Grain boundary studies of high-temperature superconducting materials using electron backscatter Kikuchi diffraction

A. Goyal*, E.D. Specht, Z.L. Wang¹, D.M. Kroeger

Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6116, USA

Received 12 August 1996; accepted 2 December 1996

Abstract

Grain orientation and grain boundary misorientation distributions in high critical current density, high-temperature superconductors were determined using electron backscatter Kikuchi diffraction. It is found that depending on the type of superconductor and the processing method used to fabricate it, there exist different scales of biaxial texture from no biaxial texture, local biaxial texture, to complete biaxial texture. Experimentally obtained grain boundary misorientation distributions (GBMDs) were found to be skewed significantly to low angles in comparison to what is expected on the basis of macroscopic texture alone, suggesting that minimization of energy may be a driving force during the processing of high critical current density materials. In addition, a higher than expected fraction of coincident-site lattice boundaries is observed. Examination of maps of grain boundary misorientations in spatially correlated grains, i.e. the grain boundary mesotexture, suggests the presence of percolative paths of high critical current density. A combination of orientation measurements, theoretical modeling of GBMDs and modeling of percolative current flow through an assemblage of grain boundaries is performed to gain an insight into the important microstructural features dictating the transport properties of high-temperature superconductors. It is found that maximization of low energy, in particular, low-angle boundaries, is essential for higher critical currents. The combination of experimental and analytical techniques employed are applicable to other materials where physical properties are dominated by intergranular characteristics.

1. Introduction

Practical applications of high-temperature superconductors require fabrication of these brittle, ceramic materials into flexible conductors or wires for most large-scale bulk applications like transmission lines, motors, transformers, superconducting magnetic energy storage systems, magnetic resonance systems, etc. [1]. A successful method to form conductors has been to fabricate thick films of these materials on flexible silver substrates or by using the oxide-powder-in-tube (OPIT) method [2]. In the OPIT process oxide precursor powder is inserted into a silver tube, which is then thermomechanically drawn and rolled into conductor form followed by appropriate heat treatments to form the superconducting phase. While conductors can
be made using these techniques with all families of high-$T_c$ materials, the superconducting interior has a critical current density dependent on the texture and the properties of the grain boundary assemblages formed. So far, the OPIT process has only yielded high critical current densities, $J_c$, with the (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (Bi-2223) compound. The thick film process has primarily been successful with (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$ (Bi-2212) and TlBa$_2$Ca$_2$Cu$_3$O$_x$ (Tl-1223) materials. No thermomechanical process has so far yielded high critical currents for the YBa$_2$Cu$_3$O$_{7-x}$ (Y-123) compound. Moreover, even in the best conductors of Bi-2223, Bi-2212 and Tl-1223 the transport critical current density is only $\frac{1}{10}$ of that achieved in single crystal, epitaxial films of the same materials. Furthermore, magnetically determined intragranular critical current density is close to that of epitaxial films, suggesting that the $J_c$ of these conductors is limited by extrinsic defects like grain boundaries.

The various compounds of high-$T_c$ materials not only have widely different transition temperatures ($T_c$) but also significantly different irreversibility fields ($B_{irr}(T)$) which define the useful range of fields and temperatures for which the materials have high critical current densities in the absence of weak-links. Based on such considerations the Y-123 is the most desirable superconducting compound for operations at 77 K in moderate to high magnetic fields. In order to fabricate conductors of Y-123 and to optimize the properties of Bi-based and Tl-based materials, it is necessary to obtain a better understanding and control of extrinsic defects which dictate the transport properties of these conductors.

The earliest studies of critical current density $J_c$ in high-$T_c$ oxide superconductors revealed that $J_c$ for a polycrystalline specimen is much lower than intragranular $J_c$. These results indicate that for most grain boundaries $J_c(gb)$, the critical current density for transmission through the boundary, is lower and decreases much more rapidly with field than intragranular $J_c$. This "weak-link" behavior, which is in contrast to the behavior of low-temperature metal superconductors, is attributed to the likelihood that the defect structure and strain associated with the grain boundary are comparable in extent to the superconducting coherence length, which in high-temperature superconductors is highly anisotropic and smaller than in metal superconductors. The effects of grain boundary characteristics on current transmission across the boundary have been studied most extensively for Y-123. For clean, stoichiometric grain boundaries, $J_c(gb)$, appears to be determined primarily by grain boundary misorientation. The dependence of $J_c(gb)$ on misorientation angle has been determined in (Y123) for grain boundary types which can be formed in epitaxial films on bicrystal substrates. These include [0 0 1] tilt, [1 0 0] tilt, and [1 0 0] twist boundaries [3]. Grain boundaries with misorientation angles larger than about 10° were found to be weak-links. Recently, the Dimos experiment has been extended to artificially fabricated [0 0 1] tilt bicrystals in Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_8$ [4], Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_x$ [5], Tl-1223 [6] and Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ [5]. In each case it was found that, as in Y123, $J_c$ depends strongly on grain boundary misorientation angle. Although no measurements have been made on the Bi-2223, data on current transmission across artificially fabricated grain boundaries in Bi-2212 indicate that most large-angle [0 0 1] tilt [5] and twist [7, 8] boundaries are weak links, with the exception of some coincident site lattice (CSL) related boundaries [7, 8]. It is likely that the variation in $J_c$ with grain boundary misorientation in Bi-2212 and Bi-2223 is similar to that observed in the well-characterized cases of Y123 and Tl-based superconductors.

In order to determine what makes conductors of Bi-2223 and 2212 and Tl-1223 "tick", studies of grain boundary networks in these materials and how they effect and control percolation of supercurrent were studied using electron backscatter Kikuchi diffraction (BKD). The various types of superconductors were found to have distinct macroscopic and local textures and microstructures. Grain boundary misorientation distributions (GBMD) were highly dependent on the compound and the method used for fabrication. Comparison of experimentally obtained GMBDs to theoretically expected GBMDs based on texture alone, indicated that in each case the population of low-energy boundaries was much higher than expected. Modeling of current flow for the various
types of microstructures was performed to determine optimum microstructures and guide processing. Results of this study have led to the development of a new method to form macroscopically, biaxially textured superconductors. The particular methods used to characterize and model microstructures are equally applicable to other materials and therefore have broad applications.

2. Experimental

2.1. Bi-2223 conductors

High critical current density conductors were obtained from American Superconductor Corporation. Multifilamentary Bi-2223 conductors for microstructural analysis were prepared using standard oxide powder-in-tube techniques [9]. Oxide powders with an initial metals ratio of $1.7 : 0.4 : 1.9 : 2.1 : 3.1$ (Bi : Pb : Sr : Ca : Cu) were used. These powders were packed into Ag billets, which were subsequently deformed to hexagonal rods using extrusion, swaging and drawing techniques. Nineteen of these hexagonal rods were bundled together and inserted into a Ag tube. The resulting composite bundle was drawn and then rolled to a tape. An iterative thermomechanical process was used to optimize the superconducting properties of the tape. Heat treatments were performed between 800–830°C in 0.0075 atm $O_2$, the thermodynamic stability field of the Bi-2223 phase. Rolling was used to densify the tape in between heat treatments. Fully processed tapes are near 100% dense and have a transport critical current density in the range of $10 - 20 \times 10^3$ A/cm$^2$ at 77 K in self-field using a 1 $\mu$V/cm criterion. Individual filaments in the tape are about 20 $\mu$m thick and 200 $\mu$m wide. To facilitate microstructural analysis, Ag was chemically etched from one side to reveal the superconductor. The etching procedure does not interact with the superconductor. Fig. 1 shows

![SEM image of the Bi-2223 surface of a filament revealed by etching away the silver from a multifilamentary powder-in-tube specimen.](image)

(b) Grain boundaries are clearly visible, permitting determinations by EBSP of the orientations of contiguous grains.
A. Goyal et al. / Ultramicroscopy 67 (1997) 35–57

Fig. 2. Typical backscatter diffraction pattern from a grain of Bi-2223. Since the sample is c-axis textured the region near the (0 0 1) pole is seen.

Fig. 3. (a) (0 0 1) pole figure from a region in a Bi-2223 sample. Data was obtained from 113 spatially correlated grains; (b) (0 0 1) pole figure from the same region.

a scanning electron microscope (SEM) image of a filament surface. Most grain boundaries are clearly visible, permitting the determination of electron backscatter diffraction patterns from adjacent grains. Diffraction patterns were obtained for all of the grains which could be distinguished in several small areas containing from 15 to ~ 100 contiguous grains [10]. Since the surface of the sample is not flat, good patterns are not obtained at most locations. Manual location of the bands was found to be necessary to obtain accurate indexing of the patterns.

2.2. Bi-2212 thick films

The highest critical current density films of this compound made by Kumakura et al. at the National Research Institute for Metals, Japan were examined [11]. Experimental details of film fabrication have been reported by them [11].

2.3. Tl-1223 thick films

The highest critical current density films made by Deluca et al. [12] at General Electric Corporation
were examined. Experimental details of film fabrication have been reported by them. Briefly, precursor materials comprising of \(\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x\) are spray deposited onto a polycrystalline yttria-stabilized-zirconia (YSZ) substrate followed by vapor-phase incorporation of Ti in a two-zone Ti-reactor.

2.4. BKD data analysis

Data were obtained on various scanning electron microscopes (SEMs), a Cambridge 800 SEM fitted with a fibre optically coupled silicon intensified target camera (SIT) and a Philips XL30 Field-Emission SEM fitted with a fiber optically coupled SIT. Since all the materials examined were strongly \(\alpha\)-axis textured, the dominant pole in the diffraction pattern exhibited 4-fold symmetry and was indexed as the \([0\,0\,1]\) pole of the approximately tetragonal subcells. Fig. 2 shows a typical backscatter diffraction pattern from Bi-2223. From the indexed diffraction pattern, the absolute orientation of a grain was determined. Grain boundary misorientation between two contiguous grains A1 and A2, were calculated using Bollman's theory, \(M_{12} = A_1^{-1}A_2\) [13]. Depending on the crystal symmetry, the angle/axis of misorientations has many symmetrically equivalent forms (24 for cubic, 8 for tetragonal, etc.); and the variant containing the smallest positive misorientation angle was chosen as the description of the disorientation.

3. Results and discussion

3.1. Bi-based materials

3.1.1. Bi-2223

Fig. 3a and Fig. 3b summarize orientation measurements from 113 spatially correlated grains of Bi-2223. As indicated in the \((0\,0\,1)\) pole figure shown in Fig. 3a, excellent \(\alpha\)-axis texture exists. However no in-plane texture is observed as illustrated by the pole figure shown in Fig. 3b. Fig. 4a shows the proportion of small-angle and coincident-site lattice boundaries found in this area containing 113 grains and resulting in 227 identifiable boundaries. More than 40% of the boundaries are \(\Sigma\) 1 boundaries, i.e., have misorientation angles less than 15° and 30% of the boundaries have misorientations less than 10°. Small-angle boundaries have low energies and can be expected to be less detrimental to \(J_c\) than high-angle boundaries. In addition, 8% of the boundaries were found to be within the Brandon criterion for CSLs larger than 1 and less than 50 and with rotation axis \([0\,0\,1]\). The boundaries were classified as low sigma if the composite axis/angle deviation from the exact sigma orientation was within the Brandon criterion [14]. The deviations were calculated using a method discussed by Bollman [13] and Zhu et al. [15]. However, the properties and therefore the importance of coincidence site lattice (CSL) boundaries have not been determined, although there are indications that some CSL boundaries may be better than other large-angle boundaries [7, 8]. The data in Fig. 4a suggests that their numbers may be only slightly enhanced. Fig. 4b shows the frequency of CSL boundaries with the \(\Sigma\) less than 50.
The large fraction of low-angle grain boundaries suggests that percolative paths for strongly linked flow may exist. The examination of maps of misorientation angles over small areas indicates that two-dimensional percolative paths among grains at the Ag/superconductor interface can indeed be found. Fig. 5 shows the spatial distribution of grain boundaries in a region of the BSCCO tape. Small-angle boundaries are marked by dashed lines, solid lines designate large-angle boundaries and dot–dash lines indicate those boundaries that are within the Brandon criterion for a CSL. Many small-angle boundaries are present in this region. Percolative paths consisting of low-angle boundaries can easily be traced through the microstructure from the bottom left to the top right in Fig. 5. Since the c-axis are not perfectly aligned, most boundaries have a mixed character, i.e. have both tilt and twist components. Mixed boundaries which have a significant c-axis misalignment component and still have a small, absolute misorientation angle (in other words, have small basal plane misorientations), provide opportunities for the current to percolate in the thickness direction of the tape,
assuring three-dimensional current flow. An example of such a boundary is at the top left corner of Fig. 5. Such a mechanism for three-dimensional current flow is important since c-axis conduction is very limited in the Bi-based materials due to their highly anisotropic crystal structure [16, 17].

In addition, it is important to note that the samples contain many "bent" grains. By moving the electron probe within grains which morphologically appear “bent” in the SEM image, it is found that in many such grains the (0 0 1) pole in the EBSP pattern changes continuously and not abruptly. This indicates that the bent grains contain a series of boundaries which accommodate the change in orientation without the presence of any large-angle boundary. It is surprising to find that such low-angle boundaries are not replaced by a high-angle boundary after the final extended high-temperature anneal that is given to the sample, i.e., the typical polygonization process observed in metals does not occur. Also, recent nanoindentation studies of Bi-2212 and Bi-2223 powder-in-tube samples reveal that these materials possess a unique deformation behavior [18]. This is dominated by extensive cleavage on (0 0 1) planes at small applied loads. Once cleaved into thin sheets, individual sheets are highly flexible, and their deformation characteristics are similar to those observed for mica [18]. The typical deformation processing schedule that is normally used to fabricate these tapes can be expected to result in numerous bent grains. Such bent grains can easily be found in metallographic examination of transverse cross-sections of these tapes. If many such bent grains accommodate the change in orientation comprising the bend by a series of small-angle boundaries as observed here, then they provide an important mechanism for current flow between c-axis misaligned grains and further ensure three-dimensional current flow in the tapes.

3.1.2. Bi-2212

Thick films of Bi-2212 show a macroscopic texture similar to that of Bi-2223; however, there are differences in the GBMDs. Data were collected from many spatially correlated grains resulting in 300 grain boundaries. The total percentage of small-angle boundaries was found to be 33%. The percentage of CSL boundaries larger than 1 and less than 50 was found to be 25%, significantly higher than that observed in Bi-2223. Fig. 6 shows the population of CSLs observed in the sample. A higher population of CSLs in this material is consistent with the significantly larger amounts of liquid phases present during the processing of this material compared to that of Bi-2212.

Some samples of Bi-2212 were also found to be flat enough to perform orientation imaging (OIM) scans. Fig. 7a and Fig. 7b show OIM scans from a region of the film ~ 400 µm x 140 µm. Data were taken on a hexagonal grid of 2 µm spacing. Two sets of grain boundaries are drawn, the thinner boundaries indicate misorientations greater than 5° and less than 15°. The thick boundaries indicate misorientations larger than 15°. In Fig. 7a, a given color represents percolative regions within 2°. Fig. 7b shows the same region with a given color now representing percolative regions within 15°. Clearly some evidence of “local” biaxial texture is observed.

3.1.3. Expected GBMDS as a function of c-axis texture in Bi-2223 and Bi-2212

Computer simulation of a model polycrystal was performed by generating a set of 200 grains, the crystallographic orientations of which were described using Euler angles \( \phi_1, \phi_2, \phi_3 \) [19]. These Euler angles define a rotation matrix \( g \) which defines the orientation of a crystallite in the model polycrystal with respect to the specimen or global coordinate system. The notation similar to that defined by Bunge [20] was used. Each grain has a random orientation in relation to a global polycrystal basis \( \{e_1, e_2, e_3\} \). There is linear dependence between the crystal coordinate basis, \( C \) and basis \( G \); \( C = g \cdot G \), where \( g \) is an appropriate orthogonal transformation matrix determining the orientation of the crystal in the global basis \( G \). The matrix \( g \), determined from the Euler angles describes three successive rotations \( R \), which describe the final orientation of the crystal coordinate system, \( C \), with respect to the sample coordinate system \( G \). If two grains 1 and 2 have orientations \( g_1 \) and \( g_2 \), respectively, then their mutual misorientation angle is described by the rotation matrix \( g_{12} = g_1^{-1}g_2 \). The geometrical
Fig. 7. OIM images from a region in a Bi-2212 film of size ~ 400 µm × 140 µm. Data was taken on a hexagonal grid of 2 µm spacing. Two sets of grain boundaries are drawn, the thinner boundaries indicate misorientations greater than 5° and less than 15°. The thick boundaries indicate misorientations larger than 15°. In (a) a given color represents percolative regions within 2°. (b) shows the same region with a given color now representing percolative regions within 15°.
Characteristics of the boundary, i.e., the angle and axis of misorientation (the so-called disorientation), is extracted from the properties of the misorientation matrix.

Computer simulation of a random distribution of grain boundaries was performed by randomly assigning three Euler angles, in the ranges specified above, to each grain using a standard random number generator, and then determining misorientations of all possible grain boundaries that can be formed from the set. Since 200 grains were used, this results in ~ 20,000 grain boundaries. Fig. 8a shows the distribution of misorientation angles obtained from the simulation of a randomly oriented cubic polycrystal using this technique. The shape of this histogram is in good agreement with theoretical estimates of Mackenzie [21]. The fraction of grain boundaries with misorientations less than a given angle can be obtained by integrating and

![Fig. 8](image1.png)

Fig. 8. (a) Distribution of misorientation angles for the 20,000 "grain boundaries" which could be formed among 200 randomly oriented grains in a cubic material. The shape of the histogram agrees well with the calculated curve of Mackenzie [23]; (b) Fraction of misorientation angles less than Θ as a function of Θ, obtained from 20,000 simulated grain boundaries for cubic, tetragonal and orthorhombic symmetries.

![Fig. 9](image2.png)

Fig. 9. The effect of macroscopic c-axis texture on the misorientation angle distribution from simulations for tetragonal symmetry. In randomly selecting the 200 grain set from which grain boundaries were formed, deviations of the c-axes from perpendicular to the sample plane were restricted as indicated.

![Fig. 10](image3.png)

Fig. 10. Calculated (a) in-plane and (b) out-of-plane $J_c$ normalized to intragranular $J_c$ as a function of c-axis texture. An optimum c-axis FWHM exists for a given θc, where the $J_c$ begins to drop off.
normalizing Fig. 8a, and is shown in Fig. 8b (solid curve). Similar curves are also shown for tetragonal and orthorhombic materials. With decrease in crystalline symmetry, the fraction of low-angle boundaries decreases as expected. Since the simulated polycrystal is random, in each case, the population of small-angle boundaries is small.

The effect of texture was studied by restricting the values of Euler angles to certain specific ranges. For example, to study the effect of c-axis texture, only the value of φ was restricted to various values. In order to study the effect of biaxial texture, values of only two Euler angles φ₁, φ need to be restricted when φ is small. Fig. 9 shows the effect of macroscopic c-axis texture on the misorientation angle distribution for tetragonal materials. The fraction of misorientation angles less than an angle φ is plotted for cases in which the c-axis of the grains were restricted to ranges of 10°, 20°, 30°, etc., and the a-axis are random and not restricted. The straight line denotes what would be expected for perfect c-axis texture. It is evident from the figure that the fraction of small-angle boundaries increases with better c-axis texture. The number of small-angle boundaries increases as the range of variation of the c-axis orientation is decreased. For perfect c-axis alignment, 22.2% of boundaries would have misorientation angles less than 10°. Bi-2223 powder-in-tube conductors typically have c-axis rocking curves with full-width-at-half-maximum ~15–20°, suggesting that the 10° or 20° curves in Fig. 9 may apply to them.

3.1.4. Effect of c-axis texture and dimensionality on critical current density

For a tetragonal material with perfect c-axis alignment, there are no c-axis tilted grains to carry the current; hence, transport can be expected to be...
two-dimensional, with a bond percolation threshold of 50% for an FCC lattice [22]. Even for the most favorable 2D case of a hexagonal lattice, the percolation threshold is 35%, so the material is near or below the percolation threshold and high-$J_c$ is not possible. The situation is at the other extreme for a completely untextured material. Current flow is truly three-dimensional, so percolation will occur when only 12% of the grain boundaries are conducting (if the grains were arranged in a FCC lattice). However, for a randomly oriented tetragonal material, only 3% of the grain boundaries have misorientations below a critical misorientation angle $\theta_c$ of 10°, and so current cannot flow through low-angle boundaries in this limit either. This suggests that there exists a $c$-axis texture which lies between these two limits for which current flow is optimized. A numerical model addressing this problem was developed by Specht et al. [23]. Fig. 10 summarizes the results of the calculations and show the in-plane and out-of-plane $J_c$ normalized to the intragranular $J_c$ as a function of $c$-axis full-width-half-maximum (FWHM). An optimum $c$-axis FWHM exists for a given $\theta_c$. The effect of a different critical misorientation angle, $\theta_c$, above which $J_c$ is low, is also shown in Fig. 10. In general, with increase in $\theta_c$, the optimum $c$-axis alignment increases to higher FWHM. However, it is likely that $\theta_c$ for bi-based materials will be close to 10° as is the case with other high-$T_c$ materials.

In an effort to improve the properties of Bi-2223 conductors, processing was aimed at obtaining conductors with better $c$-axis alignments. Fig. 11 shows an SEM image of a region of tape examined. Color-coded grain boundaries are superimposed on the micrograph. Red denotes high-angle boundaries, green low-angle boundaries, dashed red lines indicate boundaries within the Brandon criterion for a CSL, and dashed lines with a dot indicate those boundaries which are within 1° of a CSL boundary. Fig. 12a shows the statistics for grain boundaries in this region and Fig. 12b shows the frequency of CSL boundaries. Again a very high fraction of low-angle boundaries is found. The $c$-axis alignment of this tape was $\sim 12°$, much sharper than results of the tape presented earlier. This appears to significantly increase the fraction of CSL boundaries. Similar populations of low-angle boundaries are found as presented earlier. Further increase in the properties of these materials will occur by better control of the processing to obtain materials with optimum microstructures.

3.2. $Tl$-1223

We have reported in the past that thick films of $Tl$-1223 are composed of "colonies" of locally bi-axially aligned grains [24]. All the colonies are uniaxially aligned with respect to their $c$-axis, which is also perpendicular to the polycrystalline YSZ substrate on which the films are grown. However, little or no in-plane texture is observed between the colonies. Fig. 13 shows a typical microstructure of the films. Fig. 14 shows the typical grain orientation structure and texture within...
a colony as determined by electron backscatter Kikuchi diffraction [25]. Fig. 14 was obtained by moving the electron beam continuously across the sample in straight lines while recording the instantaneous backscatter diffraction pattern. Post processing of the data were then performed to locate the position and nature of the grain boundaries. Since the c-axis of all the grains in the film is aligned perpendicular to the film, grain orientations in the tetragonal Tl-1223 film can be represented by a single arrow indicating the location of the a-axis. Arrows are placed at the location of the grain boundary by projecting the a-axis of the grain on to the substrate surface (i.e. the R–T plane). The arrow represents the orientation of the grain to the right of the boundary. During the measurement the substrate sides were aligned along parallel and perpendicular to the specimen coordinate system and correspond to the R and T directions. Due to the four-fold symmetry for the tetragonal structure about the c-axis, the angle in the R–T plane was chosen to lie within the first quadrant, i.e. between 0–90°. As shown in Fig. 14b, colonies are comprised of well-aligned grains. A (1 0 0) pole figure
The presence of a single colony of aligned grains is evident. Calculation of grain boundary misorientations between neighboring grains in this $40 \times 120 (\mu m)^2$ region shows that 91% of the boundaries have misorientations less than 15° and 80% less than 10°. X-ray phi scans obtained from a single colony give rise to a single peak for a 90° rotation of the sample about the c-axis. The FWHM of the peak then represents the “spread” in orientations within a colony. The distance between two adjacent arrows is representative of the grain size and on average is in the range of 5–10 μm.

The structure of typical colony intersections are indicated in Fig. 15 and Fig. 16. Fig. 15a shows the (1 0 0) pole figure of a region comprising two colonies where the average misorientation between the colonies is large. Fig. 15b shows the grain orientation structure at the colony intersection. The population of boundaries in this region with misorientation angles less than 15° is 83% and less than 10° is 75%. This is not surprising because most grain boundaries within a colony are small-angle and high-angle boundaries are formed primarily at the colony intersection. What is more interesting is that 54% of the high-angle boundaries at the colony intersection are within the Brandon criterion [12] for CSL boundaries with Σ < 50.

Fig. 16a shows the (1 0 0) pole figure of another region comprising two colonies. While the average misorientation between the two colonies in this area is also large (> 15°), the misorientation is accommodated by a continuous change in orientation across the intersection as shown in Fig. 16b. The population of boundaries in this region with misorientation angles less than 15° is 63% and less than 10° is 51%. In addition 14% of the high-angle boundaries are within the Brandon criterion for CSL boundaries with Σ < 50. Regions as large as $1000 \times 500 (\mu m)^2$ have been mapped using this technique and over 1500 grain boundaries have been characterized. In general, a large fraction of low-angle boundaries is found (~ 60% on average). Larger regions are more complex and contain a mixture of the three cases shown in Figs. 14–16. Fig. 17a and Fig. 17b show the grain orientations in two 1 mm regions of a film. Fig. 18a and Fig. 18b shows the corresponding (1 0 0) pole

![Fig. 14.](image)
Fig. 15. (a) (1 0 0) pole figure from a region in the Ti-1223 film containing two colonies; (b) a-axis arrow map for an area which contains a sharp colony intersection, indicated by the hand-drawn curve. For 75% of boundaries $\theta < 10^\circ$, and 54% of boundaries with $\theta < 15^\circ$ are within the Brandon criterion for an ideal CSL.

Fig. 16. (a)(1 0 0) pole figure from another region in the Ti-1223 film containing two colonies; (b) a-axis arrow map for an area in which orientation appears to change gradually without a well-defined colony boundary. 52% of boundaries have $\theta < 10^\circ$, and 14% of large-angle boundaries are within the Brandon criterion for an ideal CSL.

Figures. In Fig. 17 the projections of the a-axis of the grains onto the $RT$ plane, i.e. the arrows are color coded such that a given color represents orientations within $15^\circ$. A colony structure is evident.

These regions comprise a total of 1077 grain boundaries. 48% of these were less than $15^\circ$, 29% less than $10^\circ$, and 10% were within the Brandon criterion for a CSL. These particular regions with
Maps of a-axis Projections in 1mm regions

Fig. 17. (a) Color coded “arrow” maps of a-axis grain orientations in 1 mm regions of a sample. A given color represents grain orientations within 15°. Data was obtained in the manner described for Figs. 14–16. The colony structure is clearly evident in such macroscopic regions; (b) Arrow map of a-axis projections from another region.

good alignment were found to have $J_c$'s of $1 \times 10^5$ and $2 \times 10^5$ A/cm$^2$, respectively.

Since there are only small-angle boundaries within a colony, macroscopic current flow is not expected to be well-linked. However, strongly-linked current flow across an aggregate of colony intersections which is contained in a typical film, can be expected to be percolative in nature. Assuming that the results from Nabatame et al. [6] are applicable, the current will be expected to weave its way around high-angle boundaries, primarily traversing paths comprising connected networks of small-angle grain boundaries. One of the consequences of percolative current flow is that the critical current density will depend on the dimensions of the conductor. As the width of the conductor or film is reduced to a dimension comparable to the average colony size in the film, $J_c$ can be expected to be limited by high-angle boundaries due to reduction of percolative options.

Fig. 19 shows the most likely a-axis orientations in a 4 x 5 mm$^2$ region of a 3 μm thick Tl-1223 film on YSZ made by spray pyrolysis followed by two-zone thallination. The data were obtained at the National Synchrotron Light Source (NSLS) at the ORNL beam line X-14 [26]. The c-axis is aligned to within 2° of the normal to the film. X-ray phi-scans were then measured using the $\{1 1 8\}$ reflection. Fig. 19a shows X-ray φ-scans measured using effective beam sizes of $2 \times 11$ mm$^2$ (top) and 0.01 mm$^2$ (bottom), respectively. While little in-plane texture is observed with a larger beam, a distinct in-plane texture is observed with the smaller beam. Four peaks are observed for a rotation of 360° about the sample normal, consistent with the tetragonal symmetry of the material. Fig. 19b
Fig. 18. (a) (1 0 0) and (0 0 1) pole figures of orientations indicated in Fig. 17a; (b) (1 0 0) and (0 0 1) pole figures of orientations indicated in Fig. 17b.

shows a map of $a$-axis grain orientations measured by obtaining $\phi$-scans on a square grid using a 0.1 mm$^2$ beam and plotting the location of the strongest peak in the first quadrant ($0 - 90^\circ$). The crosses indicate the $a$-axis of the most common orientation in the $\phi$-scan. The colony structure in the sample is evident. It can be intuitively expected that the critical current density of a sample with such a microstructure will be dependent on the bridge dimensions due to change in percolative options by the geometry of the bridge. Such a measurement has been performed and results are in excellent agreement with microstructural predictions [27, 28].

3.2.1. Microstructural modeling of current flow in Tl-1223 thick films

The colony microstructure shown in Fig. 19b can be described quantitatively by an orientational correlation function, $C(r, \phi) = \langle I(r_0, \phi_0) - \bar{I} \rangle \langle (r_0 + r, \phi_0 + \phi) - \bar{I} \rangle / r^2$, where $I(r_0, \phi_0)$ is the diffracted intensity from position $r_0$ and orientation $\phi_0$, $\bar{I}$ is the average measured intensity, and the brackets $\langle \rangle$ indicate an average over all pairs of measurements separated by a displacement $r$ and misorientation $\phi$ [26]. The critical current density $J_c$ can be calculated from the map of orientational distributions in Fig. 19c by the relation $J_{ij} = \langle I_i (\Phi_i) I_j (\Phi_j) \rangle / I_i I_j$, where the average is over all pairs of angles $\Phi_i$ and $\Phi_j$ [26]. The grain boundary critical current $i_c$, based on

Fig. 19. (a) Typical X-ray $\phi$-scans of $c$-axis textured Tl-1223 films using effective beam sizes of 2 x 11 mm$^2$ (top) and 0.1 mm$^2$ (bottom), respectively. While little in-plane texture is observed with the larger beam, a distinct in-plane texture is observed with the smaller beam; (b) Map of $a$-axis grain orientations measured by obtaining $\phi$-scans on a square grid using a 0.1 mm$^2$ beam. The crosses indicate the most common $a$-axis orientation in the $\phi$-scan.
measurements of Tl-1223 films on SrTiO3 bicrystals at 77 K in zero magnetic [6], is $1 \times 10^5$ A/cm$^2$ for grains aligned to within 12 and $3 \times 10^3$ A/cm$^2$ otherwise. The limiting path model [26, 29] is used to sum all current paths and find $J_c$.

It has been shown [29] that $J_c$ for a lattice of randomly oriented grains approaches, for large lattices, the lowest $J_c$, i.e. that of a large-angle boundary. A long-range texture increases $J_c$ above this minimal value. A colony microstructure is an intermediate case, random overall but locally textured. To see the effect of the colony microstructure on current transport, the $J_c$ was simulated for square arrays of colonies, each with random orientation. The grain orientation within each colony follows a Guassian distribution, with the same FWHM for each colony. The intercolony $J_c$ is calculated using the limiting path model, as described above. For large FWHM within a colony, the current transport is limited by the intercolony $J_c$. This occurs for poor intercolony alignment because while a small fraction of the grains at colony boundaries are well aligned and can carry large currents across the boundary, there is no continuous high-current path across each colony. The intracolony $J_c$ is calculated by calculating $J_c$ for a 100 x 100 square array of grains. Fig. 20 shows the intracolony, intercolony, and total $J_c$ for a 100 x 100 square array of colonies. As is evident from the figure, $J_c$ is limited by intercolony transport for low FWHM and by intracolony transport for high FWHM. There exists an optimum FWHM for colonies in order to obtain the highest $J_c$. This provides processing of these materials a goal to strive towards to obtain higher $J_c$'s.

### 3.3. Effect of biaxial texture on GBMDs and $J_c$

Comparison of the best Bi-2223 PIT tapes and Tl-1223 thick films studied here indicates that only a small cross-section of the material, ~10%, is carrying all the current. As shown above, this is due to percolation of current through connected networks of low-energy boundaries. Therefore, in order to increase the active cross-section of the material and hence the $J_c$ of the sample, increased paths of strongly-linked, low-energy grain boundaries are required. Fig. 21 shows a calculation of the expected GBMDs when the c-axis of all the grains are perfectly aligned, but the a-axis have varying degrees of alignment. Plotted in the figure is the expected fraction of misorientation angles less than $\Theta$ as a function of $\Theta$, for a tetragonal polycrystal in which the c-axis of all the grains is completely aligned. It is evident from the figure that only
a small fraction of biaxial texture greatly increases the population of small-angle boundaries. For example, orienting the $a$-axis of all the grains to within a spread of $50^\circ$, results in a grain boundary misorientation with $\sim 50\%$ of the boundaries less than $15^\circ$ and $\sim 30\%$ of the boundaries less than $10^\circ$. Even a marginal macroscopic biaxial texture greatly suppresses weak-link behavior by

Fig. 22. OIM images from a macroscopic region of a RABiT substrate. Patterns were obtained in a hexagonal grid with a step size of 3 $\mu$m. Two types of grain boundaries are indicated in the figures, thin lines denote boundaries with misorientations greater than $5^\circ$ and less than $15^\circ$, and thick lines are greater than $15^\circ$. In (a), a given color represents a percolative region within $2^\circ$ in (b) a region within $7^\circ$ and in (c) a region within $10^\circ$. Percolation through small-angle boundaries can clearly be envisaged.
enhancing the population of small-angle boundaries as was demonstrated for Y-124 PIT fabricated by American Superconductor Corporation [25]. The greatest effect is realized when a sharp biaxial texture is obtained. This is presently possible using two techniques, Ion-Beam-Assisted-Deposition (IBAD) [30–32] and Rolling-assisted-biaxially-textured-substrates (RABiTS) [33]. In the IBAD technique, a biaxially oriented buffer layer is deposited using an ion assist gun on randomly oriented metal alloy substrates. Epitaxial YBCO is grown on this layer. In the case of RABiTS, the metal itself is
biaxially textured by thermo-mechanical processing, thereby eliminating the IBAD step. Typical in-plane textures obtained by both the techniques are very comparable, 8° in the RABiT substrate [33] and 12° in the IBAD buffer layer [31]. In both cases epitaxial YBCO films have yielded high $J_c$'s (> $10^5$ A/cm², 77 K, 0 T) with field dependence's similar to epitaxial films on single crystal films [30–32].

In the RABiT process a Ni strip is biaxially textured using thermomechanical processing. Epitaxial metal and oxide buffer layers are then grown
on the textured Ni template. The superconductor is
grown epitaxially on the last oxide layer. The high-
est $J_c$ obtained by this method is $7.1 \times 10^5$ A/cm$^2$,
especially approaching that of epitaxial films on
single crystal ceramic substrates. The key feature of
these substrates which allows for such a high $J_c$, is
the initial grain structure in the Ni substrate.

Fig. 22 shows three OIM images of these substra-
tes. Patterns were obtained in a hexagonal grid
with a step size of 3 μm. Two types of grain bound-
aries are indicated in the figures, thin lines denote
boundaries with misorientations greater than 5°
and less than 15°, and thick lines are greater than
15°. In Fig. 22, a given color represents a perco-
lative region within 2° in Fig. 22a, 7° in Fig. 22b
and 10° in Fig. 22c. Epitaxial superconducting
films on such substrates can also be expected to
have a similar grain misorientation structure, com-
prising primarily of small-angle boundaries.

4. Conclusions

The results presented here demonstrate for both
the Bi-based and Tl-based conductors that small-
angle grain boundaries are present in much higher
numbers than expected statistically from macro-
scopic textures. These results, in conjunction with
the growing body of evidence that large-angle
boundaries (possibly excluding CSL boundaries) in
most, if not all, oxide superconductors are weak-
links, strongly suggest that long-range conduction
occurs by percolation through a connected net-
work of small-angle (and perhaps CSL) boundaries.
Critical current density is determined by local grain
boundary misorientations, not by macroscopic tex-
ture. Texture determines the probability that adjacent
grains will have similar orientations. Grain
boundary energy provides a driving force which
skews the misorientation distribution toward
small-angle and probably CSL boundaries. The
specific arrangement of good boundaries compris-
ing the percolative network, i.e., the local texture,
vary with material and processing method. In the
Tl-1223 deposits a very high density of small-angle
grain boundaries is associated with the colony
microstructure, and long-range conduction de-
pends on percolation through a much smaller
population of small-angle (and possibly CSL)
boundaries at colony intersections. In Bi-2223 con-
ductor a randomly distributed but smaller popula-
tion of small-angle boundaries is sufficient to
ensure percolation of current. It is well-known that
$J_c$ in Bi-2223 conductors does not correlate perfect-
ly with the degree of c-axis alignment and second-
phase content as determined from X-ray diffraction
and microscopic examination of polished cross-
sections. We suggest that the population of small-
angle boundaries is the “hidden variable” with
which $J_c$ correlates.

Microstructural modeling of current flow in
uniaxially aligned superconductors suggests that
there exists an optimum c-axis alignment for the
highest $J_c$, due to the combined effects of $J_c$ anisot-
ropy and current flow dimensionality. Microstruc-
tural modeling of locally biaxially aligned
superconductors suggests that there exists an opti-
num local in-plane alignment for maximum $J_c$.

Percolation through a connected network of low-
energy boundaries is offered as a general model for
long-range conduction in polycrystalline supercon-
ductors. At this stage we have only considered grain
boundary misorientation angle as a determinant of
$J_c(gb)$. It is recognized, however, that because struc-
ture and superconducting properties are anisotropic,
the axis of rotation and grain boundary plane may
also affect $J_c(gb)$. It is not clear how these variables
effect transport properties or if their effects differ
between low-energy and high-energy boundaries.
Furthermore, there may be an effect of grain bound-
ary structure and energy on chemical stoichiometry
of the grain boundary characteristics. Large-angle
boundaries may have greater tendency to form
monolayers of second phases or have depletion of
chemical constituents like oxygen resulting in a de-
pletion of hole carriers at the boundary. Bicrystal
experiments which are aimed at specifically deter-
mining the effects of these variables on transport
properties are required. In the absence of such ex-
periments, the results presented here establish
a strong case for a “necessary” condition for long-
range current transport in polycrystalline supercon-
ductors. However, it is realized that several other
variables may also be important, and hence further
work is required to establish the “necessary and
sufficient” conditions for long-range current flow.
In order to increase $J_c$ of polycrystalline superconductors, optimization of the percolative options is required. The calculation of expected GBMDs for tetragonal materials with varying degrees of biaxial texture suggests that even a small degree of biaxial texture results in a significant increase in the population of small-angle boundaries. In an effort to obtain ideal microstructures, macroscopically biaxially textured, flexible metal substrates were fabricated for epitaxial growth of superconductors. Superconductors fabricated on such substrates have $J_c$'s approaching those of epitaxial films on single crystal ceramic substrates, and offer a potential route for the fabrication of HTS conductors.

Acknowledgements

We are very grateful to our collaborators: J. Sutliff, J.E. Tkaczyk and J.A. Deluca at General Electric Corporation for useful discussions, collaborations and for providing the Ti-1223 samples; G.N. Riley Jr. and M.P. Rupich, American Superconductor Corporation for providing the Bi-2223 PIT samples; H. Kumakura, National Research Institute of Metals (NRIM), Japan, for providing the Bi-2212 samples. We are also grateful to D.P. Field and D.J. Dingley, TEXSEM, Utah and T.A. Mason, Idaho National Engineering Laboratory, Idaho for fruitful collaborations and discussions. Research sponsored by US Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Utility Technology – Superconductivity Program and the Office of Energy Research, Basic Energy Sciences, managed by Lockheed–Martin Research Corporation for the US Department of Energy under contract DE-AC05-96OR22464. This research was conducted in part at National Synchrotron Light Source (NSLS), which is sponsored by the US Department of Energy under contract No. DE-AC02-76H00016.

References


