Enhancement of the 77 K irreversibility field and critical current density of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ tapes by manipulation of the final cooling rate

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By manipulating the cooling rate from the final heat treatment, we have raised the 77 K, self-field critical current density (J_c) of multifilament $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (2223) tapes by a factor of 3, and the irreversibility field (H^*) by more than 50%. The J_c of samples cooled in 7.5% O_2 from their reaction temperature of 825 °C increased from ~8 to ~24 kA/cm^2 and H^*(77 K) increased from ~120 to ~200 mT as the cooling rate was decreased from 5 to 0.016 °C/min. The results unambiguously show that the flux pinning properties of 2223 tapes can be improved by simple changes in wire processing. © *1996 American Institute of Physics.* [S0003-6951(96)00145-3]

Improving the J_c of 2223 superconductors in an applied magnetic field provides the most direct path to broad application of high-temperature superconductor (HTS) wire. Ag-clad 2223 made using the powder-in-tube process is currently the most promising HTS wire technology because established processes can be used to manufacture long lengths of strongly linked material. However, in contrast to Y- and Tl-based superconductors, 2223 has relatively weak flux pinning properties above about 30 K. For this reason, use of 2223 wires in moderate to high applied fields is currently limited to low temperature.

Three strategies have been used previously to improve flux pinning in Bi-based superconductors. One successful approach has been postprocessing irradiation.[1] However, although the in-field transport J_c can be significantly enhanced, it is not clear to what extent this method can be applied to practical wire manufacturing. A second approach has focused on introducing defects associated with dopants, dislocations, and particles.[2–4] While this has achieved some success, enhancements to the transport J_c of HTS wires in an applied field has not yet occurred. Finally, controlled manipulation of the oxide constitution to produce impurity phase particles in Bi-2212[5] has met with limited success. In this contribution, we show that simple modifications to the heat treatment can enhance both the zero field and the in-field properties of 2223 tapes.

Parrell *et al.*[6] have shown that the rate at which 2223 tapes are cooled after heat treatment can have a large effect on the transport J_c, critical temperature (T_c) transition, and filament microstructure. They reported that slow cooling (<0.1 °C/min) in 7.5% O_2 increased the J_c (77 K, self-field) by as much as 50% over tapes cooled more quickly, and considerably sharpened the T_c transition, despite decomposition of the 2223 phase at temperatures below the 2223 phase stability limit. This letter builds on this previous work of Parrell *et al.* by exploring in detail one contribution to the J_c improvement. In particular, we have evaluated the flux pinning contribution by measuring the cooling rate dependence of the irreversibility field, H^*.

Ag-clad 85-filament samples of nominal composition $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_{2.0}Cu_{3.1}O_x$ were processed to develop a dense and aligned 2223 phase structure. The final heat treatment was given at 825 °C for 100 h in a 7.5% O_2/balance N_2 atmosphere. Samples were cooled under electronic furnace programmer control from 825 to 730 °C at seven rates between 5 and 0.005 °C/min, and were then furnace cooled at ~20 °C/min. Scanning electron microscopy was used to examine the filament microstructures, and x-ray diffraction (XRD) using Cu- $K\alpha$ radiation was used to study the phase assemblage of the samples.

The 77 K, self-field critical current (I_c) defined at 1 μV/cm were measured for six 2.5 cm long samples for each cooling rate. The I_c was converted to J_c by dividing by the average superconductor area of 12 transverse cross sections. I_c values were also measured at 77 K in magnetic fields from 0 to 300 mT applied perpendicular to the broad face of the tape (i.e., nominally parallel to the *c* axis of the 2223 grains). Extended voltage-transport current measurements were made on at least two samples for each cooling rate using a Keithley 1801 nanovolt preamplifier and a 2001 digital multimeter. The noise was kept to ±3 nV in the best cases by using continuous Cu voltage leads from the LN_2 to the preamplifier inputs. Although it is desirable to remove the Ag sheath in order to obtain the true $E-J$ characteristics of the 2223 filaments,[7] this was not feasible for the multifilament samples studied here. To correct for current sharing between the Ag and the 2223 filaments, the current flowing in the superconductor, I_s, was calculated from $I_s = I - V/R_{Ag}$, where I is the measured current, V is the measured voltage, and R_{Ag} is the measured resistance of the Ag cladding. R_{Ag} was determined from a sample that had been severely bent, destroying the continuous 2223 paths, and then annealed at 400 °C to eliminate any cold work effect on the Ag resistivity. As R_{Ag} varied by less than 2% between 20 and 300 mT, the magnetoresistivity of the Ag was ignored, and R_{Ag} determined at $\mu_0 H = 300$ mT was used. H^* of some samples was also measured by magnetization (defined by the field of loop

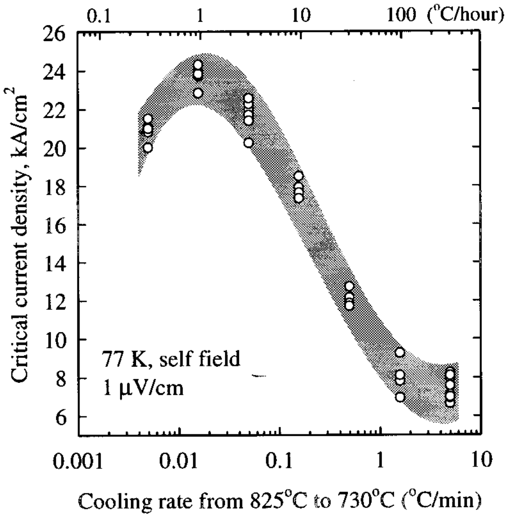

FIG. 1. J_c (77 K, self-field, 1 μV/cm) as a function of cooling rate from 825 to 730 °C. J_c was maximized at a cooling rate of ~0.016 °C/min.

closure) in a superconducting quantum interference device (SQUID) magnetometer.

Figure 1 shows J_c (77 K, self-field), at 1 μV/cm, as a function of cooling rate from 5 to 0.005 °C/min. J_c increased from ~8 kA/cm^2 to a maximum value of ~24 kA/cm^2 for a cooling rate of 0.016 °C/min, and then decreased for the still slower cooling rate of 0.005 °/min. As detailed below, we believe that the increase in J_c with decreasing cooling rate is at least partially due to increases in the flux pinning strength. We attribute the decrease of J_c at extremely slow cooling rates to decreases in both H^* and the intergranular connectivity, the latter due to extensive decomposition of the 2223 phase.[6]

Figure 2 shows the normalized J_c values, $J_c(B)/J_c(0)$, as a function of applied field for three of the cooling rates. These data show that, in addition to the increase in the zero field J_c, some of which may be due to increases in the connectivity of the core, slow cooling also increases J_c in applied magnetic fields, indicating an independent increase in the flux pinning strength.

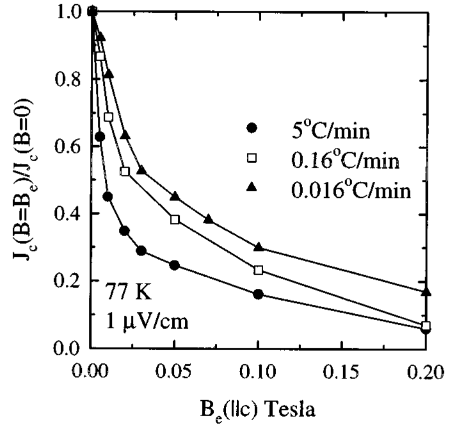

FIG. 2. Normalized J_c values as a function of applied field for samples cooled at 5, 0.16, and 0.016 °C/min. Slow cooling improved the in-field J_c values of the tapes.

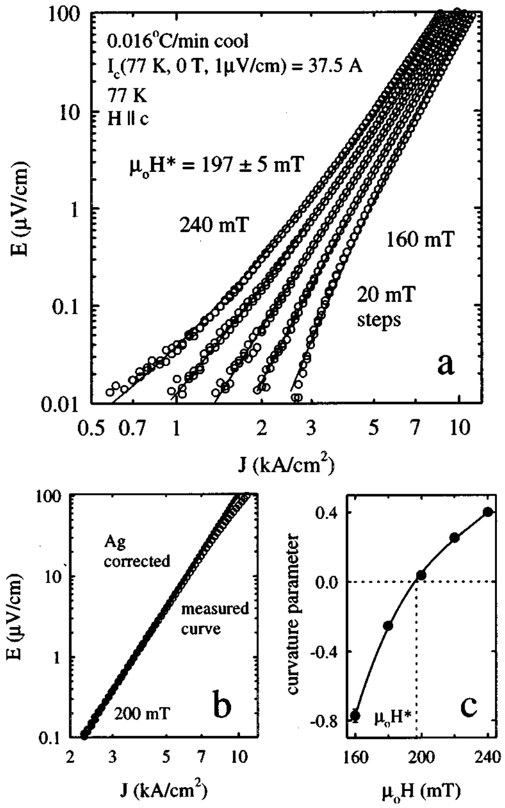

FIG. 3. Examples of (a) the extended $E-J$ data used to determine H^*, (b) a characteristic corrected for current sharing with the Ag cladding, and (c) how H^* was determined by the squared term parameter of a quadratic fit.

An example of the $E-J$ data collected for a sample cooled at 0.016 °C/min is shown in Fig. 3. Following convention,[8,9] we define H^*as the field at which the curvature of the log E–log J characteristics changes from negative to positive. A quadratic fit to the measured data was used to provide an unbiased determination of the curvature, and H^* was taken as the field at which the value of the coefficient of the square term of the quadratic passed through zero.[7] The open symbols in Fig. 3(a) show the Ag-corrected $E-J$ data as a function of magnetic field, and the lines through the data points are quadratic fits. Figures 3(b) and 3(c) show examples of the Ag correction and quadratic fit analysis procedures used to determine H^*. If left uncorrected, current sharing with the Ag sheath causes the $E-J$ characteristic to shift to higher values of J, which can introduce error into the curvature analysis, particularly for samples with low I_c values. $\mu_0 H^*$ for this sample was determined as 197±5 mT.

Figure 4 shows H^*, determined as in Fig. 3, and from SQUID magnetization loop closure, as a function of cooling rate. As the cooling rate was decreased from 5 to 0.005 °C/min, $\mu_0 H^*$ increased from ~120 to over 200 mT. This dependence on cooling rate is qualitatively similar to that of the self-field J_c in Fig. 1. This behavior, in addition to the in-field normalized J_c values of Fig. 2, confirms that the flux pinning properties of the 2223 have been improved by slow cooling, since both the normalized and the absolute J_c values increase upon slow cooling. For example, at 77 K and 0.2 T, in addition to the absolute J_c being approximately 10 times

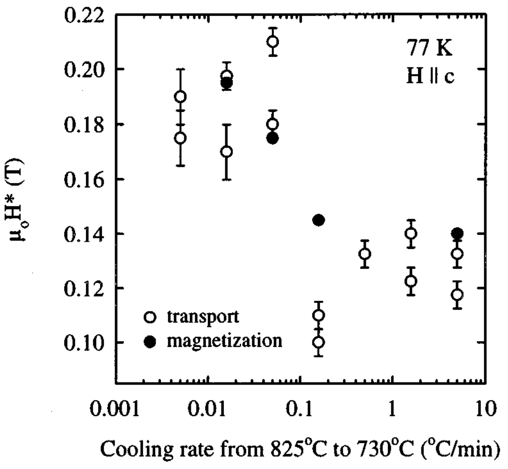

FIG. 4. Irreversibility field (H^*), determined by transport and magnetization, as a function of cooling rate.

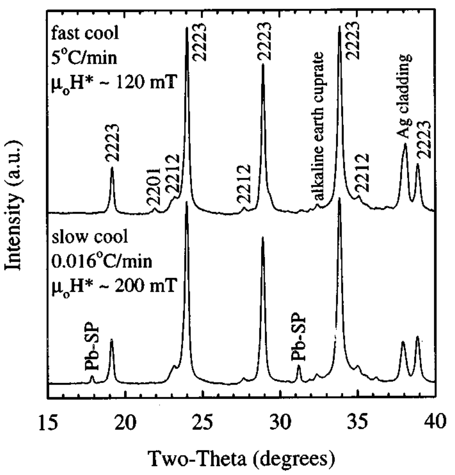

FIG. 5. X-ray diffraction patterns of samples cooled at 5 and 0.016 °C/min. Slowly cooled samples have higher J_c values despite containing more Pb-rich impurity phases.

greater, the normalized J_c of samples cooled at 0.016 °C/min is about twice that of samples cooled at 5 °C/min. Although the magnitude of the H^* enhancement observed is modest, our results are particularly significant in that the process through which they were obtained is readily applied in practice. Furthermore, the development of a mechanistic understanding may lead to further flux pinning improvements.

To develop this understanding, we have carried out a preliminary microstructural investigation of samples cooled at different rates. As shown in the XRD patterns of Fig. 5, samples cooled at slower rates with higher J_c and H^* values generally contain more impurity phase, particularly Pb-rich phases such as the co-called $(Bi,Pb)_3Sr_2Ca_2CuO_x$ (3221) phase (labeled ''Pb-SP''). The formation of the Pb-rich phases during slow cooling implies a change in the 2223 composition. Indeed, wavelength dispersive spectroscopy showed that slowly cooled 2223 had a statistically significant lower Pb content; samples cooled quickly at 5 °C/min had an average composition of $Bi_{2.02}Pb_{0.38}Sr_{1.95}Ca_{1.99}Cu_{3.00}O_x$, while those cooled more slowly at 0.05 °C/min had a composition of $Bi_{1.99}Pb_{0.35}Sr_{1.94}Ca_{1.97}Cu_{3.00}O_x$.

Since more work is needed to fully characterize the microstructure-property relationships of these samples, we can only speculate about the mechanism of the H^* enhancement. One source could be cation or anion defects introduced by changes in the equilibrium composition of the 2223 phase during slow cooling. A second possibility is that the precipitated phases produce increased flux pinning, either directly or through strain fields or other perturbations associated with their presence. As important as our initial flux pinning enhancements are to performance improvements of 2223 wires, further understanding of the complex interplay between intergranular connectivity and intragranular flux pinning will almost certainly result in more substantial J_c improvements of HTS wires.

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