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ABSTRACT

$(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Bi–2223) and $TlBa_2Ca_2Cu_3O_x$ (Tl–1223) bars were hot forged in air at 820–850°C. Final stresses of 2–3 MPa were sufficient to produce >95% dense Bi–2223 bars. In contrast, stresses to ≈42 MPa were able to produce only 75–80% dense Tl–1223 bars. The Bi–2223 bars were more phase–pure and exhibited much stronger c–axis textures than the Tl–1223. Maximum critical current densities at 77 K were 8×10^4 A/cm^2 for the Bi–2223 and 2×10^4 A/cm^2 for the Tl–1223. Fracture strength and toughness values were 140 MPa and 2.9 $MPa\sqrt{m}$ for the Bi–2223 and 50 MPa and 0.5 $MPa\sqrt{m}$ for the Tl–1223.

INTRODUCTION

Hot deformation has been shown to increase the critical current density of bulk polycrystalline superconductors. For $YBa_2Cu_3O_x$ (Y–123), transport J_c values at 77 K have reached $\approx 3.5 \times 10^3$ A/cm^2, and intragranular J_c values have increased because of formation of defects such as dislocations and stacking faults during pressing.[1,2] For hot–pressed Bi–2223, J_c values at 77 K have reached $\approx 10^4$ A/cm^2 in bulk pieces[3-5] and 3×10^4 A/cm^2 in thick films.[6] Recent results on Ag–clad Bi–2223 tapes also indicate that the defects produced during deformation may improve flux pinning significantly, and thus J_c in applied magnetic fields.[7] The results for hot–pressed $Bi_2Sr_2CaCu_2O_x$ (Bi–2212) are mixed,[8,9] with some benefits to J_c reported at 4.2 K.

Given the benefits that appear to accrue from hot deformation, it is natural to attempt sinter–forging of Tl–based superconductors. These materials have excellent intrinsic properties and high T_c values. Preliminary data acquired for $TlBa_2Ca_2Cu_3O_x$ (Tl–1223) are reported in this paper; results are compared with those for Bi–2223.

EXPERIMENTAL METHODS

Synthesis and fabrication

Bi–2223 powder was prepared from the intermediate phases $Bi_{1.8}Pb_{0.4}Sr_2CaCu_2O_x$, Ca_2CuO_3 and CuO, which were synthesized from Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO mixtures.[3,9] To obtain highly phase–pure Bi–2223, the $Bi_{1.8}Pb_{0.4}Sr_2CaCu_2O_x$, Ca_2CuO_3, and CuO were ball–milled and heated in dry, CO_2–free air for 50 h at 840°C, then ball–milled and heated again for 50 h, this time at 855°C. The fraction of Bi–2223, as determined by X–ray diffraction, was ≈95%.

For the Tl–1223 synthesis, high–purity $BaCO_3$, $CaCO_3$, and CuO powders were weighed to proper proportions to form $Ba_2Ca_2Cu_3O_x$. The powders were ball–milled for 16 h, dried, placed in shallow Al_2O_3 crucibles, and calcined at 800–850°C for 12 h in flowing O_2 at a pressure of $\approx 2.5 \times 10^2$ Pa. From 600°C to the maximum temperature, a heating rate of 5°C/h was used. The purpose of this slow heating rate was to minimize CO_2 concentration in the atmosphere during carbonate decomposition.[10,11] The crucible was removed from the furnace at ≈200°C and quickly transferred to a dry–N_2 glovebox. The powders were transferred from the crucible, crushed in an agate mortar and pestle, and then mixed with Tl_2O_3 to produce the Tl–1223 stoichiometry. To minimize contact with any CO_2 or H_2O that may have been present in the glovebox, the mixing was completed within 0.3 h.

The mixed powder was placed into a small Pt crucible that was fitted with a tight Ag lid. The crucible was heated in flowing O_2 at 180°C/h to 900°C, held for 0.1 h, cooled to 885°C and held for 12 h, and then cooled at about 180°C/h to room temperature. The powder was then crushed and given an identical heat treatment. The final powders were removed from the furnace to the glovebox while still hot. XRD revealed the presence of both Tl–1223 and $Tl_2Ba_2Ca_2Cu_3O_x$ (Tl–2223) in the final powder.

The Bi–2223 and Tl–1223 powders were initially pressed uniaxially at 70 MPa in a steel die to form bars. The resultant bars were ≈7 x 8 x 38 mm and ≈50% dense. They were further processed by sinter forging in air at 820–850°C under compression rates of 0.001–0.005 mm/min.[3,9] To minimize contamination and loss of volatile species, the bars were wrapped in Ag foil. The final stress on each Bi–2223 bar was 2–3 MPa. Significantly higher stresses were needed to deform the Tl–1223; final stresses were 28–42 MPa. Specimen thicknesses were reduced by ≈70% during forging.

Property measurements

T_c values were determined with a SQUID magnetometer: samples were cooled in zero field below T_c, a field of 0.5 Oe was applied, and magnetization was monitored during warming. Transport J_c was measured by a four–probe method with a pulsed–current source. Contacts were applied as a slurry of Ag powder in an organic solvent. The coated specimens were dried and annealed in O_2 at ≈800°C for 1–2 h. Critical currents were often very high; therefore, for J_c testing, smaller specimens were often cut from the bars with a slow–speed diamond–blade saw. A few specimens were also measured in small applied magnetic fields.

Microstructures were examined by optical microscopy and scanning electron microscopy (SEM). Phase formation and qualitative grain alignment were examined by X–ray diffraction. Cu Kα radiation, at 30 kV and a current of 15 mA, was used.

To determine fracture strength, bars measuring ≈25 x 3 x 3 mm were cut. The tensile edges of the samples were smoothed and beveled by grinding with 600–grit SiC paper and the bars were loaded in four–point bending at a rate of 1.27 mm/min. The inner and outer load spans were 9.6 and 19.2 mm, respectively. Fracture toughness (K_{IC}) values were determined by the single–edge notched–beam method.[12,13] The test bars were loaded in three–point bending at a rate of 1.27 mm/min. K_{IC} was calculated from $K_{IC} = 3\ P\ L\ Y\ (C)^{0.5} / B\ W^2$, where P is the load at fracture, L is the support–span distance, Y is a constant related to the specimen geometry, C is the notch depth, B is the specimen width, and W is the specimen height.[12] At least four bars were tested to determine each strength and toughness value.

RESULTS AND DISCUSSION

The Bi–2223 bars proved to be easy to densify at 840–850°C; densities were routinely >95% of theoretical. The Tl–1223 bars were much harder to densify. Deformation temperatures ranged from 810–830°C, but to avoid excessive reaction with the Ag foil, the maximum temperature had to be ≤820°C. Densities were 70–75% of theoretical for stresses ≈35 MPa and 74–80% for stresses of ≈42 MPa.

Microstructural examination suggested that the difficulty in densifying the Tl–1223 bars arose from two sources. First, the Bi–2223 was more phase–pure (Fig. 1), and nonsuperconducting phases such as $BaCuO_2$ or Ca_2CuO_3 are known to be much harder than high–temperature superconductors.[13] Second, Tl–based superconductors themselves are harder and stronger than Bi–based superconductors.[14] XRD data also indicated that the Bi–2223 bars were more phase pure and better aligned than their Tl–1223 counterparts (Fig. 2).

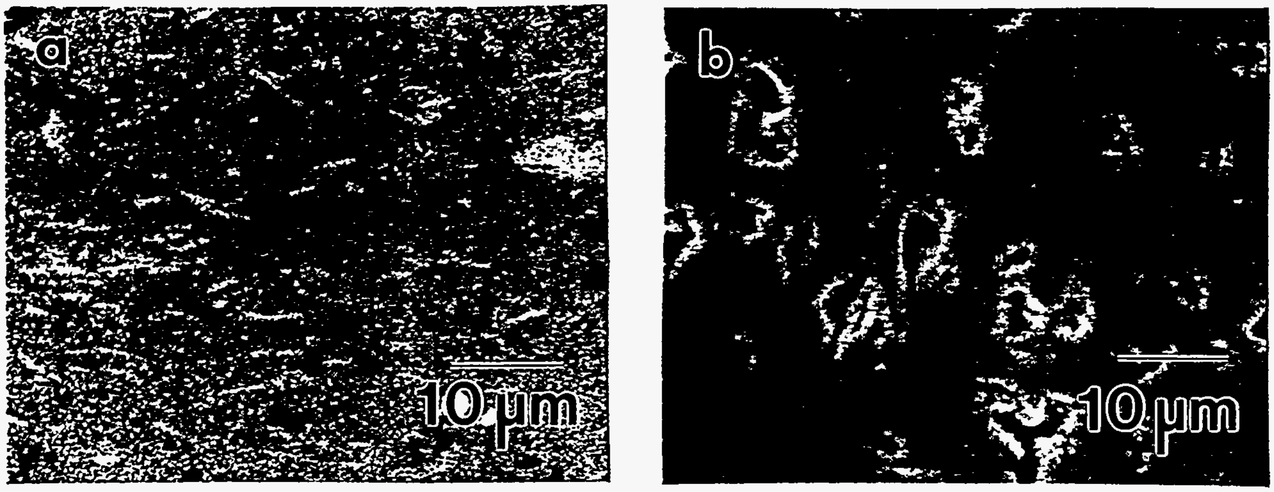

Fig. 1. SEM photomicrographs of cross sections of (a) Bi–2223 and (b) Tl–1223 bars. Light–gray regions of (a) are Bi–2212 phase; strong orientation is evident. There is much more porosity in (b) and no clear alignment of grains.

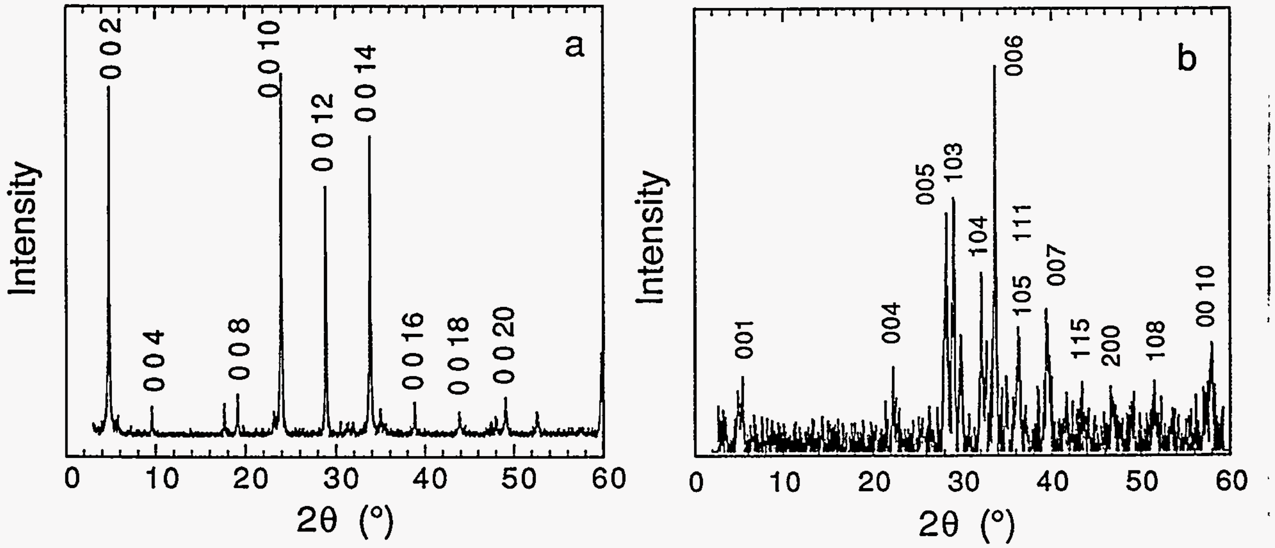

Fig. 2. XRD plots for (a) Bi–2223 bar forged at 845°C and 3 MPa and (b) Tl–1223 forged at 820°C and ≈35 MPa. The Bi–2223 exhibits excellent c–axis texture; the Tl–1223 exhibits only moderate c–axis texture.

The Bi–2223 bars exhibited sharp superconducting transitions, with onsets generally at ≈107 K. The Tl–1223 exhibited broader transitions, in part because of the presence of both the Tl–1223 and Tl–2223 phases, with onsets at ≈120 K (Fig. 3). Transport J_c values at 77 K were 3×10^3 to 8×10^3 A/cm^2 for the Bi–2223 and 1×10^3 to 2×10^3 A/cm^2 for the Tl–1223. J_c for Bi–2223 was unaffected by a 100 G magnetic field parallel to the pressing direction; J_c for the Tl–1223 decreased by ≈10% in a 100 G field.

The mechanical properties of the bars reflected their differences in density and phase purity. Fracture strength and K_{IC} values were 140 MPa and 2.9 MPa√m for the Bi–2223 and 50 MPa and 0.5 MPa√m for the Tl–1223. The basic mechanical properties of Tl–1223 appear to be closer to those of Y–123 than to Bi–2223. Thus, with improvements in phase purity and density, strengths can be expected to reach 200 MPa and toughnesses at least 1.5 MPa√m.[14]

It has been established that during hot forging, a Pb–rich liquid was present in the Bi–2223 bars and that this liquid is essential for producing high J_c values.[3,5,9] There was some liquid present during forging of the Tl–1223 superconductors, but its effectiveness was limited. Our future work with forging of Tl–1223 superconductors will include use of alloys such as $Tl_{0.78}Bi_{0.22}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$ and $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$. The Tl–1223 phase is easier to form with these compositions, and problems associated with Tl_2O volatility may be less severe. The next set of experiments will emphasize use of transient liquid phases during hot forging.

SUMMARY

Hot–forged Bi–2223 and Tl–1223 bars exhibited significant differences. At nearly equal temperatures, the Bi–2223 densified fully for stresses of 2–3 MPa, but the Tl–1223 reached a maximum density of <80% theoretical for a stress of ≈42 MPa. The Bi–2223 exhibited better phase purity, much better c–axis alignment, higher J_c values, and superior mechanical properties. T_c values were typical for each material and the transitions were sharp. Results to date suggest that reactive sintering with a liquid phase during the deformation process is essential for obtaining good final properties.

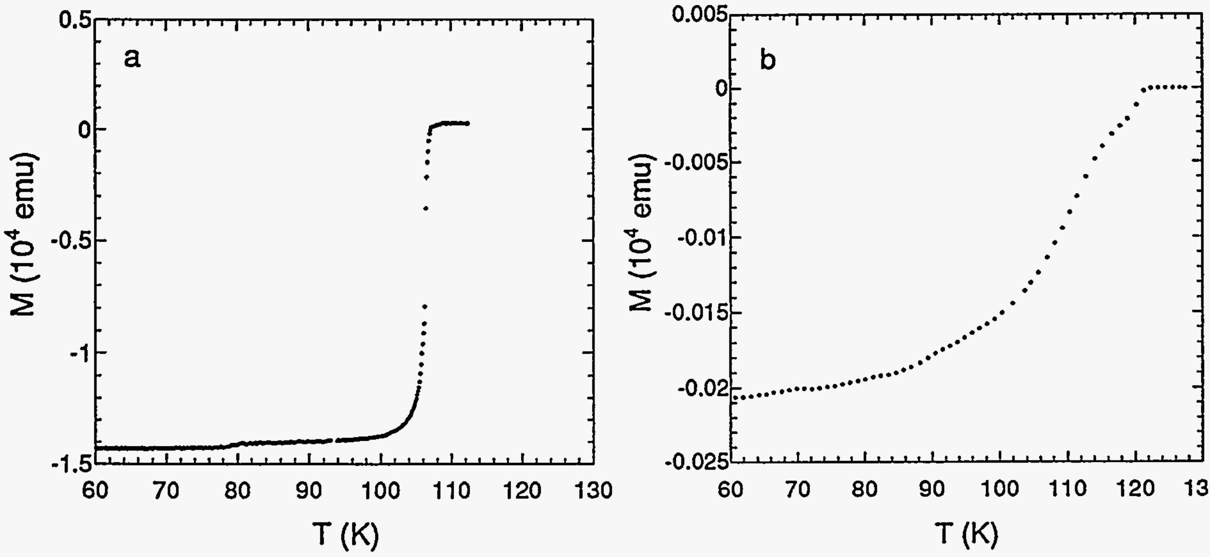

Fig. 3. T_c plots for (a) Bi–2223 bar forged at 845°C and 3 MPa and (b) Tl–1223 forged at 820°C and ≈35 MPa.

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