ANALYSES OF THE GRAIN BOUNDARY MISORIENTATION AND
OXGEN CONTENT OF BULK PROCESSED \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\)

JENN-YUE WANG**, ALEXANDER H. KING**, YIMEI ZHU*, YUAN-LIANG WANG*
AND MASAKI SUENAAGA**

*Materials Science Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973; **Department of Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, NY 11794

ABSTRACT

The grain boundary misorientation distribution of 203 grain boundaries in bulk processed high Tc superconductor \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) with five processing conditions, was studied. Two complementary analytical approaches; Grain Boundary Misorientation Distribution (GBMD) from the random description, using a hypothesis test and \(\chi^2\) analysis, and Grain Boundary Character Distribution (GBCD), using the Coincidence Site Lattice (CSL) model, were applied. The GBMD and GBCD both showed grain boundary evolution departing from a random distribution above 935°C processing temperature. The GBCD analyses indicated an approximately linear increase in the population of CSL-related boundaries, among which the tetragonal CSL \((c/a = 3)\) boundaries grew in the same trend while orthorombic boundaries \((c/a = 3)\) became stagnated. The results from comparing the corresponding GBCD and volume averaged \(J_c\) for each batch indicated that the tetragonal CSL boundaries were oxygen deficient and accounted for, among other current limiting factors, lower current carrying ability.

INTRODUCTION

Grain boundaries in the high Tc superconductor, \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\), are detrimental to the critical current carrying capability. Efforts have been made to understand the correlation between the misorientation and the measured \(J_c\). It is generally found that there is a sharp decline in \(J_c\) where the boundary misorientation exceeds 10° (Chaudhari et al. [1]; Dimos et al [2,3]). Such low \(J_c\) persists over a wide range of misorientation angle up to 90° where unusually high transport current was reported. It is exemplified in the systems of polycrystalline thin films (both \(a\)-\(b\)- and \(c\)-axis orientated) (Hwang et al. [4], Eom et al. [5,6]) and of bulk bicrystals (Babcock et al [7], Larbalestier et al. [8]) of \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\). Knowledge of the crystallographic and electronic structures of the grain boundaries is crucial for understanding the superconducting current densities in bulk \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) and for overcoming this major hindrance to practical applications of cuprate superconductors.

Grain boundary studies rely primarily on two theoretical approaches: the coincidence site lattice (CSL) model (Bollmann [9]) and the structure unit model (SUM) (Sutton and Vitek [10]). The SUM provides detailed atomic configuration at the grain boundary if the interatomic potential is known. Such information is only available in high symmetry simple crystals, which limits its application in lower symmetry crystal systems. The CSL model, on the contrary, has been successfully and widely used in grain boundary studies in various crystal lattices, particularly in the cubic system. A boundary is considered physically significant and potentially special when the boundary formed by two neighboring grains has a high number of lattice sites from both grains in coincidence. A CSL is formed when two grains rotate about a common axis with respect to one another for a certain angle. To denote how well two grains are in coincidence, the reciprocal value of the ratio of the volume of the supercell formed after rotation to the volume of the crystal unit cell is defined as the \(\Sigma\). The
smaller the $\Sigma$ values are, the more lattice sites are shared by both grains.

An experimental problem in categorizing a grain boundary is to designate a CSL to the boundary. In cubic crystals, a common rule of thumb is the Brandon criterion which defines a maximum deviation angle which a boundary can still be classified to a particular CSL. For non-cubic crystals, the geometrical model requires $a^2:b^2:c^2$ to have rational values to allow the formation of a three dimensional CSL. Assigning a CSL to a boundary can be complicated in non-cubic systems for two reasons. First, numerous CSLs can be related to various type of $\Sigma$s, depending on the choice of $a^2:b^2:c^2$. Second, in addition to the introduction of grain boundary dislocations, it is necessary to constrain the ratios of the lattice parameters at the boundary region to the closest rational values to form a CSL, and it is called constrained coincidence site lattice (CCSL). The CCSL model has been shown to apply in Zn (Chen and King [11]), YBa$_2$Cu$_3$O$_{7-\delta}$ (Singh and King [12], Wang and King [13]). Extensive work on textured YBa$_2$Cu$_3$O$_{7-\delta}$ was performed by Zhu et al [14] for about 300 grain boundaries.

In YBa$_2$Cu$_3$O$_{7-\delta}$ the lattice parameters are very sensitive to and vary with the oxygen stoichiometry. The simple geometrical constraint in local lattice parameters can be accommodated by a stoichiometric change which can be confirmed by looking into the compositional variation at the boundary. Using electron energy loss spectroscopy (EELS), Zhu et al [15] measured grain boundary oxygen hole density, by the oxygen pre-peak located at 529 eV, as a function of grain boundary misorientation. It was demonstrated that oxygen depletion occurred at the boundary where, based on the CCSL model, the axial ratio (c/a) required to adjust to the misorientation, while grain interiors are oxygenated. Figure 1a shows a series of electron-energy-loss spectra of the oxygen K edge collected at 50 Å apart, across a large-angle grain boundary. The CCSL system is $\Sigma 31/69/220/310$ with axial ratio of $a^2:c^2 = 15:140$. The intensity of oxygen pre-peak decreasing at the boundary confirms the prediction by the CCSL model. Figure 1b denotes a boundary with $a^2:c^2 = 15:135$ or $a/c = 1/3$ a nominal value for YBa$_2$Cu$_3$O$_7$. There is no marked decrease of oxygen pre-peak across the boundary as predicted by the CCSL. Zhu et al [16] provided more direct evidence between CCSL prediction and oxygen content by convergent beam electron diffraction (CBED) to measuring local lattice parameters at the grain boundary region and by EELS for the oxygen content.

In this paper, we present an analysis of more than 200 grain boundaries in bulk processed YBa$_2$Cu$_3$O$_{7-\delta}$ using a two-step screening procedure: initially by the grain boundary misorientation distribution (GBMD), then followed by grain boundary character distribution (GBCD). The GBCD analysis was analyzed with respect to critical current $J_c$. Our goal is to establish the GBCD analysis in bulk processed YBa$_2$Cu$_3$O$_{7-\delta}$ and to elucidate a possible link with $J_c$.

**EXPERIMENTAL**

The precursors of YBa$_2$Cu$_3$O$_{7-\delta}$ were prepared by a pyrolysis technique, detailed by Wang et al [17] to ensure spherical uniformity, pressed under 9000 psi static pressure, then sintered at the temperature range from 935°C to 975°C. After sintering, the ambient temperature was gradually decreased at the rate of 4°C/min to 800°C, followed by a slow cooling rate 0.05°C/min to the final sintering temperature.

TEM specimens were cut from the bulk samples using an ultrasonic disk cutter with 3 mm diameter. The specimens were then mechanically dimpled to about 50 μm at the center and ion milled to perforation by using 4 kV argon ions at an incident angle of 12°. At the final stage, the incident angle was reduced to 10° and the ion-energy was lowered to 3 kV to avoid the formation of artifacts induced by ion-bombardment.
Total of 203 grain boundaries were analyzed. The data were grouped according to processing temperature and duration. The respective numbers of grain boundary are listed in the following:

<table>
<thead>
<tr>
<th>Process</th>
<th>935°C/36hr</th>
<th>950°C/24hr</th>
<th>950°C/240hr</th>
<th>965°C/24hr</th>
<th>973°C/24hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observation</td>
<td>61</td>
<td>27</td>
<td>37</td>
<td>33</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 1: Experimental observations for different processing temperatures and times.

Figure 1: A series of electron-energy-loss spectra of the oxygen K edge collected at 50Å apart across (a) an oxygen-deficient grain boundary (Z31/69.22°[310] with axial ratio of $a^2:c^2 = 15:140$); (b) a fully oxygenated grain boundary (Z31/83.56°[100], $a^2:c^2 = 15:135$).

Grain boundary misorientations were determined by taking the Kikuchi patterns from the abutting grains, then following the geometrical method of Zhang and King [18] based on
Young et al [19], Ball [20], and Chen and King [21] to deduce the misorientation between the two. The collective misorientations of samples from each processing temperature were then analyzed against the theoretical random distribution for the tetragonal system derived by Grimmer [22]. A hypothetical test and $\chi^2$ analyses were applied to indicate how well the experiment distribution falls into being random. The hypothesis defines that sample exhibits a random GBMD. Any deviation from being random, determined by $\chi^2$, suggests the existence of texture. Equation (1) denotes that the $\chi^2$ values according to the expected and the observed frequencies

$$\chi^2 = \sum \frac{(f_{\text{actual}} - f_{\text{expected}})^2}{f_{\text{expected}}^2}$$

where $f_{\text{actual}}$ is the observed frequency and $f_{\text{expected}}$ the predicted value. Up to this step, the information is batch-wise corresponding to the processing temperature. Next we determine individual boundary characteristics by the CCSL model such that the GBCD is obtained.

**RESULTS AND DISCUSSION**

Histograms of grain boundary misorientation are plotted against the random distribution curve in figure 2 with a bin size of $10^\circ$. The $\chi^2$ analysis was applied to evaluate the deviation of experimental result. Figure 3 illustrates the $\chi^2$ values corresponding to each batch. The horizontal line indicates the significance level that was set at 0.1, thus the last four batches were regarded being non-random - a clear indication that the microstructure evolution has occurred. It is important to note that there is no linear relation between the $\chi^2$ values.

![Figure 2: The grain boundary misorientation distribution of each processing temperature is plotted against the random distribution curve.](image1)

![Figure 3: Each of $\chi^2$ value is plotted with respect to thermal processing temperature and time. The horizontal line indicates that only the batch processed at 935°C is within the significance level 0.1 and satisfies the random description.](image2)
Figure 4 shows that the population of CCSL-related grain boundaries increases monotonically with increasing temperature. Chan et al. [23] demonstrated that grain rotation into energetically favored orientations is thermally activated. However, not all thermally stable boundaries do necessarily exhibit good electrical properties. King et al. [24] and Zhu et al. [25] pointed out that some boundaries formed above 950°C, having the oxygen deficient composition of YBa$_2$Cu$_3$O$_{7-δ}$ ($δ \approx 0.7$), may be CCSL-related. After an oxygen uptake process, though other boundaries may have the $δ \approx 0$, these relatively low energy boundaries remain oxygen deficient due to the orientation constraint. It is conceivable that the increasing amount of such boundaries undermines the current carrying capability of YBa$_2$Cu$_3$O$_{7-δ}$.

Grain Boundary Character Distribution of bulk processed YBa$_2$Cu$_3$O$_{7-δ}$

![Grain Boundary Character Distribution](image)

Figure 4: The grain boundary character distribution shows the population of CCSL-related grain boundaries increases with increasing temperature. Among which, the growth rate of $c/a=3$ grain boundaries becomes stagnated at temperature above 950°C while the $c/a \neq 3$ grain boundaries increases monotonically. The critical current $J_c$ drops drastically when the bulk YBa$_2$Cu$_3$O$_{7-δ}$ processed above 950°C.

Based on the aforementioned, we proceeded to investigate the axial ratios of CCSL. Each GBCD was divided into two groups by their axial ratios, $c/a=3$ and $c/a \neq 3$, as shown by two shaded bars of each group in figure 4. The increase of non-3.0 boundaries with respect to elevated annealing temperature suggests that more tetragonal phase boundaries evolved, and remained in the microstructure after the orthorhombic transformation. For $c/a = 3$ boundaries, on the contrary, the growth rate of the population becomes stagnant above $T=950°C$. This result may correlate with the measured bulk $J_c$ because fewer boundaries are able to accommodate oxygen. Consequently, the critical current carrying capability is drastically reduced.
SUMMARY

Grain boundary analysis using both GBMD and GBCD with hypothesis testing by $\chi^2$ analysis yields a higher degree of confidence in interpreting experimental results. It is shown that, due to the orientation constraint, the CSL boundaries of $c/a \neq 3$ remain in the structure formed at high temperature during oxygenation process. Though the grain interiors underwent the tetragonal-to-orthorombic transformation, the vicinity of the boundary is depleted in oxygen content. The GBCD analysis strongly suggests that CCSL-related boundaries are energetically favorable when processed at high temperature. However, among them, the growth of $c/a=3$ boundaries becomes stagnated while $c/a \neq 3$ boundaries increase above 950°C. In addition to other current limiting factors, this promotes the degradation in $J_c$ of the bulk YBa$_2$Cu$_3$O$_{7-\delta}$ processed above 950°C.

ACKNOWLEDGEMENT

This research was performed under the auspices of the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences under Contract No. DE-AC02-76CH0001

REFERENCES