle. The thermomechanical process usually includes a first heat treatment (HT1), an intermediate rolling (IR), and a second heat treatment (HT2). In the remainder of this article, HT1 refers to the heat treatment process or tape that has received this heat treatment. Likewise for IR and HT2, and TA1-TA3 and PA, which are defined below.

Current flow in the 2223 tapes fabricated by the OPIT method is limited by multiple obstacles such as porosity, cracks, nonsuperconducting alkaline earth cuprates (AEC), residual liquid or amorphous phase, and low T_c 2212. These defects, which are current limiting mechanisms (CLM), break the 2223 grain connectivity and thus the current paths. Intermediate rolling increases the filament density but it also breaks many of the grains, forming a large number of cracks that cannot be completely healed in HT2. It has been observed that even the best fully-processed multifilamentary tapes processed at 1 atm contain up to 30% porosity.[3]

The 2212 phase is another CLM in 2223 tape. It is present as a remnant phase because the precursor powder cannot be fully reacted to form the 2223 phase, and it forms as intergrowths within 2223 grains.

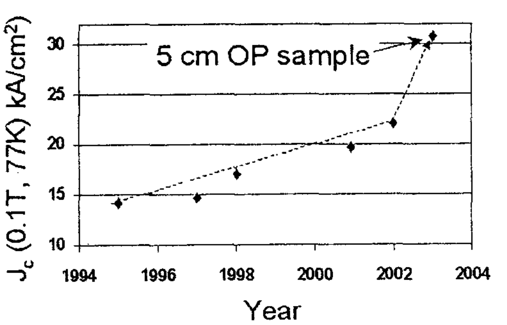


Fig. 1. J_c(0.1T,77 K) as a function of time for AMSC 2223 tape. The increase in 2003 was due to OP processing and 2212 phase reduction.

American Superconductor Corp. (AMSC) has made steady progress improving the J_c performance of 2223 tape. Figure 1 shows J_c (0.1T, 77K) as a function of time for AMSC tape. The 0.1T J_c data are shown because J_c at 0.1T is not affected by self-field effects that can severely decrease J_c in applied fields much smaller than 0.1T in high J_c tape. The significant up tick in performance in 2003 is from overpressure (OP) processing, in which the sample is heat treated in a high pressure atmosphere of Ar and O_2; 148 atm total pressure used in this study.[4,5] Ar presses on the sample and the oxygen fixes the thermodynamic conditions to form 2223.

We present results improving J_c in 2223 tape by reducing cracks, porosity, and the 2212 phase using a multiple-step thermal cycle that was carried out with 1 atm and 148 atm (OP) total pressure.

2. EXPERIMENTAL PROCEDURES

Experiments TA1-TA3 (Fig. 2a) used monocore OPIT 2223 tape made at UW-Madison whose overall powder composition was $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_{2.0}Cu_{3.0}O_x$. These experiments were a series of heat treatments at 1 atm total pressure that began with pieces of monocore tape that had received HT1 and IR. TA1 is a three-step HT2 heat treatment. TA1 tapes were then heat treated using the TA2 heat treatment cycle, and TA2 samples were used for the TA3 heat treatment cycle. We call lower-temperature processing following HT2, such as TA2, or a combination of TA2 plus TA3, post annealing (PA). The parameters shown in Fig. 2a were optimized based on the UW monocore tape used in the study.

The heat treatment shown in Fig. 2b was done at UW at 1 atm and 148 atm total pressure on 2223 tape that had been fabricated and fully heat treated at American Superconductor Corp. (AMSC) before being shipped to UW.

The 1 atm processing was carried out using an Ar/O_2 mixture with 1 atm total pressure with an oxygen partial pressure (pO_2) of 0.075 atm

The OP processing was carried out in a flowing-gas an OP system. It uses a high pressure Ar/O_2 gas mixture (Matheson TriGas Corp.) to set the required total pressure and to fix the oxygen partial pressure (pO_2) within the system. The OP conditions were designed to be 148 atm total pressure with $pO_2 = 0.08$ atm.

Samples that were heat treated using the schedule in Fig. 2b are referred to as 1 atm or OP samples.

The voltage-current measurements were made using the standard 4-probe technique in liquid nitrogen in magnetic fields up to 1 T applied perpendicular to the broad tape surface (approximately parallel to the c axis). The 1 μV/cm criterion was used to determine the critical current I_c. The critical current density J_c was defined as I_c/A, where A is the average of two or three measurements of the 2223 cross-sectional area. Microstructural studies were made using a LEO 1530 SEM equipped with energy dispersive spectroscopy (EDS - Tracor Northern). X-ray diffraction was done using a

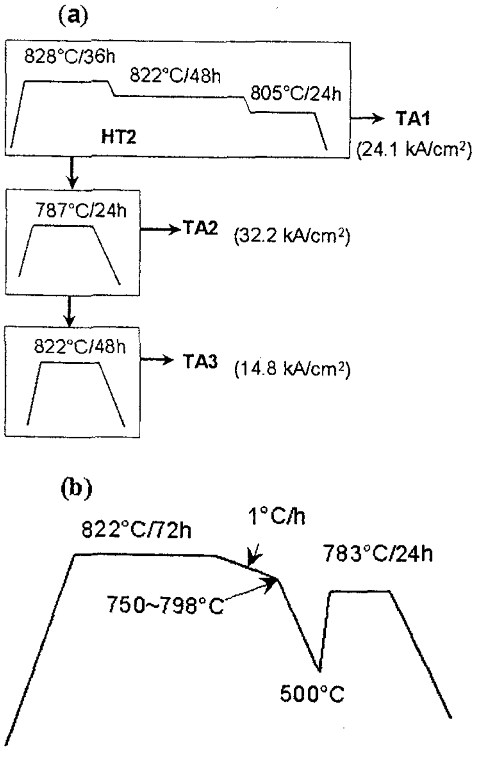


Fig. 2. (a) Heat treatments used for the TA1-TA3 samples and J_c(SF,77K)data after each step. The samples were cooled to room temperature between each TA step. (b) Final heat treatment used for the 1 atm and OP samples. It is a simplified combination of TA1 and TA2.

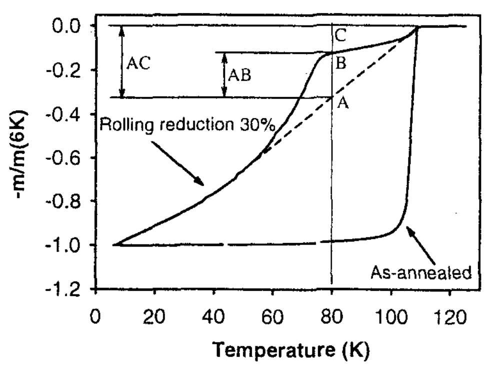


Fig. 3. Normalized magnetic moment as a function of temperature for samples as annealed and after 30% rolling reduction. 2212 SQUID index was characterized by line segment ration AB/AC.

STOE diffractometer with Cu K_α radiation.

Cai et al. developed a technique to determine the 2212 content in 2223 tape based on SQUID measurements.[6] In the SQUID measurement, the sample was zero field cooled (ZFC) to 5K, then at 5K a 0.5 mT field was applied parallel to the longitudinal tape axis. The magnetic moment was measured as a function of temperature with a Quantum Design magnetometer as the temperature was increased. The SQUID measurements were made on tape before and after being rolled with a 30% reduction in thickness. Fig. 3 shows how the 2212 SQUID index was determined. In it, a straight line was drawn connecting the high temperature and low temperature magnetization data for the rolled tape. A vertical line was drawn at 80K and the SQUID index was given by the ratio of the length of the line segments AB/AC.

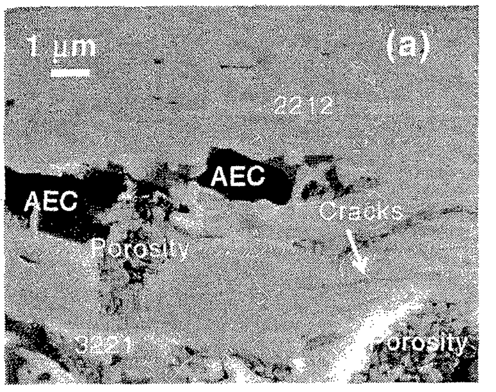
3. RESULTS

The data in Fig. 2a show J_c (SF,77K) (SF = self field) increased from 24.1 kA/cm^2 after TA1 to 32.2 kA/cm^2 after TA2. The microstructure of the TA2 sample contained a significant amount of Pb-rich phase, $(Bi,Pb)_3Sr_2Ca_2Cu_1O_x$ (3221), identified by SEM-EDS analysis and XRD. This phase was not observed in the TA1 or TA3 samples. The J_c(SF,77K) for TA3 dropped significantly to 14.8 kA/cm^2.

Figure 4 shows the J_c(SF,77K) and J_c(0.1T,77K) of 1 atm and OP processed samples. J_c(SF,77K) of the OP sample is 23% greater than the 1 atm sample. I_c(SF,77K) and J_c(SF,77K) for the OP sample are 181.7 A and 69.6 kA/cm^2, respectively. J_c(0.1T,77K) of the OP sample is 30% greater than the 1 atm sample, having reached 30.8 kA/cm^2, which is the highest 0.1T,77K value that has been achieved for 2223 tape.

The microstructures of 1 atm and OP samples are shown in Fig. 5. The 1 atm sample (Fig. 5a) shows many cracks and pores, and the nonsuperconducting phases such as AEC and 3221.

The OP sample (Fig. 5b) contains the same nonsuperconducting phases as the 1 atm sample. However, the OP sample looks much denser because the number of pores and cracks is significantly smaller. Both the 1 atm and OP samples contain the 2212 phase, which is apparent from the white streaks in the SEM images.



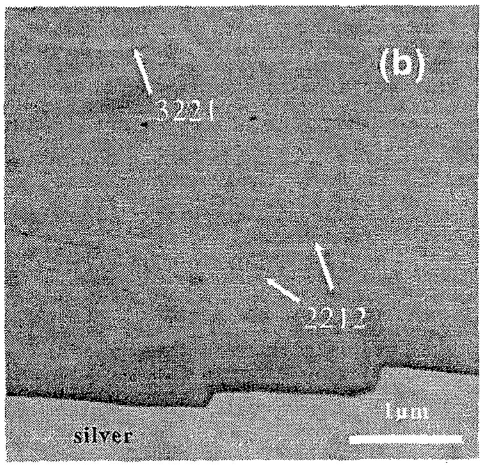


Fig. 5. SEM image of (a) 1 atm sample and (b) OP sample.

The SQUID 2212 index measured for the TA1-TA3, 1atm and OP samples is shown in Fig. 6. The index measured for the 1 atm and OP samples, was 0.29 and 0.11, respectively.

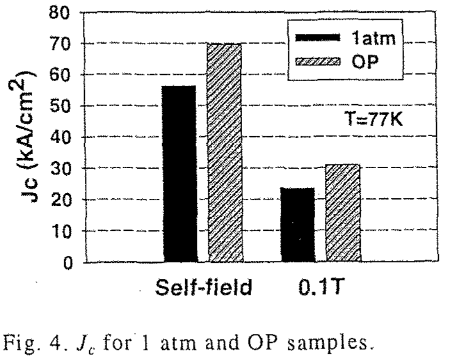


Fig. 4. J_c for 1 atm and OP samples.

4. DISCUSSION

The TA1-TA3 experiments showed the importance of a PA heat treatment to increase J_c. Adding the 787°C heat treatment (TA2) increased J_c by 34%, whereas TA3 decreased J_c by 53%, to a J_c that 39% lower than J_c for TA1. The amount of 2223 phase was essentially the same [(2223/(2212+2223)~98% measured by XRD] after each step, so this cannot explain the dramatic changes in J_c. The only significant difference we observed in the microstructure was 3221 in TA2. We believe that at the highest temperature in TA1, 2223 was being formed by a liquid-assisted reaction between 2212 and

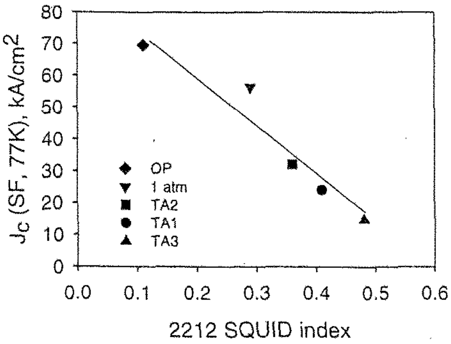


Fig. 6. J_c (SF,77K) as a function of 2212 SQUID index for TA1- TA3, 1 atm and OP samples.

nonsuperconducting phases. The design purpose of the 805°C step in TA1 was to remove the liquid that was present at the higher processing temperatures. We believe the 3221 phase that was present in the TA2 samples developed from liquid that had not been completely removed during TA1. We believe that forming the 3221 phase has a beneficial effect on J_c because it removes from the grain boundaries remnant liquid or phases that formed from the liquid. On reheating the sample to 822°C during TA3, the 3221 phase disappeared and J_c decreased significantly. We believe that at 822°C in TA2, liquid reformed in the sample. On cooling there was more liquid in TA3 than in TA1, because TA1 had an additional annealing step at 805°C that was removing liquid, so the additional remnant liquid compared to TA1 (or phases that formed from the liquid) blocked more current paths in TA3 than TA1 or TA2.

We combined, simplified, and modified TA1 and TA2 heating schedules resulting in the heat treatment shown in Fig. 2b. It incorporated a high temperature step to form the 2223 phase, used slow cooling from this high temperature to remove liquid, and added a PA step at 783° to form the 3221 phase.

Figure 4 shows OP processing increased J_c(SF,77K) 23% compared to identical 1 atm processing. Part of this increase is from OP processing having densified the sample by eliminating pores and cracks, which is seen by comparing Figs. 5a and 5b. OP densified the 2223 filament in agreement with our earlier OP results that used green tape, and HT1 and IR tape. There we also found significant J_c increases in OP samples compared to samples processed identically in 1 atm.[4,5] In addition, OP processing increased the filament density to as much as 97% of the theoretical density. In the present study we applied OP processing to fully heat treated AMSC tape, which shows OP can be added to an optimized heat treatment to increase J_c even higher.

OP processing significantly reduces pores and cracks which are significant CLMs in 1 atm processing. However, 2212, which is known to be another CLM[6,7] is still present. The SQUID 2212 index is a sensitive indicator of the amount of 2212 in the sample. However, we do not yet have a quantitative relation between the SQUID 2212 index and the volume fraction of 2212 in the sample. The index also does not tell us what form 2212 has in the 2223 tape.

Figure 6 shows that J_c of the TA1-TA3, 1atm and OP samples scaled with the SQUID 2212 index, increasing with decreasing index. Comparing TA1 through TA3, it indicates that TA2 contained the least 2212 and TA3 contained the most 2212. A plausible, but not proven, interpretation of these data is that remnant liquid partially transforms to 2212 on cooling. Thus TA3 which we believe contained the most liquid when it was cooled to room temperature had the most 2212 and highest SQUID 2212 index. TA1 which had more liquid removed by the 805°C step than TA3, had less 2212 than TA3 and thus a lower index. TA2, which had the lowest index, which meant it had the smallest amount of 2212 also contained 3221. This may indicate that 2212 and other phases that formed from the remnant liquid on cooling after TA1 were converted to 3221 during TA2. We believe that part of the liquid present in TA3 came from melting of 3221 and other phases.

The 1 atm and OP samples had lower SQUID 2212 indices (0.29 and 0.11, respectively) than the TA1-TA3 samples (0.36 – 0.48). This indicates the 1 atm and OP samples contain less 2212 than any of the TA series samples. The interesting observation for which we have no explanation yet is why OP has a significantly lower index than the 1 atm sample, even though both had essentially identical heat treatments, except for the added pressure on the OP sample.

5. CONCLUSIONS

We have studied the effect of post anneal on J_c and 2212 content in monocore 2223 tapes. We found that post annealing increased J_c, which was linked to the 3221 precipitation and 2212 reduction in a low-temperature post annealing step. We have shown that OP processing 2223 tape in a total pressure of 148 atm after it has been fully heat treated in a 1 atm process results in a significant increase in J_c(0.1T,77K) to 30.8 kA/cm^2 and I_c(SF,77K) to 181.7 A. J_c(SF,77K) of 69.6 kA/cm^2 has been achieved in OP samples. 30.8 kA/cm^2 is the highest J_c(0.1T,77K) value reported to date for 2223 tapes. We believe the increase in J_c in OP samples is due to the OP process reducing the current limiting porosity, cracks, and 2212 content.

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