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QUANTITATIVE ANALYSIS OF THE EFFECTS OF STRAIN-STATE ON THE MICROSTRUCTURE AND J_c OF BSCCO TAPES

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Abstract

After considerable optimization efforts, conventional thermomechanical processing of long, high temperature superconductors has not produced critical current densities (J_c) adequate for most liquid nitrogen temperature applications. New approaches are needed to improve the J_c of superconducting tape produced by co-deforming a ductile silver sheath containing the superconducting oxide using the powder-in-tube process. This study investigates improvements in J_c generated by modifying the strain-state during rolling of silver-sheathed $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ (BSCCO-2223) tape using quantitative image analysis of the different phases. Pure compression and combined compression-shear loading was achieved by embedding BSCCO-2223 tapes at different locations within thick steel blocks. High hydrostatic compressive stress was imposed by confining the tape width. Tapes deformed with combined shear-compression exhibited measurably higher J_c values than tapes subjected to pure compression, but their microstructures showed little difference in the amount of non-conducting (including porosity) phase content. However, constraining the tape width resulted in the most significant increase in J_c which corresponded to a much lower porosity and non-conducting phase volume in the oxide near the tape edge.

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Introduction

Successful application of high temperature superconductors (HTS) requires the fabrication of long lengths of tapes possessing high critical current density, J_c [1-8]. The oxide-powder-in-tube (OPIT) method, which co-deforms a ductile silver sheath containing superconducting oxide into a long HTS tape through a series of mechanical and thermal processing steps, is a common technique utilizing conventional rolling. One of the most promising superconducting oxides at liquid nitrogen temperatures is lead-doped $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ (BSCCO-2223). The elongated orthorhombic lattice structure of BSCCO is highly anisotropic, both mechanically and electrically, so that deformation processing is used to crystallographically align (texture) the oxide grains. Rolling-induced deformation causes alignment of oxide grains with their c-axes perpendicular to the plane of the tape. The grain alignment results in enhanced current flow along the tape length. However, in spite of tremendous efforts by numerous researchers, the conventional process of iteratively rolling and sintering HTS tape has not yielded J_c values sufficient for most liquid nitrogen temperature applications.

Therefore, new deformation and sintering processing approaches to improve the J_c of BSCCO tapes must be developed and evaluated. Very high critical current density has been achieved in films by approaching a single crystal microstructure, including maximum grain alignment and minimum porosity in the oxide. After conventional rolling processes, only a fraction of the oxide cross-section carries high superconducting current as revealed by sectioning studies [2, 9-11]. In many cases the oxide microstructure is dense, elongated, and well-aligned only in the region near the Ag/BSCCO interface. This may be due to localized shear stresses that develop at the interface in conventionally rolled monofilament tape, or it may be due to the effects of silver diffusion into the oxide near the interface. In the case of a multifilament tape, conventional rolling creates a non-uniform stress state that leads to microstructural and property variations between filaments in different positions of the tape [1, 6].

Material modeling studies have predicted enhanced texture development by combined shear-compression rolling, in addition to the understandable reduction of porosity by high hydrostatic compression [12, 13].

In the present study, we utilize the stress and strain gradients that occur at different planes through the thickness of a steel block during small-draught rolling. Pure compressive deformation is generated at the mid-plane of a block, while a combination of compressive and shear stresses develops away from the mid-plane. By embedding monofilaments of silver-sheathed BSCCO-2223 tapes at different positions within a steel block, we can effectively vary the proportion of shear strain relative to compressive strain. Furthermore, by varying the degree of lateral confinement of an embedded tape, we can also examine the effect of compressive hydrostatic stress.

Finally, using digital image analysis of the microstructures of sintered superconducting tapes, we have attempted to correlate phase development and residual porosity with the applied deformation and, most importantly, the superconducting performance.

Experimental Procedures

Tape Preparation

A monofilament tape consisting of 28% volume $\text{Bi}_{1.9}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_{2.2}\text{Cu}_3\text{O}_{10+x}$ super-conducting oxide powder sheathed in 99.99% pure silver was fabricated using the OPIT process. The tube was first drawn to a 1 mm diameter wire and then rolled progressively to a uniform tape of 0.152 mm thickness by 2.5 mm width. The tape was cut into nine 5.5 cm lengths and given an initial heat treatment of 48 hours at approximately 830°C. De-sintering resulted in a 15% average increase in the tape thickness to 175 microns, but less than a 0.25% increase in the tape width.

Strain-State Modified Tape Rolling

After the initial heat treatment, individual tapes were inserted into thin (0.3 mm) slots machined along two thickness planes in four 10 cm long x 10 cm wide x 2.5 cm thick mild steel blocks. One of the slot positions was located in the center plane of the block thickness and the second slot was located in a plane midway between the center plane and one surface of the block. The two slot positions were offset to prevent interaction during rolling. The tapes were surrounded by steel shims to minimize void space and to provide constraint on the tape width; however, during block rolling the tapes were allowed to freely expand in length. To study the effects of transverse constraint on the tape width, several tapes were left unconfined along their width edges.

Three steel blocks containing width-confined tapes were reduced in thickness by 6%, 18%, and 27% using approximately 0.2% reductions per pass. One steel block containing a pair of unconfined-width tapes was also reduced by 18%. After block rolling, the tapes were removed from the steel blocks and given a second heat-treatment (including the undeformed control tape) identical to the initial heat treatment (48 h at 830°C). In addition, one of the nine starting tapes was not re-rolled, but was given the same secondary heat treatment as a control for critical current density (J_c) and strain measurements. The total heat treatment time was very short compared to typical final heat treatments ($\approx$ 200 hours) so that full processing was incomplete and a subsequent study could examine the effect of sintering time on phase development.

Tape Strain and J_c Measurements

Polished transverse cross-sections of each tape were prepared and examined by optical and scanning electron microscopy. Thickness, width, and area measurements of the oxide cores and the total (composite) tape were made from these observations and used to calculate deformation strains relative to the initially sintered tapes (micrometer measurements were found to be very unreliable because of non-uniform tape morphology). Superconducting performance was evaluated by averaging several measurements of the critical current, I_c , at a temperature of 75°K in self-magnetic field across 1 cm sections along the tape length with a standard four-probe technique [14]. The average oxide core cross-sectional area was then used to calculate the critical current density.

Quantitative Image Analysis

Microstructural features such as porosity and non-superconducting phases were documented using digital imaging and analyzed for correlation with the deformation and superconducting behaviors.

High resolution digital microscopy images of transverse sections of silver sheathed BSCCO tapes were acquired using a JEOL 6300 FX field emission SEM at 15 Kev in backscattered electron imaging (BEI) mode. Each image consisted of 1024 x 1024 pixels with 256 gray levels at 2000 magnification. Holes, secondary phases, superconductor and silver sheath were readily distinguishable in the BEI images as regions of black, dark to medium gray, light gray and white respectively. Image fields for porosity and secondary phase comparisons of plane-strain-edge-confined vs unconfined were taken near the corner edges of the transverse sections whereas the comparisons of secondary phase development of pure compression vs compression-shear loading were determined by images taken in the central region of the core. Image analysis was performed on a Power Macintosh computer using Prism image analysis software (Signal Analytics Corporation, Vienna, Va.). Prior to measurement, gray level images were segmented by brightness thresholding [15] into three phases: holes, secondary, and superconducting phases. Thresholds were set interactively by viewing the image and using a color overlay to show the result of adjusting for the range of gray values that best represented the phase of interest. The area of each feature within a particular phase was automatically measured and stored for subsequent data analysis. Four image fields were analyzed and averaged for each of the four experimental conditions described previously. Volume percent, the ratio of total area occupied by a given phase relative to a reference area representing the

entire core region bounded by the silver sheath, was automatically calculated using the image analysis software.

Results and Discussion

Figure 1 shows the total tape and the oxide core thickness strains of BSCCO/Ag tapes as functions of the shear condition and the block rolling reduction. The total tape thickness strain (true strain) was determined from the initial and final thickness of the entire composite tape (the oxide core plus the silver sheath), while the core thickness strains were determined from the initial and final thickness of the oxide core. It can be seen from Fig. 1 that the core thickness strains are larger than the total tape thickness strains by about a factor of two, and that the core and total tape thickness strains initially increase rapidly with increasing rolling reduction, but the rate of increase slows at larger rolling reductions ($> 20\%$). This is due to the fact that the oxide core is porous ($\geq 40\%$) after the first heat-treatment and readily densifies relative to the pore-free silver sheath upon initial rolling. After the oxide core reaches a high density with large block reductions, it becomes stiffer relative to the ductile silver sheath. Figure 1 also shows that much greater tape strains develop than the overall applied block strain. This is presumably caused by the strong mechanical properties of the hard steel block relative to the compliant superconducting tape. Additional experiments are necessary to investigate the effect of block material properties on the deformation response of embedded BSCCO-silver tapes.

Figure 2 shows the effect of shear stress on the compressive deformation, as measured by the transverse cross-section area strain (combined thickness and width strains). Interestingly, shear loading resulted in higher total tape and core area strains than with pure compression loading for a given amount of block strain. This indicates that the application of shear improves conventional deformation processing as has been predicted by polycrystalline deformation modeling studies of BSCCO [16]. These studies demonstrate that shear stress enhances the sliding of the plate-like BSCCO-2223 grains and thereby delays textural "lock-up" leading to premature fracture. It can also be seen from Fig. 2 that the effect of shear stress on the oxide core and total tape strains is more prominent for larger rolling reductions. This is because the shear stress increases with increasing rolling reduction and plays a more prominent role in assisting the deformation of the oxide core under larger rolling reductions.

Figure 1 Total (composite) tape and core (oxide) thickness strains (true) versus applied block thickness strain for embedded BSCCO/Ag tapes.

Figure 2 Total tape and core area strains versus relative shear stress state.

The effects of edge confinement on total tape and oxide core deformation are shown in Figs. 3a-c. Figure 3a shows that width strain was largely suppressed, but not completely eliminated in the edge confined tapes. However, the difference between the core and total tape width strains was typically low ($< 10\%$) for these tapes. In contrast, the oxide in the unconfined tape clearly did not co-deform with the highly ductile silver sheath in the width direction. Total tape width strains were approximately three times the core width strains in these unconfined tapes, indicating extensive transverse flow of the silver. This reflects the fact that the Ag sheath is very soft and exhibits high plasticity, while the oxide core exhibits relatively low plasticity typical of intermetallics. Figure 3b shows that the oxide core thickness strain is approximately twice the total tape thickness strain and is largely unaffected by the confinement conditions. Figure 3c shows that the edge confinement does not have a significant effect on the core area strain either. These observations are important for interpreting differences in measured J_c performance and microstructure development discussed below.

The effects of shear stress and edge confinement on the critical current density, J_c , performance of BSCCO/Ag tapes are demonstrated in Figs. 4a and 4b. Note that the control tape without secondary deformation exhibited a typically low J_c of only 600 A/cm^2 after the second heat treatment, indicating that secondary deformation after heat treatment is essential to obtain proper re-densification, reaction, and microstructural development for good superconducting performance. It is obvious from Fig. 4 that for the same core thickness and area strain, the tapes subjected to high shear stress have the highest J_c values, while the unconfined tapes have the lowest J_c values. This supports the concept that high shear-stress can increase the texture of BSCCO core [16], and thereby improve J_c substantially. Although the laboratory scale experimental technique presented in this work may not be scaled up for large scale commercial tape processing, the concepts proven here can be modified and developed for successful commercial applications. For example, it has been reported that shear stress in rolling can also be induced by differential speed rolling, *i.e.* using different speeds for the top and bottom work rolls [17, 18]. The differential speed rolling technique may have the potential to produce higher texture and J_c in rolled superconductor tapes than does conventional rolling.

Figure 3 The effect of tape edge confinement on the deformation of BSCCO tapes. a) Width strains versus total tape thickness strain; b) Core thickness strains versus total tape thickness strain; c) Core area strains versus total tape thickness strain.

Figure 5 shows the core at the edge of the unconfined and edge-confined tapes. Notice that the unconfined tape (Fig. 5A) contains a number of relatively large pores while the pores of the confined tape (Fig. 5B) are fewer and smaller. The volume percentage of pores in the unconfined tapes were 9% compared with the confined tapes of 1.3%. There was also a significant increase in the amount of secondary phase in the unconfined tapes (Table 1).

Figure 4 Critical current density versus: a) core thickness strain; b) core area strain.

When considered together, the pores and secondary phases combined, the total amount of non-superconducting material was approximately a factor of two greater near the edges of unconfined tapes. Thus, it is reasonable to conclude that the major reason for the lower J_c in the unconfined tapes is due to the high porosity near the oxide core edges of the unconfined tapes.

An explanation for the measurably higher J_c values of combined compression-shear loading compared with pure compression was not evident from the quantitative image analysis of the different phases. Analysis was performed on the central region of the tape. Figure 6 show representative SEM micrographs of pure compression (6A) and combined compression-shear (6B) strain samples used in this analysis. In both samples, there was an equally small amount porosity of about 2% (Table I). The amount of secondary phase was 29% for the pure compression samples and 27% for the shear strain samples. Analysis was also performed at the edge regions. The results showed lower total non-superconducting phases for both pure compression (24%) and compression-shear strain samples (22%), but it is unlikely that the differences in current density could be attributed to such small differences in volume percentage of pores or secondary phase alone. Analyses of the size of the total non-superconducting phase for the two samples showed them to be essentially identical. For porosity areas in the range of 0.5 to 70 μm^2 , the results were $4.8 \pm 8.7 \mu\text{m}^2$ for the pure compression and $5.1 \pm 8.7 \mu\text{m}^2$ for the compression-shear tapes. Analyses of the orientation of the porosity did show a tighter distribution along the narrow axis of the tape for the combined

Figure 5 - SEM micrographs of BSCCO oxide cores at the edge regions of edge unconfined (5A) and confined (5B) tapes.

Figure 6 SEM micrographs of BSCCO oxide cores at the central regions of pure compression (6A) and combined compression-shear loaded tapes.

Table I Volume percentage of holes and secondary phase.

Samples	Volume percent holes ± 1 Std.	Volume percent secondary phase ± 1 Std.	Volume percent total non-conducting phase ± 1 Std.
without edge confinement	9.0 ± 3.1	14.1 ± 1.1	22.5 ± 4.3
with edge confinement	1.1 ± 0.2	08.9 ± 1.2	10.2 ± 1.6
pure compression	1.8 ± 1.2	26.8 ± 0.2	28.6 ± 0.8
combined compression-shear	1.9 ± 0.6	24.1 ± 2.7	26.0 ± 0.8

compression-shear tapes (Fig. 7). This would suggest a more uniform alignment or Crystal texture of the superconductor that would result in better J_c .

Figure 7 Rose distribution plots of porosity orientation in pure compression (7A) and combined compression-shear strain BSCCO tapes (7B).

When the edges of a tape are confined, hydrostatic compressive stress exists at the core edge and effectively densify the core edge during the rolling. However, the core edges of an unconfined tape flow almost freely in the width direction during rolling, and the lack of hydrostatic stress results in more and large pores. These pores not only reduce the current-carrying area directly, but also slow the sintering kinetics during subsequent heat-treatment, both of which can degrade J_c performance. BSCCO core edges have been shown to achieve higher texture and to carry higher current density [2, 19, 20]. It has been reported [19, 20] that the J_c in the core edge is two to three times higher than that in the middle portion of the core. Therefore, the high porosity in the unconfined tapes degrade the portion of the core that otherwise should carry the highest current density. This results in significantly lower overall J_c in the unconfined tapes.

Different schemes may be used to increase edge-confinement. Replacing the soft pure silver sheath material with a harder silver alloy should not only increase the density and smoothness of the core/silver interface, but should also reduce core extrusion into the silver sheath in the thickness direction, both of which are predicted to improve the J_c of the tape. Another viable method for constraining lateral deformation of the superconducting tape is to increase lateral roll friction.

Finally, it should be noted that J_c values resulting from these experiments were relatively low compared to the highest values reported in the literature. Obtaining the best J_c performance was not the primary objective of this work. The relatively low J_c values were anticipated due to the short final heat treatment. Improvements can be made by optimizing the thermo-mechanical processing treatment. Nevertheless, significant effects of stress state on the deformation and J_c of BSCCO tapes have been adequately demonstrated.

Conclusions

Several conclusions can be drawn from this experimental study. First, thick block rolling produces non-uniform deformation, which leads to different strain states for HTS tapes embedded in different positions of the block. These same gradients must be considered when conventionally rolling multifilament HTS tapes. Second, high shear stress assists the deformation of BSCCO superconductor tapes and their cores. It increases the strain in the core thickness and cross-section area, and also improves the critical current density of the superconducting core, compared to pure compression loading. Third, edge-confinement does not have a significant effect on the core thickness and cross-section area strains; however, confinement can significantly reduce porosity near the core edge and thereby lead to higher J_c .

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