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CURRENT TRANSPORT AND MICROSTRUCTURAL EVOLUTION IN BSCCO TAPES FABRICATED BY GROOVE ROLLING*

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Abstract—**The powder-in-tube technique, consisting of wire drawing and rolling, has been widely used to fabricate superconducting tapes for possible electric power applications. In this study, instead of wire drawing, the starting billet was reduced in size by groove rolling. To optimize the deformation and thermomechanical treatment process, wires of varying dimensions were fabricated. The wires were flat-rolled to a final thickness of 250 mm. Short-length tapes were subjected to a series of thermal and deformation steps. Phase development and microstructural evolution during the process were monitored by XRD, SEM, and TEM. The BSCCO-2223 tapes, which were subjected to thermomechanical treatment, had average critical current densities of 18,000 A cm^{-2}. Colony boundaries, examined by TEM, near the superconductor-silver interface were found to form in certain preferred orientations. Polytypoids of 2212 phase were also observed at the colony boundary. The effects of grain boundary on superconducting order parameter and critical current density have also been examined.**

1. INTRODUCTION

The powder-in-tube (PIT) technique has established itself as the most popular process for fabricating long-length superconductors for possible electric power and high-field magnet applications. The technique utilizes traditional metalworking processes such as drawing and rolling to transform the ceramic-based high-temperature superconductors (HTS) into more useful forms such as wires and tapes. Because of its platelike morphology, the Bi-Sr-Ca-Cu-O compound is the only HTS material that has proven to be capable of being fabricated into long lengths. The desired 2223 phase is obtained by subjecting the tapes to a series of thermomechanical treatments consisting of heat treatment and mechanical deformation [1-4]. The formation of phase pure and textured 2223 phase is a critical issue in fabricating BSCCO tapes with high critical current density (J_c). Additionally, careful control of PIT variables such as composition and phase assemblage of the precursor powder, initial tape deformation, and thermomechanical treatment conditions is required to achieve the desired current transport properties [1-3]. Although high J_c values have been achieved in short BSCCO tapes, better control of the process variables is still required to improve reproducibility of the results.

Recently, several research groups reported that most of the current in the BSCCO tapes flows exclusively in a thin layer of highly aligned grains near the silver (Ag) sheath [5-7]. Existence of such a layer has been confirmed by, high resolution electron microscopy (HREM) [5], and magneto-optical imaging [6]. A correlation between the interface contact length of the superconductor core and the Ag has also been established [7]. Although the presence of Ag aids in the formation and alignment of the 2223 phase, the actual mechanism remains unclear. Because current transport in tapes has been reported to follow a percolative path, J_c of the tapes will be strongly determined by weak links, grain boundary misorientations, and electromagnetic coupling at the boundaries [1],[2],[8]. To improve the J_c of Ag-sheathed superconducting tapes, it is imperative to understand the correlation of J_c with the microstructure of the tape, especially at the interface between the core and the Ag sheath.

In the present study, a modified version of the PIT technique was adopted in which the Ag billet was reduced in size by groove rolling rather than by wire drawing. The advantage of this technique is that it is less energy-intensive because both groove rolling and flat rolling can be achieved using the same setup. Furthermore, the technique is readily scalable and therefore long-length conductors can be easily fabricated. By optimizing the deformation and thermomechanical treatment process Ag-clad BSCCO tapes with high current transport properties were fabricated. Simultaneously, formation of the 2223 phase during thermomechanical treatment was also studied.

Transmission electron microscopy (TEM) was used to evaluate grain boundary misorientations and alignment close to the superconductor-Ag interface. Based on the TEM results, an effort was also made to simulate the grain boundary (GB) effect on the superconductor order parameter (SOP) and current transport properties of the tapes.

II. EXPERIMENTAL PROCEDURE

Partially reacted precursor powder of composition $Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{2.2}Cu_{3.0}O_x$ was obtained by a solid-state reaction of high purity oxides and carbonates of Bi, Pb, Sr, Ca, and Cu. The powder was packed by mechanical agitation into a high purity Ag tube. The tube was deformed using a rolling mill which had the facility to do both flat as well as groove rolling. Fig. 1 shows a schematic representation of a single groove. The tube was deformed by passing it through the grooves and by reducing the gap between the rolls. To determine the optimal groove rolling conditions, appropriate sections were taken for flat rolling after the fourth, sixth, and eighth groove, respectively. The dimensions of the wires, all of which had rectangular crosssections, were 3.4 mm x 3.2 mm, 2.2 mm x 2.0 mm, and 1.7 mm x 1.5 mm, respectively. The wires were flat rolled to a final thickness of 250 mm. Tapes fabricated by this procedure have been labeled as GR4, GR6, and GR8, respectively. The widths of untreated GR4, GR6, and GR8 tapes were 4.72 mm, 3.68 mm, and 3.17 mm, respectively.

Short lengths of the BSCCO tapes were cut for thermomechanical treatment. The tapes were initially heat treated in air at 840 °C for 50 h; this treatment was then repeated at 100-h cycles. After each heat treatment cycle, the tapes were pressed at 1 GPa for 5 s. Following each thermomechanical treatment step, the tapes were characterized for their superconducting and microstructural properties. Critical current (I_c) was measured at 77 K and self field, using the standard four-point probe technique. The J_c was calculated by dividing the I_c by the cross-sectional area of the superconductor core. Phase development during the thermomechanical treatment was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). Evolution and amount of the 2223 phase was estimated from the XRD pattern of the tapes.

Specimens for TEM analysis were prepared from the transverse cross section of the tapes. The transverse sections were prepared by sandwiching and gluing the tapes together with epoxy. Two 1 mm x 2 mm x 3 mm sections were cut and polished to a thickness of 150 mm. The sections were then dimpled to a thickness of about 40 mm and ion milled with a 4 kV argon ion beam at an incident angle of 10-15°. TEM analysis was conducted with a JEOL-2000FX electron microscope at 200 kV. Misorientations of the grain boundaries were characterized by rotation axis and angle, which were determined by using the rotation matrix. The Kikuchi pattern of each grain was used in calculating the matrix. The beam and beam stopper directions were taken as the two fixed directions [9].

III. RESULTS AND DISCUSSION

The Ag clad BSCCO tapes have been fabricated by a modified PIT technique comprising of flat and groove rolling. Detailed stress and microstructural analysis were conducted to establish the optimal deformation conditions during groove rolling. Inadequate annealing conditions and high reduction ratios led to the rupture failure of the Ag sheath. It also led to the formation of microcracks in the superconductor core which ultimately affected the current transport properties of the tapes. Details of this study are provided in [3]. Short lengths of the Ag-clad BSCCO tapes (GR4, GR6, GR8) were subjected to a series of thermomechanical treatments, during which phase development in all of the tapes was monitored by XRD. The study revealed that during the thermal treatment, the partially reacted precursor powder consisting predominantly of 2212 and alkaline earth cuprates is slowly transformed to the 2223 phase. While a small amount of 2212 phase was still present, after 250 h of thermal treatment, the amount of textured 2223 phase formed was 88%. Backscattered electron images of the GR4 and GR6 tapes, after the final thermomechanical treatment step, are shown in Fig. 2. SEM and EDS analysis indicated the superconductor core to be predominantly dense and well textured 2223 grains. Secondary phases such as the Ca rich 2:1 (dark regions) and Pb rich 3221 (light regions) were observed but were present in only small amounts.

Fig. 3 illustrates the current transport properties of GR4, GR6, and GR8 tapes after each thermomechanical treatment step. In each case, J_c values after the initial 50 h of heat treatment were fairly low. This can be attributed to the low formation of 2223 and the frequent interruption of the grains by secondary phases. After 250 h of heat treatment and two rounds of pressing, the I_c values of the GR4, GR6, and GR8 tapes were 53, 37, and 21 A, respectively. This, as shown in Fig. 2, corresponds to a J_c of 13,000, 18,000, and 12,000 A cm^{-2}, respectively. The highest J_c was obtained in the tape that had been groove rolled to the sixth groove. The increase in current transport properties during thermomechanical treatment can be attributed to the increased amount and texturing of 2223 grains, the higher oxide core density, and the greater connectivity of grains. Measurement of the interface perimeter lengths on transverse cross sections of GR4, GR6, and

GR8 tapes gave values of 8.5 mm, 6.53 mm, 4.88 mm, respectively. This indicates that substantial improvement in current transport properties can be obtained by modifying the contact area between the Ag and the superconductor interface.

Most of the TEM analyses were conducted on the GR6 tapes and after the final heat treatment of 250 h. HREM was conducted on the transverse cross-section, in a region approximately 10 mm from the edge of the silver sheath. HREM study indicated that even after 250 h of heat treatment, polytypoids of 2212, as shown in Fig. 4, can be observed at the colony boundaries (CBs). Furthermore, intergrowths (1/2-1 unit cell) of 2212 phase were also observed within the 2223 phase. The GB, which had an 18° [010] tilt, consisted of the (1 0 18) GB plane of 2212 and (001) GB plane formed by 2223.

Preliminary studies have been conducted to study the effect of this GB on the SOP and J_c of the sample. The estimation is based on the relationship between SOP and the contribution of N_{Cu} (0) of copper atoms to the density of electron states at the Fermi-level in copper oxides [10]. A new model that gives the dependency of N_{Cu} (0) on the distance from the boundary has been used to characterize the GB [11]. The model is based on first-principle calculations that gives a relationship between N_{Cu} (0) and local configuration around the Cu atoms. The model has been successfully used to characterize strong and weakly coupled GBs in $YBa_2Cu_3O_{7-x}$ (YBCO) samples. Computer simulations were conducted on the basis of the model and a 152,000 atom fragment of the 18° [010] tilt GB. The results of the calculations for the above mentioned GB are shown in Fig. 5. The ratio of Cu atom contribution to the density of states at Fermi-level, near the GB [N_{Cu}^{GB} (0)] and in the bulk [N_{Cu}^{bulk} (0)], is plotted in Fig. 5, as a function of distance to the GB.

For comparison the N_{Cu} (0) behavior for a weakly coupled GB in YBCO, which had a J_c of 180 A cm^{-2}, is also shown in Fig. 5. The calculated results for the GB under consideration indicate that the layer of suppressed N_{Cu} (0) is quite small and narrow, in comparison to the YBCO sample. This suggests, that even though 2212 is present at the GB, the SOP is not suppressed noticeably and that the boundary is strongly coupled. This unique behavior may be obtained because the GB topology does not cause multiple breakdowns of the Cu-O bonds. Especially in the grain with the (001) GB plane the CuO_2 planes are parallel to the boundary and hence all the Cu-O bonds are preserved. Another reason could be that the Cu atoms of the other grain near the boundary are screened by oxygen atoms, and therefore the perturbations of their local electron states are very small.

TEM examination of the transverse cross section of the tape indicates that texturing is not perfect. Some of the colonies seem to form in certain preferred orientations to the Ag surface. As shown in Fig. 6 the angle in the pattern reflects the angle between the basal planes, also called the kink angle [12]. Because in the cross section of the tape, the basal planes of all colonies are perpendicular to the plane of the picture, the kink angle can be measured directly from high resolution TEM by using lattice fringes. However, only the tilt component of the total misorientation angle can be registered this way because the twist component does not add to the kink angle. Analysis of the kink angle indicates that CB1 is 15° [010] tilt grain boundary and CB2 is 18° [010] tilt grain boundary. Analysis of papers in the literature, describing high resolution microstructure of BSCCO tapes, revealed that most of the reported CBs have kink angles of either $18^\circ \pm 3^\circ$ or $30^\circ \pm 3^\circ$ [13]. In the recent paper by Yan et al., these kink angles are observed for 50% of the CB [14]. However the exact mechanism for the formation of these kink angles has not yet been established. They may form because of the existence of coincident site lattice (CSL) boundaries $\Sigma 24$ and $\Sigma 51$ for 2223. Another reason could be the formation of facets along low-index planes thus reducing the energy for kink-angle formation [15].

IV. CONCLUSIONS

Silver-clad BSCCO tapes of various dimensions were fabricated by groove and flat rolling. Detailed microstructural and phase development studies were conducted to optimize the deformation and thermomechanical treatment process. The highest J_c of 18,000 A cm^{-2} was achieved in Ag-clad BSCCO tape that had been groove rolled up to the sixth groove. Improvement in current transport properties can be attributed to the increased amount and texturing of 2223 grains and to the absence of microcracks. Colony boundaries at the superconductor-Ag interface were observed to form in certain preferred orientations. This can be attributed to the presence of coincident site lattices for 2223 or to the formation of facets along low index planes. Polytypoids of residual 2212 were also observed at the colony boundaries. The effects of this GB on the superconductor order parameter and J_c of the sample were also examined. The study revealed that the layer of suppressed N_{Cu} (0) is quite small and narrow, thus implying that the boundary is strongly coupled.

ACKNOWLEDGMENT

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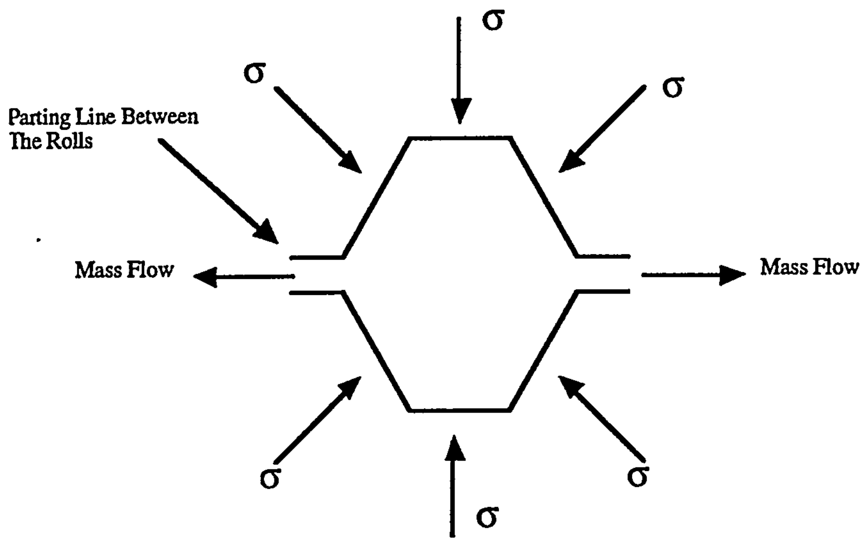

Fig. 1 Schematic representation of single groove, showing direction of stress and mass flow.

(a)

(b)

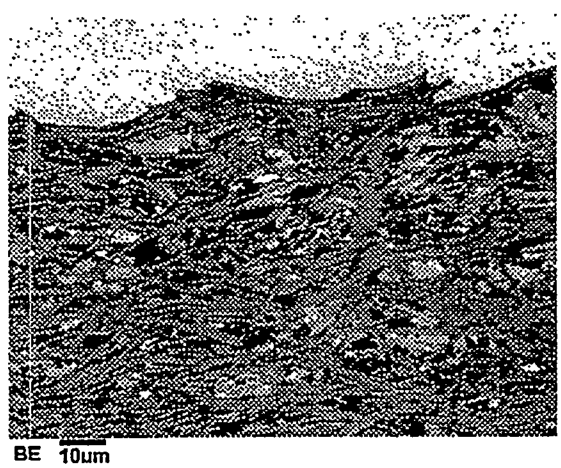

Fig. 2. Backscattered SEM photomicrographs of (a) GR6 and (b) GR 4 tape after 250 h of heat treatment and two rounds of pressing.

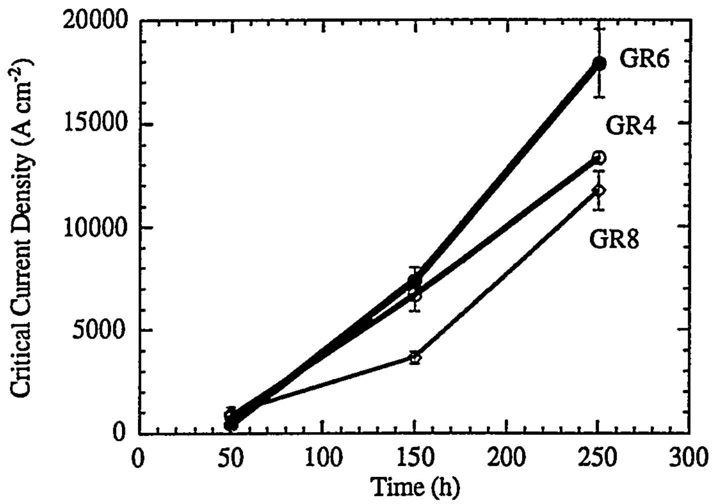

Fig. 3. Variation in current transport properties as a function of heat treatment time for GR4, GR6, and GR8 tapes.

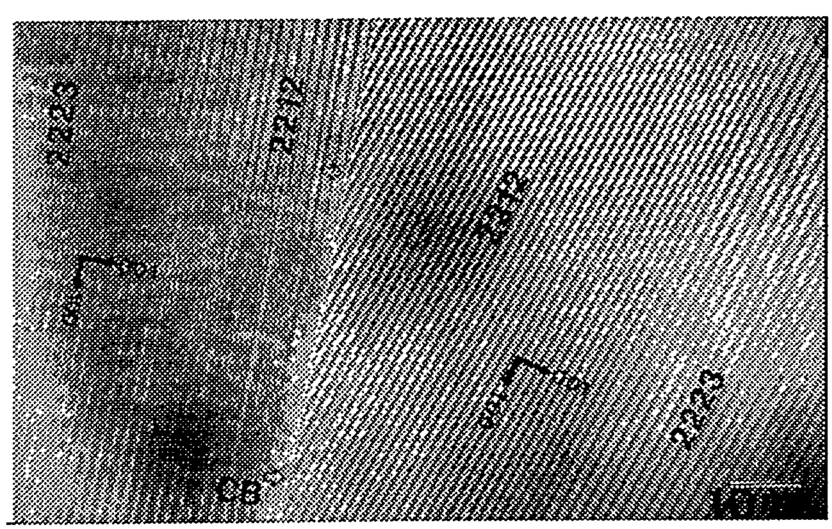

Fig. 4. HREM illustrating GB with 18° [010] tilt. Boundary consists of (1 0 18) GB plane of 2212 and (001) GB plane formed by 2223.

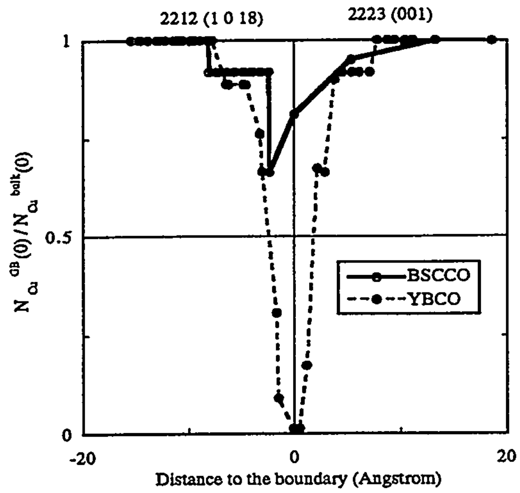

Fig. 5. Suppression of N_{Cu} (0) as a function of distance to grain boundary .

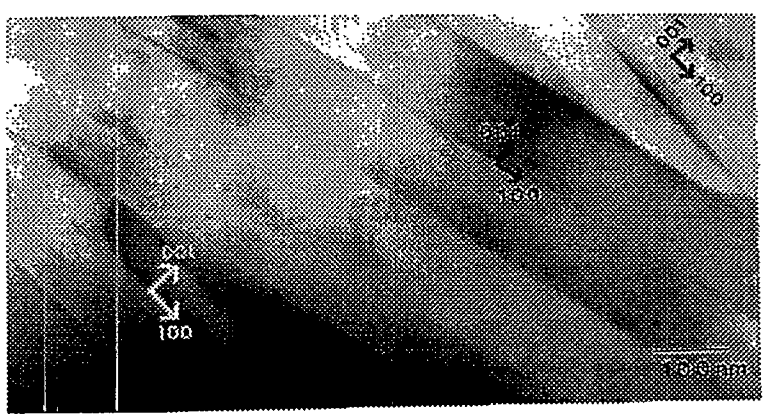

Fig. 6. Example of colonies that form preferred orientations to Ag surface. Analysis of kink angle indicated that the CB 1 is 15° [010] and CB2 is 18° [010] tilt GB