Quarterly Report
for the Period Ending December 31, 2000

“Practical Superconductor Development for Electrical Power Applications”

Principal Investigator

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Costs and Schedule

October–December Costs  $1,019,698.98
Total Year to Date        $1,019,698.98
This is a multiyear experimental research program focused on improving relevant material properties of high-T\textsubscript{c} superconductors (HTSs) and on development of fabrication methods that can be transferred to industry for production of commercial conductors. The development of teaming relationships through agreements with industrial partners is a key element of the Argonne National Laboratory (ANL) program.

**Technical Highlights**

Recent results are presented on YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{x} (Y-123) coated conductors, including fabrication by pulsed laser deposition (PLD) and sol-gel techniques. An approach to understanding the critical current density (J\textsubscript{c}) of grain boundaries is also presented and a technique is identified for increasing J\textsubscript{c}.

**Fabrication of Coated Conductors by Pulsed Laser Deposition**

In the last quarterly report, we provided details on the deposition conditions for fabricating Y-123 films by PLD. We also reported the dependence of superconducting properties of these films on substrate temperature (T\textsubscript{s}) during deposition. A temperature of \approx 790°C was found to be optimal for single-crystal substrates. We have continued to optimize PLD deposition and postannealing conditions for producing high-quality Y-123 films.

High-quality Y-123 films are now consistently obtained on LaAlO\textsubscript{3} (LAO) and SrTiO\textsubscript{3} (STO) substrates. Y-123 films exhibit T\textsubscript{c} \geq 90 K and J\textsubscript{c} values >3 MA/cm\textsuperscript{2} for films \leq 0.3 \mu m thick and 1 MA/cm\textsuperscript{2} for films that are \geq 1 \mu m thick. The J\textsubscript{c} of Y-123 films made on LAO single-crystal substrates is sensitive to film thickness, decreasing with increasing film thickness, even for films <0.3 \mu m thick. Representative data are shown in Table 1.

Ex-situ postannealing conditions have been explored and significant improvements in T\textsubscript{c} and J\textsubscript{c} (usually measured by inductive methods) have been observed for the Y-123/LAO samples annealed under optimized conditions (Fig. 1).
Table 1. Properties of thin Y-123 films on single-crystal LAO

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>T_c (K)</th>
<th>J_{c,m} (MA/cm^2)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020A1</td>
<td>Y-123/LAO</td>
<td>90.0</td>
<td>8.3</td>
<td>0.1</td>
</tr>
<tr>
<td>1011A2</td>
<td>Y-123/LAO</td>
<td>90.0</td>
<td>6.6</td>
<td>0.15</td>
</tr>
<tr>
<td>0802B2</td>
<td>Y-123/LAO</td>
<td>87.0</td>
<td>5.0</td>
<td>0.2</td>
</tr>
<tr>
<td>0912A2</td>
<td>Y-123/LAO</td>
<td>90.5</td>
<td>3.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Fig. 1. Inductive voltage vs. drive current for Y-123 film on LAO; annealing increased the inductive J_c from 4.0 to 6.6 MA/cm^2 at 77 K.
Ag coating is required for measuring transport $J_c$. Post-Ag-coating annealing conditions have been studied for Y-123 films on LAO and STO crystals. Representative data from these studies are shown in Table 2 and Fig. 2.

Table 2. Properties of Ag-coated thicker Y-123 films on single crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ (K)</th>
<th>$J_{cm}^a$ (MA/cm$^2$)</th>
<th>$J_{c}^a$ (MA/cm$^2$)</th>
<th>Thickness (µm)</th>
<th>Width (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-123/LAO</td>
<td>90.5</td>
<td>3.3</td>
<td>3.17</td>
<td>0.3</td>
<td>5.2</td>
</tr>
<tr>
<td>Y-123/LAO</td>
<td>91.0</td>
<td>&gt;1.0</td>
<td>1.35</td>
<td>1.0</td>
<td>5</td>
</tr>
<tr>
<td>Y-123/STO</td>
<td>90.8</td>
<td>&gt;1.0</td>
<td>1.57</td>
<td>1.0</td>
<td>5</td>
</tr>
</tbody>
</table>

$^a$J$^{cm}$ and J$_{c,t}$ are $J_c$ measured by inductive and transport methods, respectively.

Fig. 2. Plot of current vs. voltage at 77 K for Y-123 film on STO crystal; transport $I_c = 79$ A and $J_{c,t} = 1.57$ MA/cm$^2$. 

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Various processing methods are being investigated for the fabrication of high-$J_c$ Y-123 coated conductors on metallic substrates. Nonvacuum ex-situ processes such as metal organic deposition (MOD) and sol-gel processing offer promising options. Solution techniques are now being studied by several groups, and some of their results are comparable to superconductive performance levels obtained by vacuum processes such as PLD. The MOD process based on trifluoroacetate (TFA) has produced some of the highest $J_c$ values attained by a solution technique. We report results of an effort to optimize the heat treatment parameters for applying the TFA process to LAO substrates. With a goal of extending the TFA-based precursor route to metallic substrates, we concentrated particularly on lowering heat-treatment temperatures.

Acetates of Y, Ba, and Cu were weighed to a 1:2:3 molar ratio, dissolved in trifluoroacetic acid, and the mixture was refluxed for 4 h. The resulting solution was dried in air and a methanol-based solution with a 1.5 M cation concentration was prepared. The solution was applied to LAO single crystals. The precursor film that formed was converted to an epitaxial Y-123 film through two separate heat-treatment steps. During the first step, a uniform fluoride-containing solid film formed. During the second step, carried out in a low-O-pressure Ar atmosphere, the fluorides were driven off and a uniform, textured Y-123 film formed. Various maximum temperatures were investigated for the second step. The estimated O content of the Ar was $\approx$10 ppm. After the second step, the composition of the Y-123 film was determined by the inductively coupled plasma/atomic emission spectroscopy.

Superconducting properties of the films were characterized by measuring $T_c$ and $J_c$ inductively. Microstructures were studied by scanning electron microscopy (SEM) and energy-dispersive spectroscopy, and in-plane texture development was evaluated by X-ray diffraction (XRD). The in-plane texture was quantified by measuring the full width at half maximum values (FWHMs) of Y-123 (113) $\phi$ scans. For analysis of c-axis alignment, FWHMs of the (005) and (007) peaks of Y-123 were measured from $\Omega$ scans for each sample. Information about second-phase formation, O stoichiometry, c-axis alignment, and defect structures was obtained by Raman microspectroscopy.

SEM images of the top surface microstructures of representative samples prepared at five step-two heat treatment temperatures are shown in Fig. 3. Pores and crystalline particles are observed to varying degrees on the surface of
Fig. 3. SEM photomicrographs of top surfaces of representative films processed at (a) 720, (b) 740, (c) 750, (d) 760, and (e) 780°C during step-two heat treatment.
Fig. 3. (Contd.)
each sample; this is typical for Y-123 films prepared by postannealing processes. For the films prepared at 720 (Fig. 3a) and 740°C (Fig. 3b), needle-shaped grains (which appear to be a-axis oriented) are frequently observed, providing evidence for some grain misalignment, although the dominant texture of the films is c-axis vertical to the substrate. However, as can be seen in Figs. 3c and 3d, the 750 and 760°C samples contain far fewer a-axis grains, indicating that the c-axis verticality is improved at these temperatures. On the other hand, for the sample prepared at 780°C (Fig. 3e), large particles are observed, while needle-shaped grains are absent. These large particles were mainly BaCuO2. This finding suggests that the Y-123 phase may be undergoing partial decomposition starting at temperatures between 760 and 780°C.

The sharpest superconducting transitions were observed in samples prepared between 740 and 760°C. This temperature range also yielded the best Y-123 phase purity.

In-plane texture and c-axis alignment of the Y-123 films were determined from the FWHMs of the φ and Ω scans. Figure 4 shows a (113) φ scan for a film heated at 750°C; the average FWHM was ≈0.6°. Figure 5 presents a plot of the variation of the FWHMs of the φ scan with heat-treatment temperature. The FWHM values ranged from 0.55 to 0.8°.
FWHMs of the Ω scans for the Y-123 (005) and (007) reflections as a function of heat-treatment temperature are shown in Fig. 6. The FWHMs were 0.38° at minimum and 0.68° at maximum, and were not obviously correlated with temperature. The FWHMs from φ and Ω scans obtained by other groups are commonly ≈1.5 and 0.5°, respectively. In general, our TFA-based Y-123 films exhibited quite good in-plane and c-axis alignment.

Raman microspectroscopy was used to investigate c-axis alignment, defect structures, oxygen stoichiometry, and second-phase formation. Figure 7 shows representative Raman spectra for samples processed at each of the five heat-treatment temperatures. The spectra were recorded in the xx/yy mode, i.e., with the laser excitation and observation directions perpendicular to the substrate and hence (presumably) also perpendicular to the a-b planes of all
epitaxial Y-123 grains. In this configuration, a perfectly epitaxial, defect- and impurity-free Y-123 film should exhibit only one band (marked with an inverted triangle in Fig. 7) between 200 and 800 cm\(^{-1}\). This band, nominally at \(\approx 340\) cm\(^{-1}\), is the out-of-phase O\(_2\)/O\(_3\) mode of Y-123.

The presence of other bands is generally an indication of defect structures, poor c-axis alignment, and/or impurity phases. For example, the band near 225 cm\(^{-1}\) has been attributed to the presence of broken M-O chain structures, which can exist on a nanoscopic, microscopic, or macroscopic scale. This band was rarely observed for films heat treated at 740–760°C. Occasionally, a small

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**Fig. 5.** FWHMs of \(\phi\) scan vs. processing temperature.
band was observed in this region for samples heat treated at 720°C, which we suggest is due to imperfect connectivity between Y-123 grains. Some samples heat treated at 760°C showed evidence of the 225 cm\(^{-1}\) feature, but this band became much stronger when the heat-treatment temperature was increased to 780°C. We found that the 225 cm\(^{-1}\) also tended to appear when the BaCuO\(_2\) band at \(\approx 630\) cm\(^{-1}\) (marked as BC in Fig. 7) was present with large intensity. This may be an indication that the BaCuO\(_2\) phase influences/causes the imperfect grain connectivity.

For the film heat treated at 780°C, two types of spectra were often observed: one that showed a strong CuO band (marked as CU in Fig. 7) and the other essentially like that shown in Fig. 7. It appears that the Y-123 phase starts to decompose at temperatures near 780°C.

Fig. 6. FWHMs of \(\Omega\) scans of (005) and (007) XRD peaks.
Fig. 7. Raman spectra for Y-123 films processed at temperatures shown.

The band marked CM in Fig. 7 is the O4 phonon of Y-123. In the xx/yy configuration, the intensity of this mode should be minimal if the Y-123 film is perfectly epitaxial. The extent to which this mode appears relative to the 340 cm<sup>-1</sup> phonon is, in essence, a measure of the degree of c-axis misalignment. Using this relationship as a guide, we find in Fig. 7 that the largest degree of c-axis misalignment was exhibited by the samples heat treated at 720, 740, and 780°C; considerably less misalignment is seen for the 750 and 760°C samples.

The peak frequency of the CM band provides an approximate measure of the oxygen stoichiometry of Y-123. For tetragonal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>, the value of x is expected to be near 6 and the CM peak frequency is near 480 cm<sup>-1</sup>, whereas for the orthorhombic form, the value of x is expected to be near 7.0 and the CM mode peak frequency is near 500 cm<sup>-1</sup>. The CM mode peak frequency was near 500 cm<sup>-1</sup> for all of the samples, indicating that the Y-123 phase is the orthorhombic form in all cases.
The band near 590 cm\(^{-1}\), the peak frequency of the CM band, provides an approximate measure of the O stoichiometry of Y-123. For tetragonal YBa\(_2\)Cu\(_3\)O\(_x\), \(x\) is expected to be near 6 and the CM peak frequency is near 480 cm\(^{-1}\), whereas for the orthorhombic form, \(x\) is expected to be near 7.0 and the CM mode peak frequency is near 500 cm\(^{-1}\). The CM mode peak frequency was near 500 cm\(^{-1}\) for all of the samples, indicating that the Y-123 phase is the orthorhombic form in all cases.

The band near 590 cm\(^{-1}\) (marked as CD in Fig. 7) has been attributed to cation disorder in the Y-123 lattice. As in the case of the CM mode, the CD band is much less prevalent for the 750 and 760°C samples.

Figure 8 shows the results of inductive J\(_c\) measurements on samples prepared at the five heat-treatment temperatures. Not surprisingly, the highest J\(_c\) value (1.3 MA/cm\(^2\)) was obtained for the sample heat treated at 750°C.

High-J\(_c\) films were successfully made at 750°C in an environment with an estimated O partial pressure (pO\(_2\)) of \(\approx 10^{-5}\) atm. The relatively low temperature for Y-123 phase conversion is attributed to this low pO\(_2\). It has been established that the stability limit of the Y-123 phase strongly depends on pO\(_2\) and processing temperature because Y-123 decreases as the pO\(_2\) decreases. The heat-treatment temperature can be further lowered by increasing water vapor pressure in the sweep gas in the case of both the TFA or BaF\(_2\) processes. Water vapor is known to enhance the decomposition of BaF\(_2\), and consequently the elimination of fluorine as well, allowing the Y-123 phase to form and develop texture at lower temperatures. Our results are consistent with the trend established by the data at higher pO\(_2\) values and with a room-temperature water bubbler.

Current Transport Across Y-123 Grain Boundaries

There is evidence that the J\(_c\) of grain boundaries (GBs) in high-temperature superconductors does not drop as quickly with magnetic field H as might have been expected from a simple Josephson junction model, in which the envelope of the Fraunhofer pattern goes as 1/H. In very low fields, pinning of Josephson vortices by the meandering of thin-film, [001] tilt, bicrystal GBs in Y-123 has been shown (K. E. Gray, M. B. Field, and D. J. Miller, *Phys. Rev. B* 58, 9543 [1998]) to enhance J\(_c\). However, as the spacing between Josephson vortices decreases in higher fields, this long wavelength pinning potential due to
Fig. 8. Inductive $J_c$ of Y-123 films vs. processing temperature.

meandering becomes less effective. Gurevich and Cooley (A. Gurevich and L. D Cooley, Phys. Rev. B 50, 13563 [1994]) proposed a new mechanism for an enhanced GB critical current arising from pinned Abrikosov vortices in the banks of a GB, which present a static, quasiperiodic pinning potential to pin GB vortices. Their calculations, which predict, e.g., a peak in $J_c(H)$, are in the low-field limit, but the central concept can be extrapolated to higher fields. This pinning mechanism exhibits optimal effectiveness if the Abrikosov and Josephson vortices have the same spacing, i.e., when the magnetic flux density in the GB and the banks are equal. In that case, there is one potential well for pinning per Josephson vortex.

We have obtained data as a function of magnetic field on three types of bicrystal GBs of high-$T_c$ superconductors that show a peak in the critical current and an unusual inverse hysteresis upon field cooling. These results support a new mechanism for an enhanced GB critical current, that arises from interactions of GB vortices with pinned Abrikosov vortices in the banks of a GB, as suggested by Gurevich and Cooley. A substantial fraction of this enhancement also occurs upon exceeding the critical current of the grains after zero-field cooling. A bulk GB and an isolated GB from a coated conductor showed qualitatively identical results,
whereas a 24° artificial GB made on a bicrystal substrate showed enhancements of at least a factor of 10 (Figs. 9 and 10).

We have discovered another method, besides field cooling, to introduce Abrikosov vortices into the grains and to enhance the critical current. After cooling in zero field, if the current exceeds the threshold for flux creep, Abrikosov vortices are injected into the banks of the GB. These can play the same pinning role as the Abrikosov vortices introduced by field cooling, and

![Graph showing voltage vs. current across bicrystal grain boundary at 35 K; field-cooled specimen exhibits much larger $J_c$. ZFC = zero-field-cooled; FC = field-cooled.]

Fig. 9. Voltage vs. current across bicrystal grain boundary at 35 K; field-cooled specimen exhibits much larger $J_c$. ZFC = zero-field-cooled; FC = field-cooled.
thus increase the critical current of the GB. The increase can be a significant fraction (∼1/2) of the increase obtained by field cooling. However, by analyzing the temporal voltages during current pulses, evidence was found for heating effects. Thus, the injection of vortices into the grains could be akin to field cooling. Shorter pulses (∼2 µs) eliminated heating, so the much smaller, but definitive, enhancements of critical current must be due to Lorentz-force-driven vortex injection. The enhancements depended mostly on the magnitude of the pulse current and only weakly on the number of pulses.

In summary, we found strong support for the conceptual model of Gurevich and Cooley, in which GB vortices are pinned by Abrikosov vortices in the banks of the GB. This conclusion has some interesting and possibly important consequences. It provides a mechanistic basis to understand the high-field behavior of granular high-T_c superconductors. It also points to the potential for improved performance (i.e., higher critical currents), in applications where the critical current is affected by GBs, by decorating the GB banks with pinned Abrikosov vortices.
Interactions

Balu Balachandran attended the 9th International Superconductivity Industry Summit (ISIS-9) in Copenhagen, Denmark, on Oct. 1–3.

Balu Balachandran visited the University of Cincinnati on Oct. 20 and presented a seminar on the development of HTSs for electric power applications.

On Oct. 24, Balu Balachandran, John Hull, and Y. S. Cha visited Southern California Edison, Los Angeles, for HTS discussions.

John Hull and Balu Balachandran participated at the Boeing flywheel SPI project review meeting in Seattle on Nov. 16.

Vic Maroni, Dean Miller, and Balu Balachandran presented papers at the Materials Research Society Conference in Boston during Nov. 27–Dec. 1.

Vic Maroni and Balu Balachandran presented papers at the THERMEC’2000 Conference in Las Vegas on Dec. 4–5.


In early December, Dr. Elvira Ibragimova of the Institute of Nuclear Physics, Tashkent, Uzbekistan, visited Argonne and discussed collaborative work with Mark Kirk of the Materials Science Division. She also met with Ken Goretta to discuss strategies for increasing transport $J_c$ in superconductors.

List of Publications and Presentations

Published or presented:


Submitted


1998–2000 Patents

Method and apparatus for measuring gravitational acceleration utilizing a high temperature superconducting bearing
John R. Hull
U.S. Patent 6,079,267 (June 27, 2000).

Engineered flux pinning centers in BSCCO, TBCCO and Y-123 superconductors
Kenneth C. Goretta, Michael T. Lanagan, Jieguang Hu, Dean J. Miller, Suvankar Sengupta, John C. Parker, U. Balachandran, Donglu Shi, and Richard W. Siegel

Passive fault current limiting device
Daniel J. Evans and Yung S. Cha
Automatic HTS force measurement instrument
Scott T. Sanders and Ralph. C. Niemann

Method and etchant to join Ag-clad BSCCO superconducting tape
Uthamalingam Balachandran, A. N. Iyer, and J. Y. Huang

Elongated Bi-based superconductors made by freeze dried conducting powders
Uthamalingam Balachandran, Milan Leovic, and Nicholas G. Eror

Thin-film seeds for melt processing textured superconductors for practical applications
Boyd W. Veal, Arvydas Paulikas, Uthamalingam Balachandran, and Wei Zhong

Superconductor composite
Stephen E. Dorris, Dominick A. Burlone, and Carol W. Morgan

Surface texturing of superconductors by controlled oxygen pressure
Nan Chen, Kenneth C. Goretta, and Stephen E. Dorris

Method for synthesizing and sinter–forging Bi–Sr–Ca–Cu–O superconducting bars
Nan Chen, Kenneth C. Goretta, and Michael T. Lanagan

Mixed-mu superconducting bearings
John R. Hull and Thomas M. Mulcahy