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## ORNL Superconducting Technology Program for Electric Power Systems

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Annual Report for FY 1997



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ORNL SUPERCONDUCTING TECHNOLOGY PROGRAM  
FOR ELECTRIC POWER SYSTEMS

ANNUAL REPORT FOR FY 1997

Compiled by  
R. A. Hawsey  
A. W. Murphy

Edited by  
W. S. Koncinski  
L. M. O'Hara

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Prepared by  
OAK RIDGE NATIONAL LABORATORY  
P.O. Box 2008  
Oak Ridge, TN 37831-6285  
Managed by  
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for the  
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# Contributors

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D. B. Beach	P. M. Martin
J. D. Budai	J. E. Mathis <sup>3</sup>
D. K. Christen	B. W. McConnell
J. A. Demko	D. P. Norton
R. Feenstra	M. Paranthaman
A. Goyal	C. Park <sup>3</sup>
R. A. Hawsey	I. Sauers
E. Hatfield	S. W. Schwenterly
Q. He <sup>1</sup>	A. Sheth <sup>1</sup>
H. Hsu <sup>2</sup>	C. J. Simon <sup>1</sup>
D. R. James	V. K. Sikka
H. R. Kerchner	A. Singhal <sup>3</sup>
D. M. Kroeger	E. D. Specht
V. Lasrado <sup>1</sup>	J. P. Stovall
D. F. Lee	E. Y. Sun
F. A. List	D. T. Verebelyi <sup>3</sup>
J. W. Lue	R. K. Williams

---

<sup>1</sup>The University of Tennessee

<sup>2</sup>Imtech Corporation

<sup>3</sup>Postdoctoral research fellow

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# Acronyms and Initialisms

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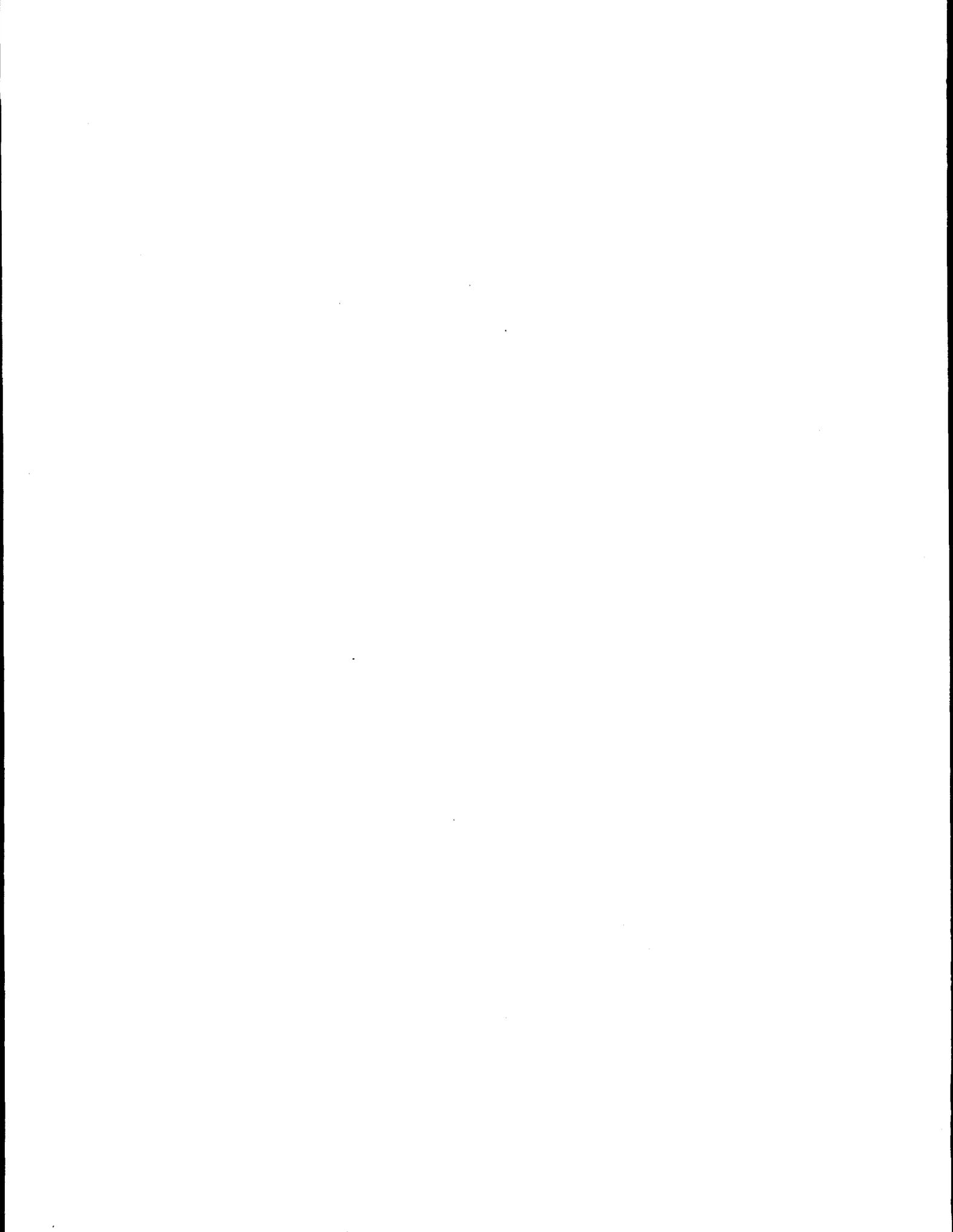
ac	alternating current
AEM	analytical electron microscopy
ASC	American Superconductor Corporation
BKD	backscatter Kikuchi diffraction
CRADA	cooperative research and development agreement
dc	direct current
DOE	U.S. Department of Energy
DOE-HQ	DOE Headquarters
DTA	differential thermal analysis
DTA/TGA	differential thermal analysis/thermogravimetric analysis
EDS	energy-dispersive spectroscopy
FEG	field emission gun
FWHM	Full width half maximum
HTS	high transition temperature superconductivity/superconductor/superconducting
HV	high voltage
IBAD	ion-beam-assisted deposition
$I_c$	critical current
IEC	International Electric Commission
IGC	Intermagnetics General Corporation
$J_c$	critical current density
$J_e$	engineering critical current density
$K_c$	critical current per unit width of conductor ( $I_c/w$ )
LANL	Los Alamos National Laboratory
LN <sub>2</sub>	liquid nitrogen
MOCVD	metallo-organic chemical vapor deposition
MOD	metal organic decomposition
ORNL	Oak Ridge National Laboratory
PLD	pulsed-laser deposition
RABiTS™	rolling-assisted biaxially textured substrates
RBS	Rutherford Backscattering Spectroscopy
RF	radio frequency
RG&E	Rochester Gas and Electric Company
rms	root mean square
RTA	rapid thermal annealer
SAD	selected area diffraction
SEM	scanning electron microscopy
STEM	scanning transmission electron microscopy
SUNY	State University of New York
$T_c$	critical temperature/transition temperature
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
WES	Waukesha Electric Systems
XRD	X-ray diffraction
YBCO	yttrium barium copper oxide
YSZ	yttria-stabilized zirconia
Z-STEM	Z-contrast scanning transmission electron microscopy



# Executive Summary

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The Oak Ridge National Laboratory (ORNL) Superconducting Technology Program is conducted as part of a national effort by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy to develop the science and technology base needed by U.S. industry for commercial development of electric power applications of high temperature superconductivity. The two major elements of this program are wire development and applications development. This document describes the major research and development activities for this program together with related accomplishments. The technical progress reported was summarized from recent open literature publications, presentations, and information prepared for the FY 1997 Annual Program Review held July 21-23, 1997. This ORNL program is highly leveraged by the staff and other resources of U.S. industry and universities. In fact, nearly three-fourths of the ORNL effort is devoted to cooperative projects with private companies. Interlaboratory teams are also in place on a number of industry-driven projects. Patent disclosures, working group meetings, staff exchanges, and joint publications and presentations ensure that there *is* technology transfer with U.S. industry. Working together, the collaborative teams are making rapid progress in solving the scientific and technical issues necessary for the commercialization of long lengths of practical high temperature superconductor wire and wire-using systems.



## Highlights for Fiscal Year 1997

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- Critical current densities ( $J_c$ s) between 2 and 3 MA/cm<sup>2</sup> (77 K, H = 0) have been achieved for thin YBCO films on rolling assisted biaxially textured substrates (RABiTST<sup>TM</sup>). The increase in  $J_c$  over previous record values ( $1.2\text{--}1.4 \times 10^6$  A/cm<sup>2</sup>) is believed to be the result of close control of substrate temperature during deposition and the use of thin oxide buffer layers, thus eliminating some microstructural features that limit  $J_c$ , such as micro-cracks and pores. For this, all buffer layers were deposited by industrially scalable electron beam (e-beam) evaporation or radio frequency (RF) sputtering, and the YBCO was deposited by pulsed laser deposition (PLD).
- The high-temperature superconducting (HTS) cold mass subsystem [i.e., the Intermagnetics General Corporation (IGC) primary and secondary HTS coils and the Oak Ridge National Laboratory (ORNL)-designed and procured 77-K radiation shield, support plates, and cryogenic system] for the 1-MVA demonstration transformer was assembled, leak tested, and shipped to Waukesha in September. ORNL has also tested an available cryocooler and loaned it to the project. In addition, the tank vacuum system was completed, tested, and shipped. The liquid nitrogen reservoir for the 77-K shield and the cryocooler heat exchanger were shipped directly to Waukesha from the manufacturers in late July. S. W. Schwenterly visited the Waukesha plant for uncrating and testing of the cold mass subsystem. The core has been assembled at Waukesha, and final assembly of the entire transformer is under way. Final test plans for the cryogenic and vacuum systems are being completed at ORNL with the balance of the test plans being prepared at Waukesha and IGC.
- The fifth cable in a series of prototype, 1-m uninsulated test samples was tested in collaboration with Southwire Company. The prototype consisted of two pairs of oppositely wound BSCCO-2223 tapes with the inner pair uninsulated between layers and the outer pair insulated between the layers by Kapton tape. The ac losses were measured calorimetrically. As expected, the outer pair is the predominant source of ac loss when both pairs carry current because the outer pair carries about 60% of the ac current.
- A new buffer layer architecture was developed on textured nickel substrates using the e-beam evaporation technique. Epitaxial laminates of MgO/Ag/Pt or MgO/Ag/Pd were deposited on biaxially textured nickel foils. In-plane aligned MgO buffers deposited using the e-beam process may be an industrially scalable alternative to laser-deposited films. The best in-plane alignment for MgO on Pd was  $\sim 11^\circ$  full width half maximum (FWHM).
- Additional alternatives to PLD of buffer layers on textured nickel were developed. For this, an all e-beam evaporation deposited, standard CeO<sub>2</sub>/yttria-stabilized zirconia (YSZ) architecture was produced, mimicking the PLD architecture developed last year. In addition, a substrate with the combination e-beam evaporation and sputtered YSZ buffer layers was also produced. YBCO films grown on these substrates show comparable properties to the best YBCO films grown on all-PLD buffered nickel.
- The first private sector demonstration of high  $J_c$  YBCO films on ORNL's RABiTST<sup>TM</sup> was completed by cooperative research and development agreement (CRADA) partner Midwest Superconductivity, Inc. For this, Midwest deposited an  $\sim 1\text{-}\mu\text{m}$ -thick film of YBCO on RABiTST<sup>TM</sup> using their metal-organic, chemical vapor deposition process. The  $J_c$  of the 2.8-mm-wide sample was 640,000 A/cm<sup>2</sup> (77 K), measured across the full sample width, and exceeds 1 million A/cm<sup>2</sup> at 70 K. Moreover, the field dependence of the  $J_c$  and the critical current ( $I_c$ ) is as good as the films grown by PLD at ORNL.

- A BaZrO<sub>3</sub> (barium zirconium oxide) precursor solution was prepared by sol-gel synthesis through an all-alkoxide route. The work is being done to determine the feasibility of growing epitaxial buffer layers by sol-gel chemistry on metal substrates. The barium precursors were prepared by reacting barium metal with 2-methoxyethanol, and zirconium precursors were prepared by exchanging ligands between zirconium *n*-propoxide and 2-methoxyethanol. The resulting BaZrO<sub>3</sub> precursor solution was partially hydrolyzed and spin-coated on sapphire, SrTiO<sub>3</sub> (strontium titanium oxide) (100), and LaAlO<sub>3</sub> (lanthanum aluminum oxide) (100) substrates. X-ray diffraction (XRD) studies showed the presence of a single (100) cube texture for BaZrO<sub>3</sub> films on SrTiO<sub>3</sub> and LaAlO<sub>3</sub> substrates. The BaZrO<sub>3</sub> film on SrTiO<sub>3</sub> substrates had a sharp texture compared with that on LaAlO<sub>3</sub> substrates. This could be explained by the presence of a reduced lattice mismatch between the substrate and the film.
- Scale-up experiments are under way at ORNL, designed in part to provide longer lengths of RABiTST<sup>TM</sup> for YBCO deposition at ORNL, Los Alamos National Laboratory (LANL), and Midwest Superconductivity, Inc. Recently, 30-cm-long CeO<sub>2</sub>-buffered, textured-Ni substrates were fabricated for the first time using a rotating cylinder in an e-beam evaporator. Also, we fabricated a RABiTST<sup>TM</sup> sample more than 6-cm long with a layer sequence of YSZ (1000 Å)/CeO<sub>2</sub> (400 Å)/Ni (125 μm) in a static mode in the e-beam system. Detailed XRD analysis on this long substrate showed that the FWHM values for the top YSZ layers were 9–10° [in-plane epitaxy; (202) φ scan] and 6–7° [out-of-plane epitaxy; (002) ω scan].
- A test apparatus has been constructed for testing tape dielectric samples in air and liquid nitrogen at 1 atm pressure. The test rig was designed at ORNL with an International Electric Commission (IEC) standard as a guide and was fabricated at Southwire. Checkout of the test set has begun, and preliminary tests of several dielectric materials have been done using dc and ac voltages. The design and assembly of a high pressure cryogenic test system for sheet dielectrics is also proceeding. Chamber support plates have been designed and fabricated. Design of the electrode assembly is under way. A low noise ac power supply has been ordered that will allow low level partial discharge measurements to be conducted and improved voltage control for ac breakdown.
- YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> films grown on RABiTST<sup>TM</sup> carry critical current densities 10<sup>5</sup> to 10<sup>6</sup> A/cm<sup>2</sup> at 77 K and low applied magnetic fields. In the low-field and low-current regime, ac transport current studies show hysteresis energy loss (per cycle and per unit length) roughly the value expected for a superconductor of elliptic cross section. The *I<sub>c</sub>* was deduced from observed dc and dynamic current-voltage relations. The power loss rises sharply as *I<sub>0</sub>* (the maximum current in each cycle) is raised above *I<sub>c</sub>*. In the present configuration, ferromagnetic hysteresis of the Ni substrate contributes little or no loss.
- In a collaborative project with the University of Tennessee Space Institute, a dip-coating unit was assembled at ORNL for application of LaAlO<sub>3</sub> sol-gel alkoxide precursors on SrTiO<sub>3</sub> single crystal substrates. Detailed XRD studies indicated the formation of epitaxial LaAlO<sub>3</sub> films with a single cube-on-cube texture. A complex matrix of 20 different sets of growth conditions was needed to grow the films, thus providing data for future work on RABiTST<sup>TM</sup> and long-length substrates.
- High *I<sub>c</sub>* Y-123 films were grown on a RABiTST<sup>TM</sup> using e-beam evaporation exclusively for the ultrathin buffer layers. For this, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> coated conductors were fabricated with a layer sequence of YBCO/YSZ/CeO<sub>2</sub>/Ni. The cube (100) texture in the starting Ni substrates was obtained by cold-rolling followed by recrystallization. The CeO<sub>2</sub> (cerium oxide) and YSZ films were grown epitaxially on the textured-Ni substrates using an e-beam evaporation technique. The total thickness of the buffer layer was 1500 Å. The YBCO films were then grown by PLD. The biaxial texture in the YBCO layer was over 90%. A transport *I<sub>c</sub>* of 1.0 × 10<sup>6</sup> A/cm<sup>2</sup> at 75 K was obtained on a 0.76-μm-thick YBCO film in zero field.

- We have investigated several systematics regarding the superconductive transport properties of YBCO epitaxial deposits on RABiTS™. The focus of the effort was to make a comparative study of the field- and temperature-dependent  $J_c$  among different YBCO/RABiTS™ samples and with properties of the “benchmark” materials deposited on SrTiO<sub>3</sub>. In addition, a preliminary test of the bend-strain tolerance was conducted, both in compression and tension, and an assessment was made of the prospects for achieving practical current levels through this type of coated-conductor approach. YBCO films can be routinely obtained on RABiTS™ with  $J_c$  (77 K) > 0.5 MA/cm<sup>2</sup> and only one in-plane orientation when CeO<sub>2</sub> is utilized to eliminate secondary in-plane orientations. These data show that not only is YBCO the HTS material of choice for conductor applications, but also that the high-field properties of YBCO/RABiTS™ may exceed those of the prototype, YBCO/SrTiO<sub>3</sub> films. For YBCO thicknesses of ~1–3 μm, the  $J_c$  (1 T) exhibits no systematic thickness dependence, with values in the range ~100–150 kA/cm<sup>2</sup> at 64 K. Even though the present structures have a small superconductor fraction, the data at 64 K suggest that practical levels are accessible in the liquid nitrogen temperature range.
- Epitaxial buffer layers of NdAlO<sub>3</sub>, GdAlO<sub>3</sub>, YAlO<sub>3</sub>, and SrTiO<sub>3</sub> have been grown on single crystal substrates using a sol-gel technique.  $\theta$ -2 $\theta$  scans of the films indicate *c*-axis preferred orientation, and pole figure analyses verify single cube-on-cube epitaxy. FWHM values of the rocking curve and  $\phi$  scans are between 1 and 4°.
- IGC has delivered the HTS coils for the 1-MVA transformer to ORNL. The coils are constructed using several kilometers of IGC’s low-cost, surface-coated BSCCO-2212 material. The coils are approximately 1-m diameter and 1.2-m long and are the largest volume HTS coils produced to date in the United States. The coils were pretested prior to shipment by IGC and meet specifications.
- Southwire and ORNL have signed a new cooperative agreement to develop superconducting underground transmission cable technology. Recently, Southwire and ORNL’s Fusion Energy and Metals and Ceramics divisions successfully completed the first phase of research, resulting in the design and testing of four prototype, 1-m cable sections and the characterization of these cables with both dc and ac current. The new agreement provides for precompetitive research and technology development that will lead to the construction of a 30.5-m-long, three-phase HTS cable complete with dielectrics, thermal insulation, and outer enclosures. The cable will be installed between two overhead utility towers and will supply about 1250 A of current at 12.5 kV to the utility and building wire plants at Southwire Company. In this manner, the cable will be tested under real-use conditions and will verify the design of the various cable subsystems. ORNL will again be a partner in the project, supplying research, design, and testing expertise in the areas of dielectric materials, cryogenics, and superconductivity.
- Four-terminal ac impedance measurements are being carried out on superconductive YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  films grown on RABiTS™ tape. The overall signal is dominated by the non-lossy component from the 1.2 μH/m self-inductance of the 1-mm-wide strips. The smaller loss voltage obeys behavior expected for magnetic hysteretic losses, including the superconductive material in the mixed state. The present results are preliminary in a study to determine the power-loss contributions, including those from the ferromagnetic Ni substrate. Comparison is planned with results from similar YBCO films grown on nonmagnetic insulating substrates, such as SrTiO<sub>3</sub>.
- Testing of the Southwire HTS transmission line prototype 4 has been completed. The dc measurements indicate that the cable  $I_c$  using the 1-mV/cm criteria is about 975 A. The ac loss measurements

have been successfully conducted using a calorimetric method. At the ac design current of 1250 A, the prototype has an ac loss of about 1.2 W/m.

- The first foreign patent license agreement on RABiTS™ technology was issued to Midwest Superconductivity, Inc., in April 1997. In addition, a new U.S. patent license agreement was executed in July 1997 with Oxford Superconducting Technology (Carteret, New Jersey) for invention disclosure ESID-1640 (RABiTS™). A supporting joint statement of work was amended to our present CRADA with Oxford to enable further research and development of RABiTS™/YBCO tape superconductors. The initial emphasis will be on establishing in-house capability at Oxford for producing the entire RABiTS™/YBCO structure, using PLD as a basic research tool.

# Technical Progress in Wire Development

## BIAXIALLY TEXTURED $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ CONDUCTORS ON RABITS™ WITH CRITICAL CURRENT DENSITIES OF 2–3 MA/cm<sup>2</sup>

The strong dependence of critical current density ( $J_c$ ) on basal-plane grain boundary misorientation angle is well documented for most families of high transition temperature superconductors (HTS).<sup>1–5</sup> Furthermore, most applications of HTS, such as transformers, generators, and motors, require high-current-carrying capability in magnetic fields in excess of 0.1 T. The highly anisotropic, Bi-based superconductors are intrinsically limited in this regard in liquid nitrogen (65–77 K) because of thermally activated flux flow. Hence, a biaxially textured YBCO conductor is needed to meet application requirements of a high  $J_c$  in modest magnetic fields at liquid nitrogen temperatures.

Several methods have been proposed to produce biaxially textured conductors. One approach is to use ion-beam-assisted deposition (IBAD) to grow biaxially textured yttria-stabilized zirconia (YSZ) buffer layers on Ni-based superalloys.<sup>6–8</sup> This approach has produced a  $J_c$  of  $1 \times 10^6$  A/cm<sup>2</sup> (77 K, 0 T) with a 1- $\mu\text{m}$  thick YBCO film. Another method is to use industrially scalable, thermomechanical processes to impart a strong biaxial texture to the metal substrate itself, followed by epitaxial deposition of buffer layers and superconductor. This method, called RABITS™ (for rolling-assisted biaxially textured substrates), has been recently demonstrated to produce  $J_c$ s of  $3 \times 10^5$  A/cm<sup>2</sup> (77 K, 0 T) using a substrate configuration of YSZ (0.2  $\mu\text{m}$ )/CeO<sub>2</sub> (0.9  $\mu\text{m}$ )/Pd (0.02  $\mu\text{m}$ )/Ni (125  $\mu\text{m}$ ).<sup>9</sup> A different substrate configuration of YSZ (0.2  $\mu\text{m}$ )/CeO<sub>2</sub> (0.9  $\mu\text{m}$ )/Ni (125  $\mu\text{m}$ ) resulted in a  $J_c$  of  $7.3 \times 10^5$  A/cm<sup>2</sup> (77 K, 0 T).<sup>10</sup> In both of these cases, all the oxide layers, as well as the superconductor, were deposited using pulsed laser deposition (PLD). Oxide buffer layers on

textured Ni have also been deposited using electron beam (e-beam) evaporation<sup>11</sup> and sputtering.<sup>12</sup>  $J_c$ s of  $6\text{--}8 \times 10^5$  A/cm<sup>2</sup> at 77 K, 0 T have been obtained on these substrates for 1- $\mu\text{m}$  YBCO films grown by PLD. It had not been clear why  $J_c$ s on these substrates have not exceeded  $1 \times 10^6$  A/cm<sup>2</sup> at 77 K, 0 T, given the fact that an electron backscatter investigation<sup>13</sup> of hundreds of interconnected grain boundaries show that RABITS™ with nominal in-plane orientations of 7–8° full width half maximum (FWHM) contain few adjacent grain boundaries with misorientations greater than 5°.

The importance of substrate temperature on the crystalline structure of YBCO thin films produced by PLD on YSZ had been recently pointed out by both Freyhardt et al.<sup>14</sup> and Low et al.<sup>15</sup> Accordingly, it was decided to investigate whether the substrate temperature influenced the  $J_c$  (77 K, 0 T) of YBCO films on RABITS™. We report the achievement of  $J_c$ s approaching  $3 \times 10^6$  A/cm<sup>2</sup> for thin YBCO films grown epitaxially on RABITS™ using PLD. This improvement in  $J_c$  is thought to come about both by closely controlling the substrate temperature during deposition and by using thin buffer layers, thus eliminating some microstructural features that limit  $J_c$ , such as micro-cracks and pores.

Nickel substrates were prepared by cold-rolling nickel to a thickness of 125  $\mu\text{m}$ . The nickel was then annealed at a temperature of 800°C for 2 h in a vacuum of  $\sim 10^{-5}$  torr. An epitaxial layer of CeO<sub>2</sub>,  $\sim 40$  nm thick, was deposited by e-beam evaporation of cerium metal onto the nickel at 650°C. Oxidation of the nickel during the heat-up phase was prevented by the presence of a reducing gas: 4% H<sub>2</sub> in argon. The cerium oxide was formed by the in situ reaction of the cerium with water vapor present ( $1 \times 10^{-5}$  torr) in the vacuum system during the deposition.<sup>11,12</sup> The deposition of CeO<sub>2</sub> was followed by the deposition of a 500-nm-thick layer of YSZ oxide by radio-

## 1-2 Technical Progress in Wire Development

frequency (RF) sputtering of a YSZ target while the substrate was maintained at 780°C in a  $2 \times 10^{-2}$  torr background of 4% H<sub>2</sub> in Ar.

The RABiT<sup>SM</sup> (nickel-plus-buffer-layers unit) was then silver-pasted to the heater in the PLD chamber (Neocera). Because observations of the heater surface with an infrared pyrometer showed significant differences in the surface temperature from that indicated by the thermocouple located in the heater block, thermocouple wires were attached directly to the nickel substrate to monitor and control the substrate temperature as accurately as possible during the depositions. A Lambda Physik EMG200 excimer laser, operating at a wavelength of 308 nm, provided 200 mJ light pulses, which, when focussed by a lens with a focal length of 350 mm, produced a 3 J/cm<sup>2</sup> fluence at the YBCO target. During the deposition, the oxygen pressure was maintained at 200 mtorr at a flow rate of 15 scc/min. To minimize both the rate of cone formation and changes in stoichiometry on the surface of the YBCO during laser irradiation, the YBCO target was rotated at 21 revolutions per minute.

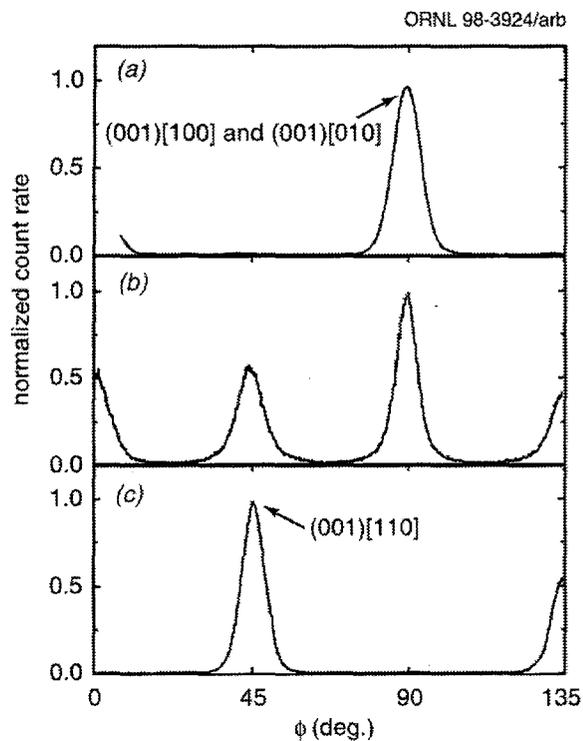
Three substrate temperatures, 740°C, 765°C, and 785°C, were used to find the optimum for the given conditions. These temperature conditions will be hereafter referred to as treatment A, treatment B, and treatment C, respectively. Temperature control was provided by a Eurotherm model 808 programmable temperature controller. The YBCO growth rate was ~0.04 nm/s. After the deposition was complete, the sample was cooled at a rate of 5°C/min in 300 torr of oxygen to 500°C to ensure full oxygen uptake by the YBCO, at which point additional oxygen was added to bring the pressure to 500 torr. This temperature and pressure was maintained for 4 h. Finally, the substrate was cooled to room temperature at a rate of 1°C/min. Four silver electrical contacts were then sputtered onto the YBCO surface.

Comparison of thermocouple substrate temperature readings with the heater-block temperature readings confirmed the IR pyrometer observation that the heater surface

was much hotter. Moreover, it was observed that the substrate temperature would fall by as much as 25°C during the course of the deposition if the temperature controller maintained a constant heater-block temperature. Although the authors were unaware of the fact at the time, this is in concordance with the Kiss et al.<sup>16</sup> IR observation of substrate temperature changes of PLD of YBCO on MgO. For the present case, the Eurotherm controller was able to keep the temperature stable to within 1°C when controlling for substrate temperature. An alternative method for maintaining tight control of the substrate temperature has been reported by Freyhardt et al.<sup>14</sup> who keep the substrates within a blackbody-like enclosure, exposing the substrates only when the laser fires.

XRD  $\theta$ -2 $\theta$  scans (Philips) for all three cases show strong 00 $l$  orientation for the YBCO. In addition,  $\phi$  scans, as shown in Fig. 1.1, show cube-on-cube structure with an 8.2° FWHM in-plane orientation and a 5.6° FWHM for  $c$ -axis orientation. Electrical transport measurements were performed using 4-probe techniques. Resistivity measurements employed a constant current of 40 mA. The  $J_c$  measurements were made in a different 4-probe device, with the capability of applying magnetic fields at various orientations. A 1 $\mu$ V/cm criterion was used for transport  $J_c$ . Film thicknesses were measured by etching the YBCO and performing profilometer measurements. X-ray energy-dispersive spectroscopy (EDS) was used to ensure that all the YBCO had been etched away from the YSZ layer. Thickness measurements were also confirmed using Rutherford Backscattering Spectroscopy (RBS). The measured critical temperatures ( $T_c$ ) showed a nearly linear relationship with deposition temperature over the narrow deposition temperature range, with values of 85.8 K for treatment A, 86.6 K for treatment B, and 87.6 K for treatment C. The transition widths were all less than 2 K.

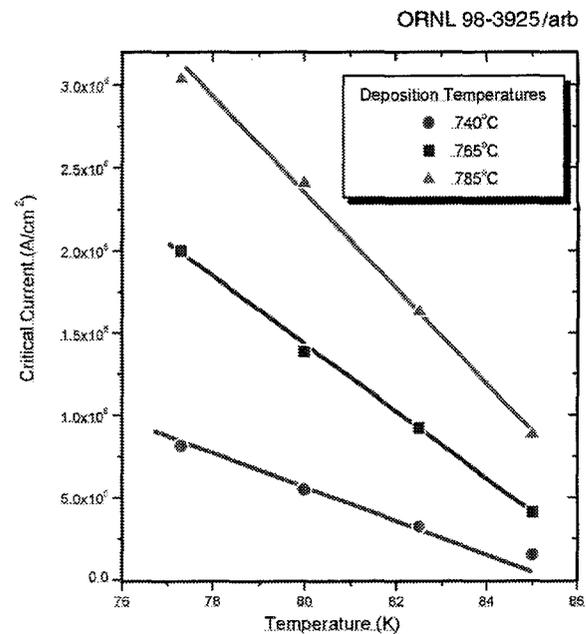
Zero-field measurements at 77 K revealed an increase in  $I_c$  with increasing deposition temperature as shown in Fig. 1.2. However, measurement of  $J_c$  for the best sample,



**Fig. 1.1. XRD azimuthal ( $\phi$ ) scans indicating the in-plane alignment of YBCO/YSZ/CeO<sub>2</sub> films on thermo-mechanically textured Ni substrate. (a) (102) + (012) planes of treatment B, illustrating (001)[100] and (001)[010] alignment. (b) (103) + (013) planes of treatment A, illustrating mixed alignment. (c) (103) + (013) planes of treatment C, illustrating (001)[110] alignment.**

treatment C, was limited by current-contact heating. To estimate the value at 77 K, an extrapolation of the data from three higher temperatures was made. The resulting linear fit ( $R^2 = 0.9999$ ) gave a  $J_c$  (77 K) of  $3.2 \times 10^6$  A/cm<sup>2</sup>. The sample deposited at 765°C had a slightly lower  $J_c$  at 77 K (directly measured) of  $2.4 \times 10^6$  A/cm<sup>2</sup>, whereas the 740°C sample had a much lower  $J_c$  at 77 K of  $0.81 \times 10^6$  A/cm<sup>2</sup>. Film thicknesses ranged from 206 nm to 250 nm, with all the substrates being 3 mm wide.

For the best film,  $J_c$  measurements were made at 77 K as a function of applied magnetic field, for  $H \parallel c$ . The field dependence was similar

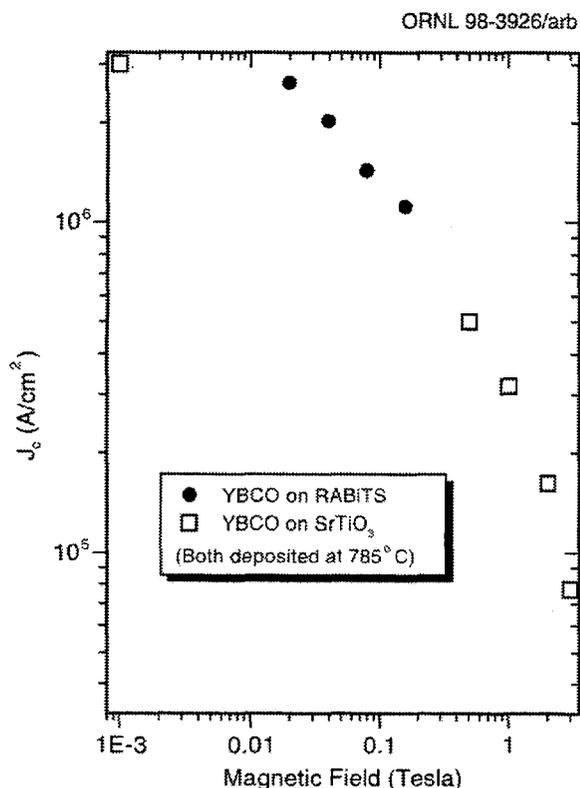


**Fig. 1.2. Variation in zero-field  $I_c$  as a function of temperature for the three deposition temperatures.**

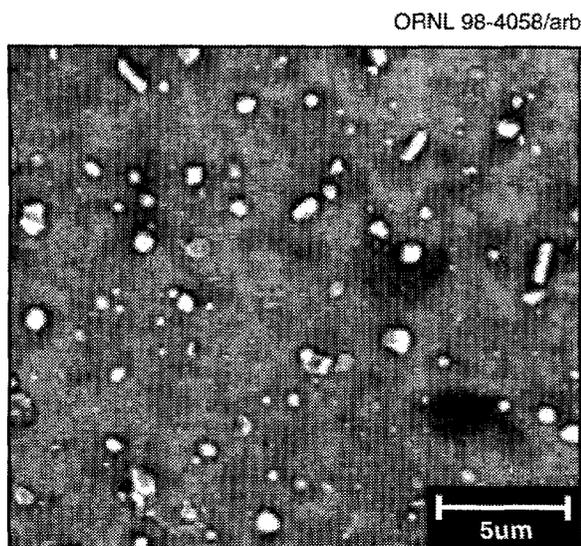
to that for epitaxial films on single-crystal substrates and demonstrates strongly linked behavior. With each of the three samples, a control sample of SrTiO<sub>3</sub> was placed in the PLD chamber alongside the RABiTSTM. Figure 1.3 shows  $J_c$  vs  $H$  for the YBCO film on the SrTiO<sub>3</sub> crystal made together with the YBCO film on the RABiTSTM sample C. The zero-field  $J_c$  at 77 K for the film on SrTiO<sub>3</sub> was measured to be  $\sim 3 \times 10^6$  A/cm<sup>2</sup>.

Scanning electron microscope (SEM) images of the best film, shown in Fig. 1.4, display a very dense YBCO morphology, with very little structure evident. No evidence of any [100]/[010] micro-cracking is observed in the YBCO layer. This is in contrast to what was typically seen in buffer layers with a 0.9- $\mu$ m-thick CeO<sub>2</sub> layer and a 0.2- $\mu$ m-thick YSZ layer as summarized in a recent overview paper.<sup>17</sup>

In conclusion, PLD of YBCO on buffer layers deposited by industrially scalable e-beam evaporation and RF sputtering methods onto nickel resulted in superconducting  $I_c$ s and flux



**Fig. 1.3.**  $J_c$  vs  $H$  for sample C and for a YBCO film grown epitaxially on SrTiO<sub>3</sub> alongside the RABiTS™.



**Fig. 1.4.** SEM photograph of the YBCO layer showing the dense surface morphology.

pinning behavior comparable with the best obtained for YBCO on single-crystal substrates. It is possible that the achievement of the higher  $J_c$ s of YBCO on RABiTS™ may be attributed to the closer temperature control of the substrate temperature and the use of thinner buffer layers.

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## PULSED-LASER DEPOSITION OF OXIDE BUFFER LAYERS AND YBCO ON ROLLED-TEXTURED (001) Ni

### Reproducibility of $J_c$ in YBCO/Buffer Layers/Ni Structures

Initial results have identified the YBCO/buffer layer oxides/rolled-textured (001) Ni architecture as a viable approach to producing a deposited HTS conductor. Efforts have continued in understanding and improving the properties of these multilayer structures deposited by a number of techniques, including PLD. Figure 1.5 shows the value of  $J_c$  for a number of YBCO films grown on RABiTS™ in which both the buffer layers and YBCO were deposited using PLD. Relatively thick ( $> 0.5 \mu\text{m}$ ) YBCO films have been obtained on rolled textured Ni, with  $J_c$  as high as  $1.4 \text{ MA/cm}^2$ . However, the sample-to-sample variation is relatively high. Much of the scatter observed in the plot is the result of samples that were synthesized under conditions that were not optimal. Nevertheless, the scatter in  $J_c$  reflects

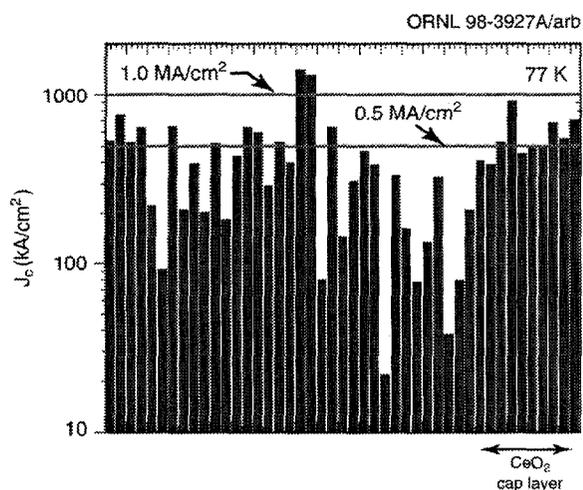


Fig. 1.5. Plot of  $J_c$  for various YBCO/buffer layers/Ni samples. YBCO film thickness is  $> 0.5 \mu\text{m}$  for all samples considered.

the need to improve the reproducibility in the film properties.

One important factor to consider for the YBCO/YSZ/CeO<sub>2</sub>/Ni architecture involves the in-plane orientation of the YBCO films on the YSZ layers. Because of a large lattice mismatch, two distinct in-plane orientations of YBCO on (100) YSZ are often observed as illustrated in the XRD  $\phi$ -scan in Fig. 1.6. The presence of two in-plane orientations leads to  $45^\circ$  grain boundaries and a subsequent reduction in  $J_c$ . Previous work has shown that various oxide buffer layers, including CeO<sub>2</sub>, can significantly suppress one of these orientations. Growing YBCO/CeO<sub>2</sub>/YSZ/CeO<sub>2</sub>/Ni structures with a thin ( $\sim 200 \text{ \AA}$ ) CeO<sub>2</sub> cap layer on the YSZ improves the reproducibility of  $J_c$ . As seen in Fig. 1.5, YBCO films can be routinely obtained on RABiTS™ with  $J_c(77 \text{ K}) > 0.5 \text{ MA/cm}^2$  and

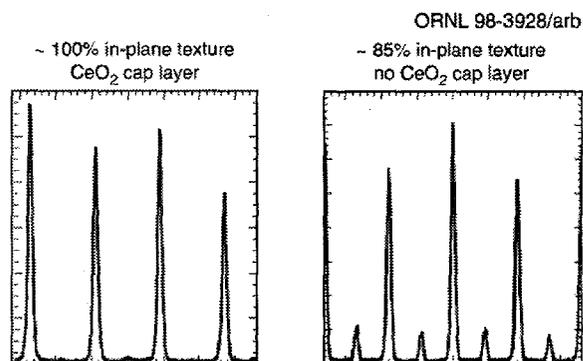


Fig. 1.6. XRD  $\phi$ -scans for YBCO films deposited on RABiTS™ with and without CeO<sub>2</sub> cap layers.

only one in-plane orientation when CeO<sub>2</sub> is utilized to eliminate secondary in-plane orientations. Efforts continue to understand other factors, such as strain or microstructure, that influence  $J_c$  for YBCO films on RABiTS™.

### Transmission Electron Microscopy of YBCO/Buffer Layers/Ni Structures

A fundamental understanding of the epitaxial oxide/metal multilayer structure is

crucial in efforts to effectively characterize and further improve the performance of RABiTS™-based HTS conductors. Microstructural analysis using cross-section transmission electron microscopy (TEM) has been performed on YBCO/buffer layer/Ni structures. Figure 1.7 shows results from a cross-section TEM image of a YBCO/YSZ/CeO<sub>2</sub>/Ni structure. This cross section reveals each of the oxide layers and includes a grain boundary that originates from the Ni substrate. There are several features of interest in this micrograph. First, significant oxidation of the nickel substrate is evident at the Ni/CeO<sub>2</sub> interface. It is assumed that this NiO layer forms after the nucleation of (100) CeO<sub>2</sub> occurs on the (100) Ni surface. The formation of a NiO layer at the metal/oxide layer interface should have significant influence on the mechanical and adhesive properties of the film because of stresses related to the volume change with the oxidation of Ni at the buried interface. From the image, we note that the morphology of the thermally etched grain boundary is reproduced in all of the oxide layers. We also

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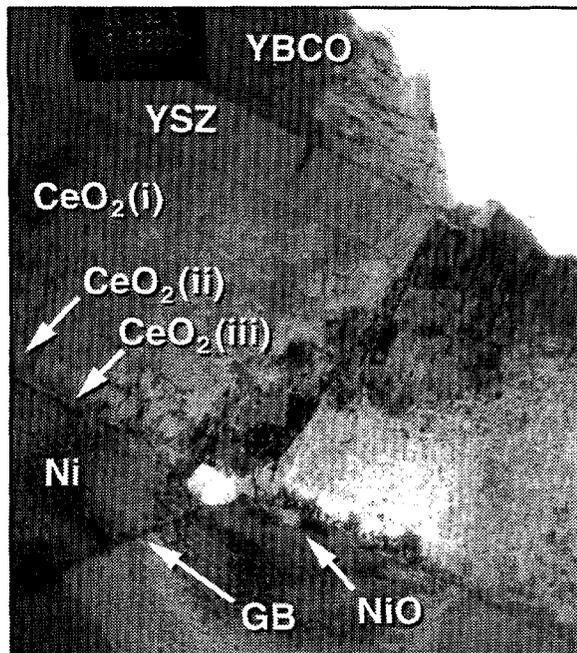


Fig. 1.7. Cross-section TEM image of YBCO/YSZ/CeO/Ni structure.

observe that the microstructure of the CeO<sub>2</sub> is dependent on film growth conditions, with distinct microstructures observed for CeO<sub>2</sub> deposited in a vacuum, hydrogen, or oxygen background. The YSZ layer also displays a distinctive columnar microstructure. Future efforts will focus on understanding how specific oxide microstructures affect the mechanical properties of these multilayer structures.

Microstructural characterization of YBCO on RABiTS™ using plan-view Z-contrast scanning transmission electron microscopy (Z-STEM) provides insight regarding the atomic structure of the YBCO grain boundaries for films deposited on these substrates. Figure 1.8 shows an atomic resolution Z-STEM image of a typical YBCO low-angle grain boundary that is commonly observed in *c*-axis oriented YBCO films deposited on rolled-textured (001) Ni tape. These low-angle grain boundaries in epitaxial YBCO film on RABiTS™ originate from the grain structure in the biaxially textured (001) Ni tape. As seen in the figure, the atomic structure of the grain boundary closely resembles that observed for YBCO films on SrTiO<sub>3</sub> bicrystals, consisting of a "clean" boundary with a regular array of dislocation cores. From the micrograph, there is no evidence for impurity phases, NiO,

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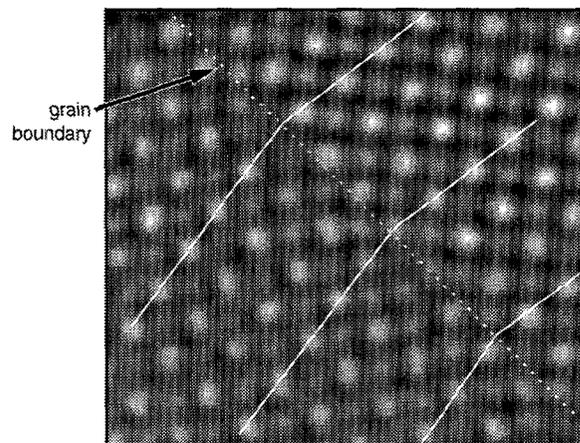


Fig. 1.8. Plan-view Z-contrast scanning electron microscopy image of a YBCO grain boundary for a *c*-axis oriented film deposited on rolled-textured (001) Ni.

or misoriented YBCO grains at the boundary. This is consistent with the relatively high  $J_c$  that are observed for YBCO/buffer layers/(001) biaxially textured Ni structures.

### Bend Strain Tolerance of $J_c$

An important aspect for any HTS wire technology involves the degree to which the conductor can be bent without damaging the conductor. To address this issue, bend strain tolerance measurements have been performed on RABiTS™. The bend strain tolerance for two of YBCO/buffer layers/Ni tapes measuring both tensile and compressive strain is shown in Fig. 1.9. For both of these samples, the buffer layers and YBCO were deposited using PLD. The samples were placed in strain by deforming the tapes over a selected radius of curvature at room temperature. The strain is then removed (sample curvature is removed) for  $J_c$  measurement in liquid nitrogen. Each data point

in the plots represents bending, straightening, and thermal cycling. The initial  $J_c$  (77 K) for each sample was greater than 0.5 MA/cm<sup>2</sup>. For compressive strain, significant degradation of  $J_c$  was not observed until the bend strain exceeded 0.7%, at which point failure was catastrophic. SEM images of this sample after strain tolerance measurements indicate the presence of long cracks that extend a significant fraction of the sample width. The observation of long cracks in the YBCO film is consistent with the catastrophic failure that was observed in the behavior of  $J_c$ . For the case of tensile strain, a significant decrease in  $J_c$  with applied strain began at ~0.3%. In contrast to the behavior observed for compressive strain, failure of the sample with tensile strain was more gradual, with complete failure ( $J_c = 0$ ) observed for a strain of ~0.5%. The SEM micrograph for this sample shows an array of short fracture lines with the density of cracks higher for the tensile strain than for the sample placed in

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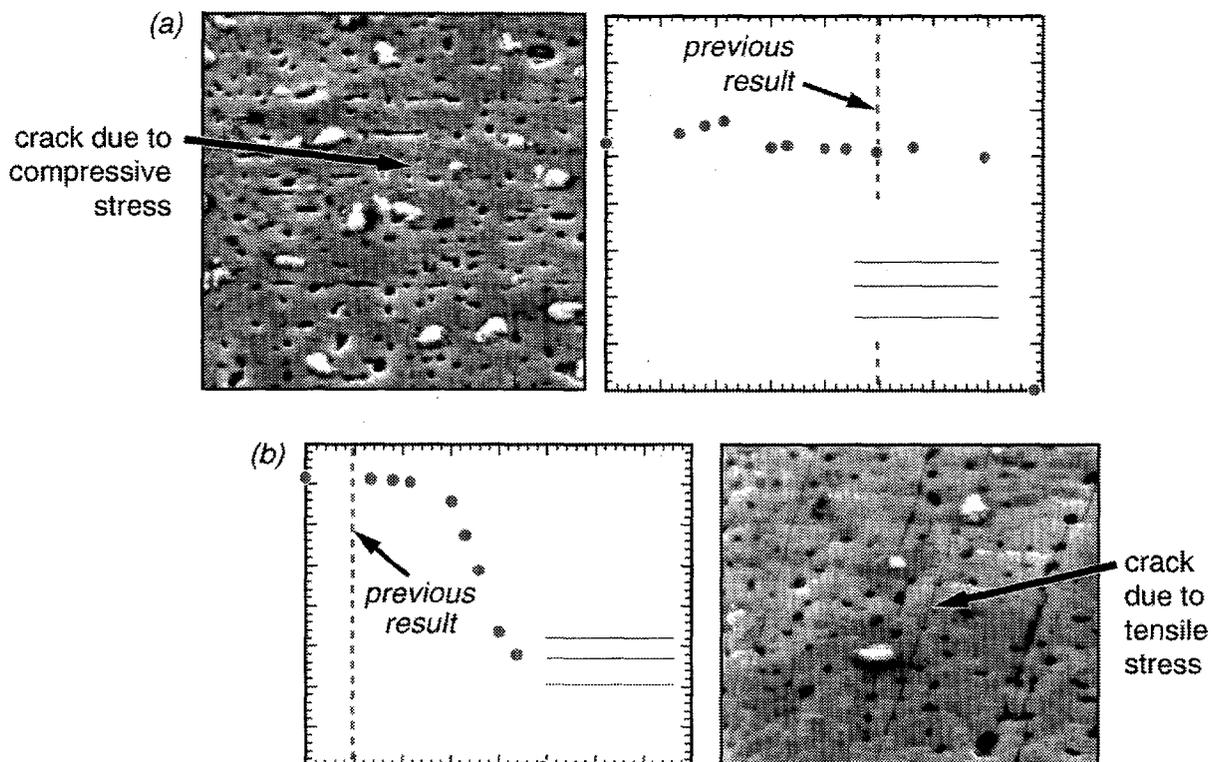


Fig. 1.9. Bend strain tolerance for two YBCO/buffer layers/Ni tapes measuring (a) compressive and (b) tensile stress.

compression. The appearance of short cracks is consistent with a gradual failure of the film for tensile strain. The strain tolerance for these samples is better than previous results in which the total oxide layer thickness was significantly larger. Future efforts will continue to focus on the effects of specific multilayer oxide architectures on the strain tolerance.

### Efforts To Engineer High $J_c$ Conductors Using Thin Rolled-Textured Ni

The use of thinner (001) Ni tapes holds the promise of achieving high engineering critical current densities ( $J_c$ ) with 1–2- $\mu\text{m}$ -thick YBCO films. Previous results have shown that Ni could be rolled-textured to a thickness of  $\sim 25\ \mu\text{m}$  with in-plane and out-of-plane texture similar to that obtained for 125- $\mu\text{m}$ -thick Ni tapes. Initial efforts have focused on the epitaxial growth of the YBCO/YSZ/CeO<sub>2</sub> oxide architecture on 25- $\mu\text{m}$ -thick Ni tapes using PLD. Figure 1.10 shows the XRD rocking curves for the buffer and YBCO layers. Four-circle XRD shows that the oxide layers are epitaxial and in-plane aligned with respect to the Ni substrate. The best result achieved to date with 25  $\mu\text{m}$ -thick Ni substrates is  $J_c$  (77 K)  $\sim 200\ \text{kA}/\text{cm}^2$ .

Significantly higher values for  $J_c$  are anticipated as superior procedures for handling these relatively thin metal tapes are developed. Future efforts will also focus on understanding the effect of substrate thickness on the conductor properties, particularly when considering the difference in thermal expansion for the oxides layers and the thin Ni tape.

### Facility Development for Long-Length Conductor

Efforts to fabricate RABiTS™-based YBCO conductors with length on the order of 10–100 cm have resulted in facility development for continuous film deposition using PLD. A radiant heater capable of uniformly heating 1-cm-wide Ni tapes up to 800°C in an oxygen ambient atmosphere has been purchased from Thermionic Laboratory. This radiant heater is necessary for achieving long-length and two-sided deposition of YBCO on RABiTS™. Initial efforts will focus on 10-cm-long samples. A linear translation substrate holder capable of accommodating 10-cm-long samples has been designed and assembled. For tape length greater than 10 cm, a reel-to-reel tape drive system has been designed. This system includes vacuum

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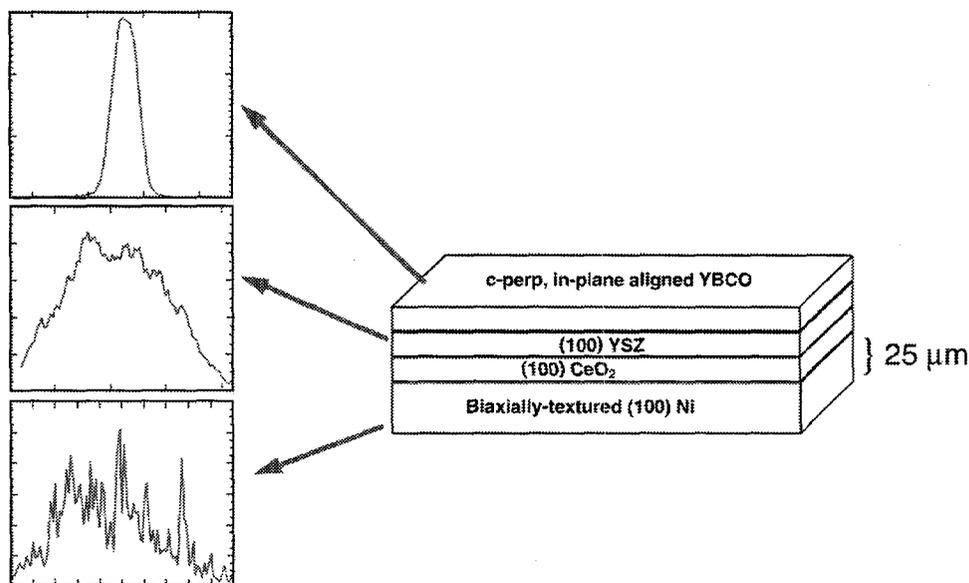


Fig. 1.10. XRD rocking curves for YBCO/YSZ/CeO<sub>2</sub> oxide architecture on a 25- $\mu\text{m}$ -thick rolled-textured Ni tape.

chamber attachments with stepping motors to manipulate 1-cm-wide metal tapes of arbitrary lengths.

### HIGH $J_c$ YBCO FILMS ON BIAXIALLY TEXTURED Ni WITH OXIDE BUFFER LAYERS DEPOSITED USING ELECTRON BEAM EVAPORATION AND SPUTTERING

High  $J_c$  has been recently demonstrated for epitaxial YBCO films grown on RABiTS™.<sup>1,2</sup> For these first demonstrations of high  $J_c$ , both the buffer layers (CeO<sub>2</sub> and YSZ) and the YBCO were deposited epitaxially by in situ PLD without intermediate exposure of the substrate to atmosphere. For a practical superconducting wire technology, a more flexible fabrication scheme and an easily scalable deposition technique compared to in situ PLD is desirable. To investigate the possibility of obtaining high  $J_c$  YBCO conductors using more flexible and easily scalable ex situ methods for deposition, buffer layers have been grown on biaxially textured nickel by (a) exclusively e-beam evaporation (CeO<sub>2</sub> and YSZ) and (b) a combination of e-beam evaporation (CeO<sub>2</sub>) and RF magnetron sputtering (YSZ). Although methods to deposit oxide buffer layers (CeO<sub>2</sub> and YSZ) exclusively by e-beam evaporation<sup>3</sup> and exclusively by sputtering<sup>4</sup> have been reported previously, no attempts to grow YBCO on these buffered substrates have been reported.

#### Experimental

Biaxially textured Ni substrates were formed by consecutive rolling of a polycrystalline, randomly oriented high purity (99.99%) bar to total deformations greater than 95%, followed by recrystallization.<sup>1</sup> Examination of (111) and (200) pole figures of an as-rolled Ni tape shows localization of intensities along the {112}<111> and the {123}<634> orientations along the  $\beta$ -fiber or

the skeleton line, consistent with the formation of a sharp copper-type rolling texture. Controlling the surface condition of the work rolls allowed substrates with surfaces with a root mean square (rms) roughness of ~10 nm to be obtained. The substrate was then annealed in situ in a laser ablation chamber at 900°C for 2 h in 4% H<sub>2</sub> in Ar, resulting in the formation of a sharp {100}<100> cube texture. Typical samples showed X-ray  $\omega$ - and  $\phi$ -scans with FWHM of 6° and 7°, respectively. Grain boundary studies of the substrate using electron backscatter Kikuchi diffraction (BKD) showed that more than 95% of the boundaries had misorientations less than 5°.<sup>5</sup>

The deposition of CeO<sub>2</sub> was accomplished by e-beam evaporation and is described in detail elsewhere.<sup>3</sup> CeO<sub>2</sub> was deposited from a cerium metal melt at a substrate temperature of 625°C in  $2 \times 10^{-5}$  torr of 4% H<sub>2</sub>/96% Ar. The CeO<sub>2</sub> was deposited at a rate of 0.1 nm/sec to a thickness of 40 nm as determined by a quartz crystal monitor. Following deposition, the substrate was cooled in  $2 \times 10^{-5}$  torr of 4% H<sub>2</sub>/96% Ar to < 200°C and then was allowed to cool to room temperature in air at 1 atm.

Epitaxial YSZ was next deposited by either e-beam evaporation or RF magnetron sputtering. In both cases, the nominal composition of the starting material was 99.9% ZrO<sub>2</sub> with 10–15 wt % Y<sub>2</sub>O<sub>3</sub>. For e-beam evaporation of YSZ, a substrate of CeO<sub>2</sub> on Ni was cleaned in methanol and mounted in the evaporation chamber. Next it was annealed at 700°C in 1 torr of 4% H<sub>2</sub>/96% Ar for 60 min. Deposition of YSZ was accomplished at a substrate temperature of 700°C in  $2 \times 10^{-5}$  torr of 4% H<sub>2</sub>/96% Ar. The YSZ was deposited at a rate of 0.1 nm/sec to a thickness of 100 nm. Following deposition, the substrate was cooled in  $2 \times 10^{-5}$  torr of 4% H<sub>2</sub>/96% Ar to < 200°C and then was allowed to cool to room temperature in air at 1 atm. For deposition of YSZ by sputtering, a substrate of CeO<sub>2</sub> on Ni was mounted directly in the sputtering chamber

without cleaning in methanol. It was next annealed at 780°C in 10 mtorr of 4% H<sub>2</sub>/96% Ar for 10 min. Deposition of YSZ was accomplished at a substrate temperature of 780°C in 10 mtorr of 4% H<sub>2</sub>/96% Ar. The YSZ was deposited at a rate of 0.1 nm/sec to a thickness of 750 nm. The sputter target was parallel to and 5 cm from the substrate surface. After deposition, the substrate was allowed to cool to < 200°C in 10 mtorr of 4% H<sub>2</sub>/96% Ar before exposure to air at 1 atm.

YBCO was deposited on the YSZ/CeO<sub>2</sub>/Ni substrates at 780°C in an O<sub>2</sub> pressure of 185 mtorr by PLD using a KrF excimer laser.<sup>2</sup> The substrates were cooled after deposition to 400°C at 10 C/min and then exposed to 700 mtorr of oxygen. The thickness of the YBCO films was 1 μm as determined for each substrate by profilometry.

The samples were characterized using a field emission Hitachi SA-4500 SEM, a Philips XL30 field emission microscope equipped with an electron backscatter diffraction detector, and by a Rigaku X-ray diffractometer. Electrical properties were measured using a pulsed current system reported previously.<sup>6</sup>

## Results and Discussion

The typical microstructures of YBCO films grown by laser ablation on RABiTS™ in which the buffer layers were deposited by exclusively

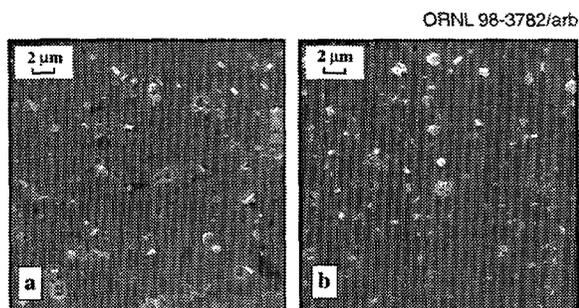


Fig. 1.11. (a) Scanning electron micrograph of a YBCO film deposited on exclusively e-beam buffered nickel. (b) Scanning e-beam micrograph of a YBCO film deposited on e-beam/sputtered buffered nickel.

e-beam evaporation or a combination of e-beam evaporation and sputtering are shown in Fig. 1.11. The micrographs were taken at a magnification of 1000 × and show no evidence of any microcracks. Moreover the films appear to be very dense and continuous and to contain some surface second phase particles.

Similar to samples prepared by in situ PLD, the out-of-plane alignment of YBCO is good with a rocking curve width of ~2° FWHM. The in-plane alignment for these samples is more complex. Figure 1.12 shows the in-plane texture of YBCO film grown on the substrate in which

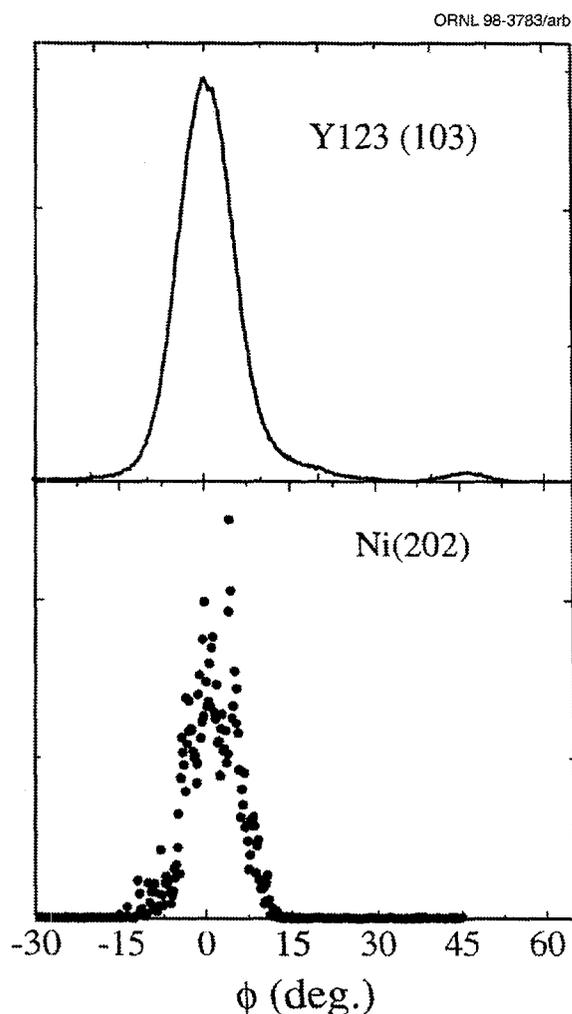
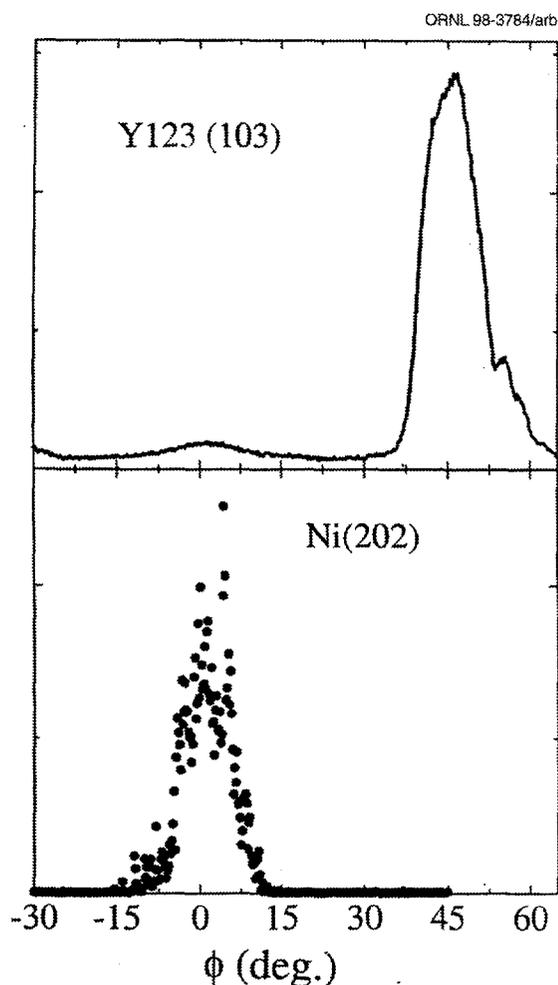


Fig.1.12. (a) X-ray phi scan of a YBCO film on RABiTS™ in which the buffers were put down exclusively by e-beam evaporation and (b) X-ray phi scan of Ni.



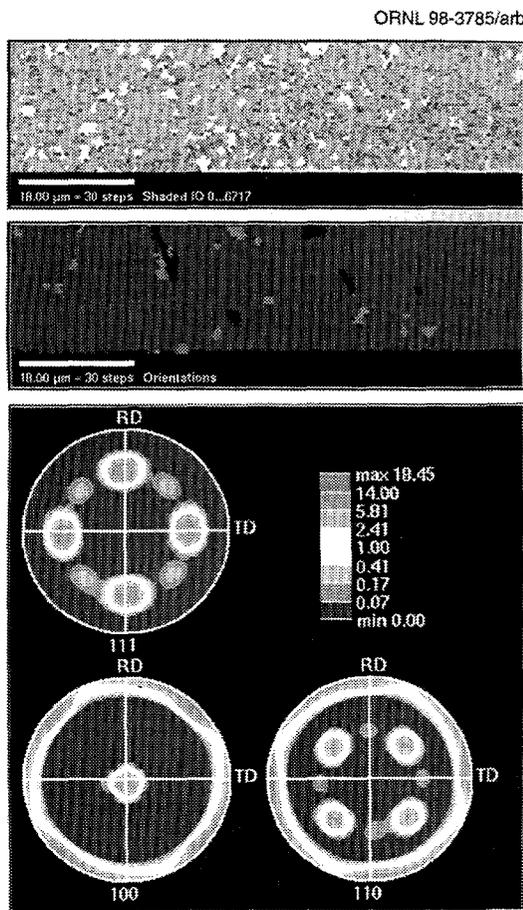
**Fig. 1.13. (a) X-ray phi scan of a YBCO film on RABiTS™ in which the buffers were put down by a combination of e-beam evaporation and sputtering and (b) X-ray phi scan of Ni.**

the buffer layers were deposited exclusively using e-beam evaporation with respect to the texture of the underlying Ni substrate. In this case the thicknesses of the CeO<sub>2</sub> and YSZ layers were 10 nm and 130 nm, respectively.

Figure 1.13 shows the in-plane texture of YBCO film grown on the substrate in which the buffer layers were deposited by a combination of e-beam evaporation and sputtering with respect to the texture of the underlying Ni substrate. In this case the thicknesses of the CeO<sub>2</sub> and YSZ layers were 10 nm and 770 nm, respectively. As in the in situ PLD samples, relative to Ni[100],

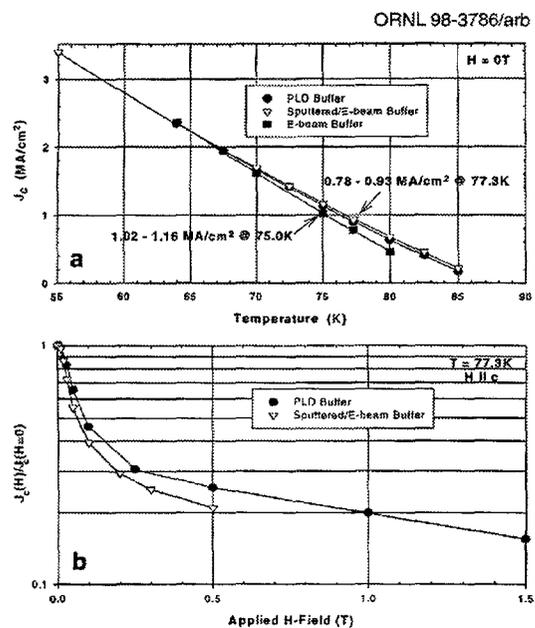
CeO<sub>2</sub>[100] and YSZ[100] are rotated 45° (i.e., Ni[100] || CeO<sub>2</sub>[110] || YSZ[110]). The YBCO assumes two in-plane orientations relative to the YSZ, namely, the cube-on-cube orientation with YBCO([100] + [010]) || YSZ[100] and the 45° rotated orientation with YBCO([100] + [010]) || YSZ[110]. These same two-component mixtures of in-plane orientation for epitaxial YBCO were observed previously by Garrison et al.<sup>7</sup> and Fork et al.<sup>8</sup> on single crystal YSZ. They found that the distribution of orientations depends strongly on the YSZ/YBCO interfacial composition and less strongly on the temperature and pressure during YBCO deposition. In our study for the sample with buffer layers grown by exclusively e-beam, the distribution of in-plane orientations of the YBCO was 1.5% cube-on-cube and 98.5% 45° rotated with respect to the underlying Ni. For the sample with buffer layers grown by e-beam/sputtering, the distribution was 97% cube-on-cube and 3% 45° rotated with respect to the underlying Ni. This difference in preference of the YBCO epitaxial variant on YSZ may be related to different internal stresses due to different thicknesses of YSZ layers.

Figure 1.14 (top) shows an orientation image micrograph of the Ni substrate. The micrograph was obtained using BKD. Gray level shading on the micrograph is a reflection of the pattern quality or intensity of the Kikuchi bands observed at each point. Grain boundaries give rise to multiple diffraction patterns and hence have a poor pattern. Similarly, poor patterns are observed from any other crystallographic defect or strained region. BKD patterns were obtained on a hexagonal grid with a spacing of 0.6 μm. Indexing of the pattern at each location gave a unique measure of the orientation at that point. A hypothetical hexagonal lattice with a grain size of 0.6 μm was superimposed at each point from which a pattern was obtained. Grain boundary misorientations were then calculated for all the resulting boundaries using standard techniques. The micrograph was then regenerated to reveal high angle boundaries, and the only high angle boundaries found were those



**Fig. 1.14. (top)** In-plane orientation map of a YBCO film deposited on e-beam/sputtered buffered nickel. **(middle)** The dark and light areas are regions of YBCO with cube-on-cube orientation and  $45^\circ$  rotated orientation, respectively. **(bottom)** Corresponding (111), (100), and (110) pole figures.

surrounding  $45^\circ$  rotated YBCO grains. In Fig. 1.14 (middle), dark and light areas are regions of YBCO with cube-on-cube orientation and  $45^\circ$  rotated orientation, respectively. Corresponding (111), (100), and (110) pole figures are shown in Fig. 1.14 (bottom). The dark grains in Fig. 1.14 (middle) correspond to the  $45^\circ$  rotated cube location in the pole figure. Approximately 3 vol % of YBCO is rotated  $45^\circ$ . Clearly, the supercurrent will not be disrupted significantly by the presence of this second orientation.



**Fig. 1.15. Temperature (a) and magnetic field dependence (b) of  $J_c$  for YBCO films on buffer layers prepared by PLD, sputtering/e-beam, and e-beam on biaxially textured nickel.**

With a voltage criterion of  $1 \mu\text{V}/\text{cm}$ , transport  $J_c$  was measured for the e-beam and the sputtered/e-beam samples in a pulsed current system. Figure 1.15(a) shows the temperature dependence of  $J_c$  for the two samples along with that for a sample with buffer layers and YBCO prepared by in situ PLD. For the in situ all-PLD sample, the distribution of in-plane orientations of the YBCO was 10% cube-on-cube and 90%  $45^\circ$  rotated. All three samples show high  $J_c$  at 77.3 K ( $0.78\text{--}0.93 \text{ MA}/\text{cm}^2$ ) and a similar temperature dependence of  $J_c$ . The dependence of  $J_c$  on magnetic field is also similar for the sputtered/e-beam sample and the all-PLD sample [see Fig. 1.15(b)]. The e-beam sample was damaged during the measurement of  $J_c$  as a function of the temperature and could not be used during the measurement of  $J_c$  as a function of field.

These results are the first demonstration of high  $J_c$  for epitaxial YBCO films on biaxially textured nickel with buffer layers deposited by

ex situ non-PLD methods. They suggest the feasibility of more flexible and practical methods of fabrication of coated YBCO superconducting wire of long length.

### Summary

High  $J_c$  YBCO films were prepared on RABiTS™ composed of CeO<sub>2</sub>/YSZ/Ni in which the oxide layers were deposited ex situ using either e-beam or sputtering. This result is significant for several reasons. First, it demonstrates that ex situ deposition of YBCO films can be successfully performed on buffered Ni that has been exposed to air. This is important from a manufacturing point of view. Second, it demonstrates that crack-free, epitaxial, oxide buffer layers can be deposited on Ni using the scalable techniques of e-beam evaporation and sputtering.

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### GROWTH OF BIAXIALLY TEXTURED MgO BUFFER LAYERS ON ROLLED-Ni SUBSTRATES BY ELECTRON BEAM EVAPORATION

The growth of a buffer layer architecture consisting of an epitaxial laminate of MgO/Ag/Pt or MgO/Ag/Pd deposited on a biaxially textured Ni substrate is described in this report. The cube (100) texture in the Ni was produced by thermomechanical processing. Both Pd and Pt films were grown epitaxially on the rolled-Ni substrates. The Ag films were grown on Pd- and Pt-buffered Ni substrates by in situ epitaxial growth of MgO. The crystallographic orientation of the Ag and MgO was mostly (100). The MgO buffer layer developed may be useful for the growth of high current conductors.

Earlier, we developed three buffer layer architectures on textured-Ni substrates using an e-beam evaporation technique. They were Ag/Pd(Pt)/Ni, CeO<sub>2</sub>/Ni, and YSZ/CeO<sub>2</sub>/Ni. We also recently demonstrated a  $J_c$  of  $1 \times 10^6$  A/cm<sup>2</sup> at 75 K and zero field on ~0.76- $\mu$ m-thick YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-y</sub> (YBCO) film. This film was deposited by pulsed laser ablation on a YSZ/CeO<sub>2</sub>/Ni substrate. All the buffer layers were deposited using the e-beam system. The total thickness of the buffer layer was 1500 Å. In this report, we discuss our successful growth of biaxially aligned MgO buffer layers on the textured-Ni substrates.

The cube (100) texture in Ni (99.99% pure) was produced by cold-rolling to over 90% deformation followed by recrystallization at 800°C. The thickness of the textured-Ni substrate used was 125  $\mu$ m. The deposits were produced without any substrate polishing using an e-beam evaporation technique. The experimental details for the growth of buffer layers on rolled-Ni substrates are described in the following two sections.

### Ag/Pd(Pt)/Ni Architecture

The as-rolled Ni substrates were cleaned ultrasonically with both acetone and methanol and were mounted on a substrate holder with a heater assembly in the e-beam system. After the vacuum had reached  $1 \times 10^{-6}$  torr at room temperature, the substrates were in situ annealed at  $400^\circ\text{C}$  for 4 h. The temperature of the substrate was measured using a thermocouple. The Pd layer was then grown on the textured Ni at temperatures ranging from  $100$  to  $500^\circ\text{C}$ . The typical deposition rate for Pd was  $0.5$ – $1.0$  nm/s at a pressure of  $10^{-6}$  torr, and the final thickness was varied from  $200$  nm to  $1\ \mu\text{m}$ . The thickness of the film was measured by a quartz crystal monitor during the deposition. The  $\theta$ - $2\theta$  scan for a  $400$ -nm-thick Pd film deposited on Ni at  $500^\circ\text{C}$  showed the presence of a (100)-oriented film. A four-circle diffractometer was used to collect pole figures, to measure rocking curves ( $\omega$  scan) of (002) planes of the (001)-textured film which analyze the out-of-plane alignment, and to measure  $\phi$  scans of the (202) planes which analyze the in-

plane alignment of the film. Figure 1.16 shows the  $\omega$  and  $\phi$  scans for as-deposited Pd ( $400$  nm thick) on Ni at  $500^\circ\text{C}$ . The FWHM for Ni (002) and Pd (002) are  $6.6^\circ$  and  $4.0^\circ$ , and that of Ni (202) and Pd (202) are  $13.0^\circ$  and  $7.1^\circ$ , respectively. From Fig. 1.16, we can conclude that Pd can be grown epitaxially on Ni. Platinum films were also grown epitaxially on textured-Ni substrates using similar Pd deposition conditions. Figure 1.17 shows the  $\omega$  and  $\phi$  scans for as-deposited Pt ( $200$  nm thick) on Ni at  $500^\circ\text{C}$ . The FWHM for Ni (002) and Pt (002) are  $10.7^\circ$  and  $9.3^\circ$ , and that of Ni (111) and Pt (111) are  $8.9^\circ$  and  $10.2^\circ$ , respectively. This is an example where Pt was grown epitaxially on Ni.

The Ag films were then grown on both Pd-buffered and Pt-buffered Ni substrates at room temperature. The Ag films were then post-annealed at  $300^\circ\text{C}$  in the system. The  $\theta$ - $2\theta$  scan for a  $150$ -nm-thick Ag film deposited on both Pd-buffered and Pt-buffered Ni showed the presence of a (100)-oriented film. Figure 1.16 also shows the  $\omega$  and  $\phi$  scans for  $150$ -nm-thick post-annealed Ag films on Pd-buffered Ni

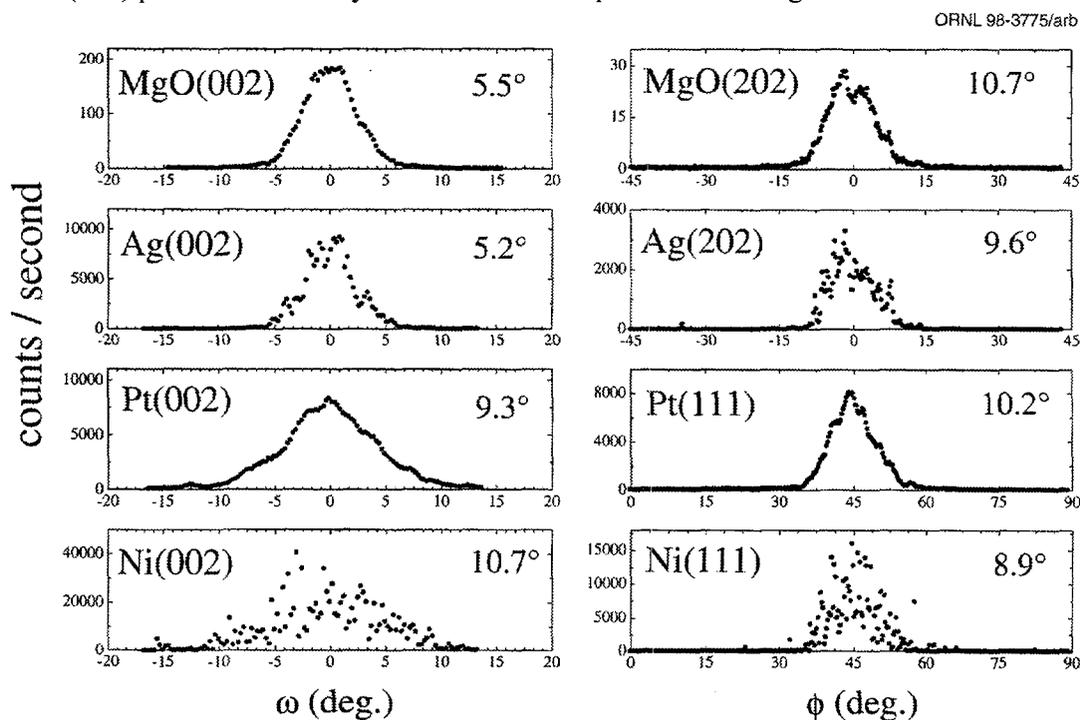
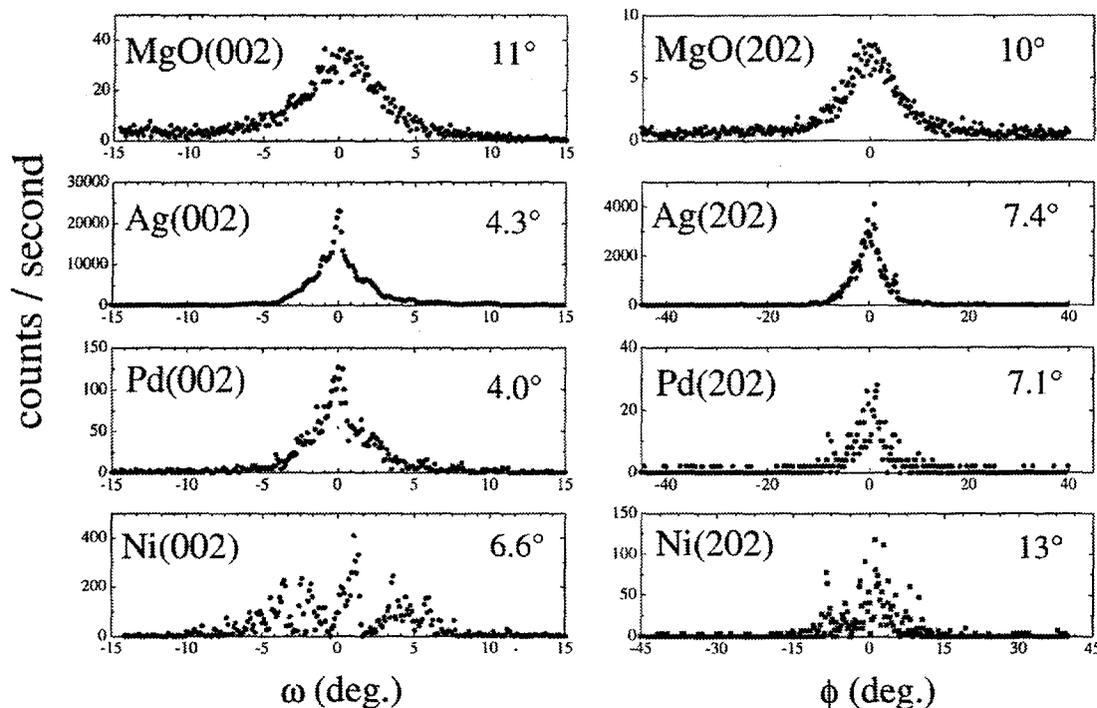


Fig. 1.16. The X-ray  $\omega$  and  $\phi$  scans for post-annealed  $200$ -nm-thick MgO on Ag-Pd-buffered Ni substrates.

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**Fig. 1.17. The X-ray  $\omega$  and  $\phi$  scans for as-deposited 200-nm-thick MgO on Ag-Pt-buffered Ni substrates.**

substrates. The FWHM for Ag (002) is  $4.3^\circ$ , and that of Ag (202) is  $7.4^\circ$ , respectively. The rocking curves for Pd, Pt, and Ag are smooth because these are *fine-grained films*. The Ni substrate, by contrast, is coarse grained, so its rocking curves (see Figs. 1.16 and 1.17) consist of many sharp peaks corresponding to individual grains. The XRD results show that Ag, Pt, and Pd can be deposited epitaxially on Ni by the e-beam evaporation technique. Similar results were also obtained on films grown by dc sputtering.

### MgO/Ag/Pd(Pt)/Ni Architecture

The MgO layers were deposited on Ag-Pt-buffered or Ag-Pd-buffered Ni substrates at room temperature using e-beam evaporation followed by in situ post-annealing up to  $300^\circ\text{C}$ . MgO was used as the source. The deposition rate was  $0.5\text{--}1.0\text{ nm/s}$  at  $1 \times 10^{-5}$  torr vacuum with the total thickness of 200 nm. Figure 1.16

shows the  $\omega$  and  $\phi$  scans for 200-nm-thick post-annealed MgO films on Ag-Pd-buffered Ni substrates. The FWHM for MgO (002) is  $11.0^\circ$ , and that of MgO (202) is  $10.0^\circ$ , respectively. Figure 1.17 shows the  $\omega$  and  $\phi$  scans for 200-nm-thick as-deposited MgO films on Ag-Pt-buffered Ni substrates. The FWHM for MgO (002) is  $5.5^\circ$ , and that of MgO (202) is  $10.7^\circ$ , respectively. Figures 1.16 and 1.17 prove that the MgO films grown on Ag-buffered substrates are biaxially oriented. Attempts will be made to grow superconductors on these buffer layers.

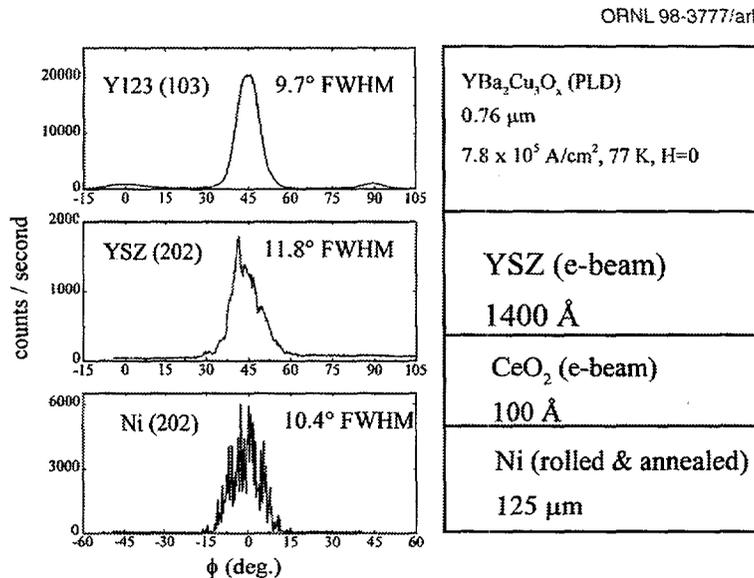
### DEMONSTRATION OF HIGH CURRENT $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ COATED CONDUCTORS ON ROLLED-Ni SUBSTRATES WITH THIN BUFFER LAYERS

In the YBCO coated conductors project, the highest  $J_c$  obtained previously at ORNL was  $7.3 \times 10^5\text{ A/cm}^2$  at 77 K and zero field on a

1.4- $\mu\text{m}$ -thick YBCO film that has an architecture of YBCO/YSZ/CeO<sub>2</sub>/Ni. Both buffer layers and YBCO superconductors were grown in situ by PLD. The total buffer layer thickness used was about 1  $\mu\text{m}$ . To improve the mechanical properties of our RABiTS™ and also to increase the overall engineering current density ( $J_e$ ), we investigated the effect of buffer layer thicknesses. The CeO<sub>2</sub> layer thickness was found to be critical. CeO<sub>2</sub> films with a thickness of about 100 Å were smooth, continuous, and also crack-free. In this study, we grew 1400-Å-thick YSZ films on 100-Å-thick CeO<sub>2</sub>-buffered Ni substrates. The e-beam evaporation technique was used to grow both CeO<sub>2</sub> and YSZ films. The YBCO films were grown using a KrF excimer laser.

The 125- $\mu\text{m}$ -thick as-rolled Ni substrates were cleaned initially with both acetone and methanol and recrystallized at 800°C to obtain the (100) cube texture. The biaxially oriented Ni substrates were then mounted on a substrate holder with a heater assembly in the e-beam system. After the vacuum in the chamber had reached  $1 \times 10^{-6}$  torr at room temperature, a mixture of 4% H<sub>2</sub> and 96% Ar was introduced until the pressure inside the chamber reached ~1 torr. The Ni substrates were then annealed at

~650°C for 60 min at ~1 torr. During CeO<sub>2</sub> deposition, the chamber was maintained at a pressure of  $2 \times 10^{-5}$  torr with a mixture of 4% H<sub>2</sub> and 96% Ar. The CeO<sub>2</sub> layers were deposited on Ni substrates at 600°C. The deposition rate for CeO<sub>2</sub> was 3–4 Å/s with an operating pressure of  $10^{-5}$  torr, and the final thickness was 100 Å. For 100-Å-thick CeO<sub>2</sub> films, XRD results from the  $\theta$ -2 $\theta$  scan, and also  $\omega$  and  $\phi$  scans, revealed (100) texture. The YSZ layers were grown on the CeO<sub>2</sub>-buffered Ni substrates at 600°C. YSZ deposition rate was 1 Å/s with the operating pressure of  $2 \times 10^{-5}$  torr, and the final thickness was 1400 Å. XRD results from the  $\theta$ -2 $\theta$  scan, and also  $\omega$  and  $\phi$  scans, for 1400 Å thick YSZ films also showed a strong texture. A thick ( $\leq 1 \mu\text{m}$ ) YBCO film was then deposited on the YSZ using PLD at 780°C. The oxygen pressure was 185 mtorr. After deposition, the films were cooled at 10°C/min, and the oxygen pressure was increased to 700 torr at 400°C. The  $\theta$ -2 $\theta$  scan on the YBCO film showed the presence of a  $c$ -axis aligned film. The thickness of the YBCO film was found to be 0.76  $\mu\text{m}$  using a profilometer scan. These films were 0.3 cm wide and 1 cm long. The  $\phi$  scan for 0.76- $\mu\text{m}$ -thick YBCO film on the RABiTS™ is shown in Fig. 1.18. It shows the



**Fig. 1.18. The  $\phi$  scans for a 0.76- $\mu\text{m}$ -thick YBCO deposited on 1400-Å-thick YSZ-buffered Ni at 780°C.**

presence of a good in-plane texture. The films were further characterized by resistivity and transport  $I_c$  measurements using a conventional four-probe technique. Values of transport  $J_c$  were calculated using a  $1\text{-}\mu\text{V}/\text{cm}$  criterion. The temperature dependence of both critical currents,  $I_c$  and  $J_c$ , values for  $0.76\text{-}\mu\text{m}$ -thick YBCO films are shown in Fig. 1.19. A maximum  $J_c$  of  $7.8 \times 10^5 \text{ A}/\text{cm}^2$  was obtained at  $77 \text{ K}$  and zero field. At  $75 \text{ K}$ , a  $J_c$  of about  $1 \times 10^6 \text{ A}/\text{cm}^2$  was obtained. These results show that high  $J_c$  YBCO films can be grown on  $1500\text{-}\text{\AA}$ -thick buffer layers.

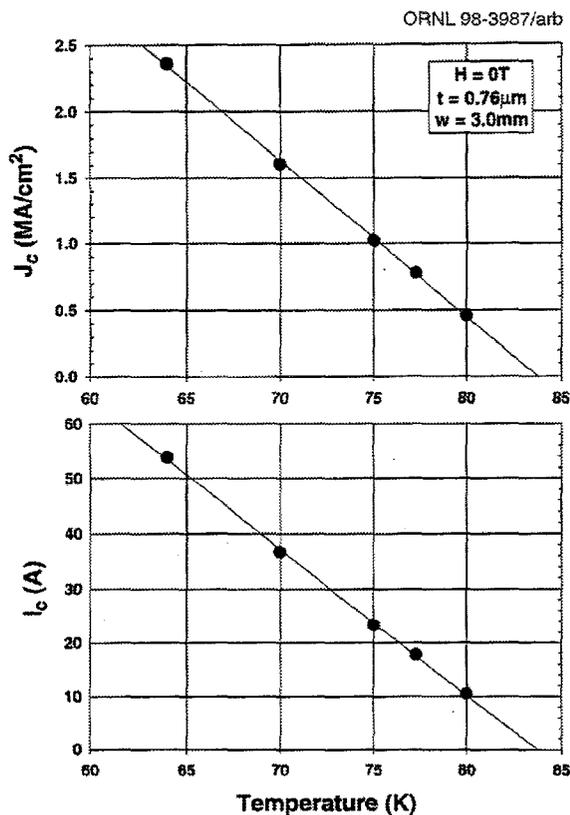


Fig. 1.19. The temperature dependence of both  $I_c$  and  $J_c$  values for a  $0.76\text{-}\mu\text{m}$ -thick YBCO film.

## DEVELOPMENT OF HIGH- $J_c$ HTS COATINGS BY PRECURSOR-DEPOSIT APPROACHES

### Background

A technically and economically viable coated-conductor technology will require the development of techniques to rapidly coat biaxially textured, buffered metal tapes with thick, high- $J_c$  HTS deposits. While work is in progress to develop YBCO coatings by the highly scalable solution techniques, to date high- $J_c$  deposits on metal tapes have been achieved only by vapor deposition methods, such as PLD and metallo-organic chemical vapor deposition (MOCVD). The present work focuses on issues related to the scale up of coatings by a new approach to vapor-deposited coated conductors that combines some attractive features of both vapor and bulk coating techniques.

The production of vapor-deposited HTS films may be regarded as occurring by two general approaches: in situ or ex situ processing. In the in situ approach, the deposition conditions are controlled in such a way that a completely formed, biaxially aligned HTS coating is grown during the deposition. In the ex situ approach, an amorphous or micro-crystalline precursor film is deposited, containing all or some of the components of the final HTS compound, in much the same way as the solution approaches. This precursor deposit should be chemically and structurally robust because formation of the HTS compound may be conducted ex situ in a (batch) furnace anneal in which the components are reacted, with additional necessary components possibly provided via the vapor phase. For a wire technology, the ex situ approach has several advantages: (1) during deposition of the precursor film, there is no need to maintain the moving tape substrate at high temperature or to provide a source of activated oxygen; (2) in principle, there is no growth-rate limitation to the deposition rate of the precursor film; and (3) the reaction to form the fully HTS

wire might be conducted by large-scale batch annealing, which is not rate-limited by linear processes.

### Objectives and Approach

Here we report results of studies to develop methods for the vapor deposition of high- $J_c$  YBCO and Tl1223 coatings using the precursor approach. Compared with Bi-based HTS conductors, both these HTS materials exhibit superior flux pinning properties in the presence of magnetic fields at liquid nitrogen temperatures (64–77K) and would open new applications for HTS coated conductors at these high temperatures. In these initial studies, we have focused on the compatible growth of high- $J_c$  films on single crystal substrates that comprise the upper layers of the present RABiTST<sup>TM</sup> architecture and on a demonstration that such films can be grown to the thicknesses needed for a conductor technology.

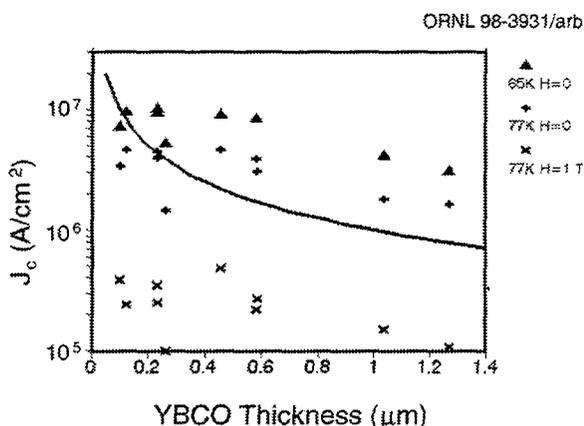
The work on YBCO films was conducted as part of a CRADA partnership with the 3M Company, Southwire Company, and LANL and exploits the deposition of Y-BaF<sub>2</sub>-Cu precursor films by e-beam co-evaporation, a deposition technology that is already used extensively for product fabrication by 3M. The project draws on expertise developed during several years of base program research at ORNL, where parameters were developed for the production of high-quality thin films, primarily on single crystal SrTiO<sub>3</sub> and KTaO<sub>3</sub> substrates. In this technique, the precursor films are chemically and mechanically stable and can be readily stored for extensive periods until the ex situ reaction anneal, conducted at 740–780°C in an O<sub>2</sub>/H<sub>2</sub>O/N<sub>2</sub> gas mixture at low oxygen partial pressure. The principal objective of this task was to extend the technique to thick coatings that retain full epitaxy and *c*-perpendicular alignment. A related specific objective was to understand the processes underlying the formation of these thick films and to begin to optimize the process for use with RABiTST<sup>TM</sup>.

The research on Tl1223 films involved a collaboration with researchers at the State University of New York (SUNY) at Buffalo, who had previously developed ex situ processing techniques to produce high- $J_c$  epitaxial films of Tl<sub>0.78</sub>Bi<sub>0.22</sub>Sr<sub>0.6</sub>Ba<sub>0.4</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>9-δ</sub> (TlBi1223) on substrates of single crystal LaAlO<sub>3</sub>. In this case, the Tl-free precursor films are deposited by PLD, and the reaction anneal occurs in a two-zone furnace in the presence of flowing O<sub>2</sub> and Tl<sub>2</sub>O vapor. The principal objective was to find parameters appropriate to produce ~1-μm-thick, high- $J_c$  films on single crystal YSZ, the same oxide that comprises the upper buffer layer of the RABiTST<sup>TM</sup> architecture. Initial results of deposition on RABiTST<sup>TM</sup> were also evaluated.

### Results

#### *Thickness Dependence of $J_c$ for Ex Situ YBCO Films*

In these controlled studies, precursor films of various thicknesses were deposited by e-beam co-evaporation of Y, BaF<sub>2</sub>, and Cu onto single crystal SrTiO<sub>3</sub> substrates in order to find processing parameters suitable to produce thick, *c*-perpendicular-oriented epitaxial films and to document the systematic dependence of  $J_c$  on thickness. Despite numerous claims in the early literature that the *c*-perpendicular orientation is unstable for growth to thicknesses greater than a few thousand angstroms, we were able to synthesize fully epitaxial films exceeding 1 μm in thickness. This success depends strongly on the groundwork of earlier research where the importance of low oxygen pressure during the reaction process was identified. In the present work, typical processing conditions are  $p(\text{O}_2) \approx 200$  mtorr,  $p(\text{H}_2\text{O}) \approx 20$  torr, at a reaction temperature of 780°C for a duration of about 1 h. Results for  $J_c$  as a function of thicknesses to ~1.3 μm, in the liquid nitrogen temperature range, are shown in Fig. 1.20, both at self field and for a 1-Tesla field applied parallel to the *c*-axis. The curve in Fig. 1.20 represents the  $J_c$



**Fig. 1.20. The  $J_c$  at liquid nitrogen temperatures as a function of film thickness for epitaxial YBCO on  $\text{SrTiO}_3$ , processed by the ex situ technique described.** Results are shown at zero applied field and for 1-Tesla fields applied parallel to the  $c$  axis.

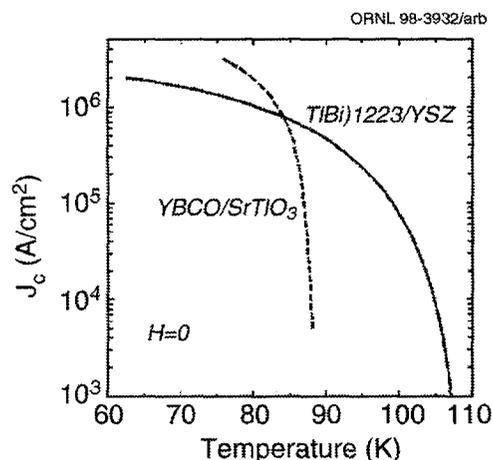
levels required to achieve the proposed operations criterion for a tape conductor with a sheet current of  $K_c > 10$  A/mm-width. Whereas the present data may indicate some degradation of  $J_c$  with thickness, low-field values remain well above the  $K_c$  criterion. Because structural studies (XRD and ion beam RBS) indicate good crystalline order, work in progress will determine if the fall off is related to a paucity of flux pinning defects as the films become more bulk-like with thickness. Additional important issues are the effects of practical substrate (buffer layer) materials on the compatibility with the ex situ processing requirements; development of ex situ YBCO films on  $\text{CeO}_2$  and YSZ buffer layers is under way, for ultimate compatibility with the full RABiTST<sup>TM</sup> tapes.

### Development of Epitaxial TIBi1223 Films on YSZ Surfaces

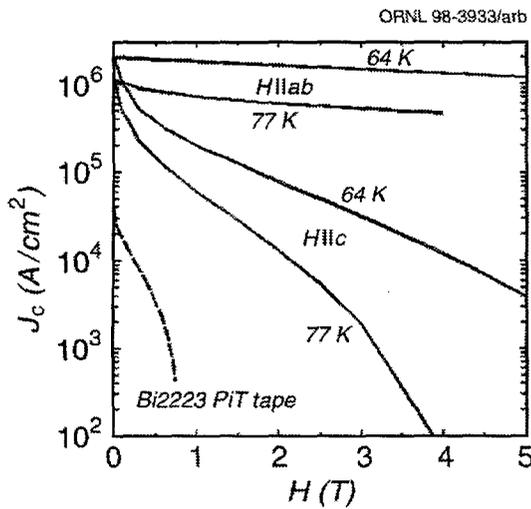
Previously, the reaction post-anneals to form high- $J_c$  epitaxial films of TIBi1223 on single crystal  $\text{LaAlO}_3$  were conducted either in air or oxygen at temperatures near  $860^\circ\text{C}$ . These processing conditions may be incompatible with the reactive base-metal substrates of RABiTST<sup>TM</sup>. Moreover, no previous knowledge base had

existed for the epitaxial growth of TIBi1223 on YSZ, which is a present upper-surface buffer layer of RABiTST<sup>TM</sup>. In this work we were able to successfully synthesize fully epitaxial films at greatly reduced oxygen pressure and temperature. The present films,  $0.7\ \mu\text{m}$  thick, are processed in proximity to unreacted TIBi1223 pellets and in-flowing argon and  $\text{Ti}_2\text{O}$  vapor at  $780^\circ\text{C}$  for 40 min. The processing temperature and ambient conditions are comparable with those of the ex situ YBCO synthesis and those of in situ depositions that have shown compatibility with RABiTST<sup>TM</sup>. The films contain a small amount of epitaxial TIBi1212 second phase, as determined by XRD, but otherwise are well ordered, with both in-plane and out-of-plane alignments of less than  $1.5^\circ$  FWHM.

Transport measurements show a zero-resistance transition temperature of about 108 K. In Figs. 1.21 and 1.22, results of transport  $J_c$  are given, showing the temperature dependence in self-field and the field-dependent  $J_c$  at 77 K and 64 K (just above the triple point temperature of liquid nitrogen), respectively. In zero applied field, the  $J_c$  value at 77 K is about  $1.1\ \text{MA}/\text{cm}^2$  and is nearly  $2\ \text{MA}/\text{cm}^2$  at 64 K. Comparison with a high- $J_c$  YBCO film illustrates an attribute of TIBi1223—the expanded high-temperature operation range, evidenced by a  $J_c$  of  $10^5\ \text{A}/\text{cm}^2$  near 100 K,



**Fig. 1.21. The  $J_c$  measured in self-field.** The dashed line is data for a high- $J_c$  YBCO film on  $\text{SrTiO}_3$ .



**Fig. 1.22.** The magnetic field dependence of  $J_c$ , for field orientations both parallel ( $H||ab$ ) and perpendicular ( $H||c$ ) to the film plane, for the two temperatures 64 K and 77 K spanning the useful  $LN_2$  range. For comparison, data for commercial Bi2223 powder-in-tube tapes are included.

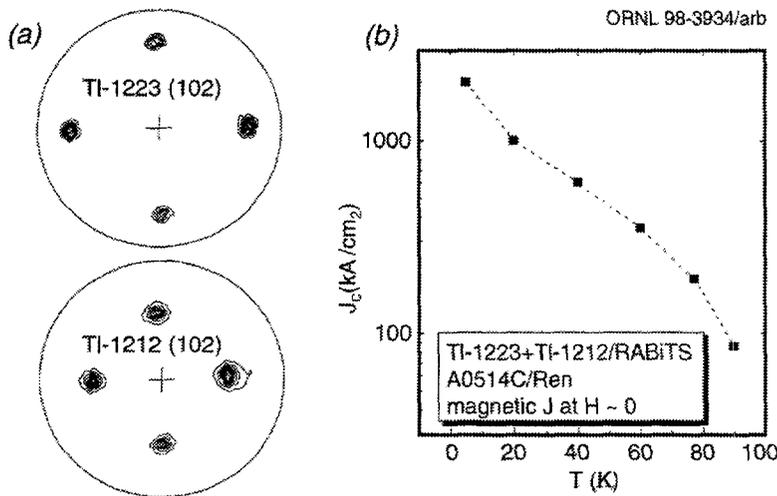
where YBCO is no longer superconducting. The field-dependent measurements clearly illustrate the advantages of TlBi1223 films over present state-of-the-art Bi2223 tapes. Of course, the important outstanding issue is the extension of these results to RABiTS™. Results of such an

initial attempt are shown in Fig. 1.23, where techniques similar to the above were employed to deposit the films on a RABiTS™ of architecture YSZ/CeO<sub>2</sub>/Ni. The X-ray (102) pole figures of Fig. 1.22 show that the sample is mixed phase, with nearly equal distribution of epitaxial TlBi1212 and TlBi1223. Results of the low-field  $J_c(T)$  for this small sample were deduced from magnetic hysteresis measurements and yield a low-field (trapped flux) value  $J_c(77\text{ K}) \approx 200\text{ kA/cm}^2$  at 77 K. This first result offers encouragement for further development of TlBi1223 coatings on RABiTS™. Work is also under way to refine the processing parameters for 1223 on CeO<sub>2</sub> buffers, which also can be used as the RABiTS™ upper surface.

**Summary and Conclusions**

Vapor deposition techniques (e-beam co-evaporation and PLD) have been used to deposit precursor films of YBCO and Tl1223, respectively. In both cases, the films are converted to the superconducting phase by an ex situ furnace post-annealing process. Investigations of the YBCO films deposited on single crystal substrates have shown that epitaxy, *c*-perpendicular alignment, and good

superconducting transport properties can be achieved to thicknesses greater than 1 μm. For the TlBi1223 material, high- $J_c$  films on YSZ surfaces have been developed through modification of the ex situ processing to lower the reaction temperature from ~860 to ~760°C and to greatly reduce the oxygen partial pressure. An initial attempt to employ this approach to deposition of TlBi1223 on a RABiTS™ gave encouraging results. These results help demonstrate feasibility of the ex situ approach and provide further motivation for its development as the HTS layer in a coated-conductor technology.



**Fig. 1.23.** (a) The XRD (102) pole figure of a Tl film on RABiTS™, showing the epitaxial co-existence of 1223 and 1212 phases. (b) The  $J_c$  in low field determined from magnetization hysteresis.

## FIRST DEMONSTRATION OF A LONG LENGTH RABiTS™

Scale-up experiments under way at ORNL are designed in part to provide longer lengths of RABiTS™ for YBCO deposition at ORNL, LANL, and Midwest Superconductivity, Inc. Recently, over 30-cm-long CeO<sub>2</sub>-buffered, textured-Ni substrates were fabricated for the first time using a rotating cylinder in an e-beam evaporator. Also, we fabricated a RABiTS™ over 6-cm long with a layer sequence of YSZ (1000 Å)/CeO<sub>2</sub> (400 Å)/Ni (125 μm) in a static mode in the e-beam system. Detailed XRD analysis on this long substrate showed that the FWHM values for the top YSZ layers were 9–10° [in-plane epitaxy; (202)  $\phi$  scan] and 6–7° [out-of-plane epitaxy; (002)  $\omega$  scan]. Attempts are being made to grow YBCO on these substrates.

In an attempt to scale up our RABiTS™ process, we proceeded in two ways. The first approach is the simple mounting of long textured Ni on a heating stage in a static mode in the e-beam system. The second approach is to wind textured Ni on a rotating cylinder that can be mounted inside the e-beam system. By using the first approach, we fabricated a RABiTS™ over 6-cm long with a layer sequence of YSZ (1000 Å)/CeO<sub>2</sub> (400 Å)/Ni (125 μm) using our e-beam evaporator. Detailed X-ray analyses were made on three different spots. The results indicated that the top YSZ layer had FWHM values of 9–10° [in-plane epitaxy; (202)  $\phi$  scan] and 6–7° [out-of-plane epitaxy; (002)  $\omega$  scan]. The film appeared to be golden yellow in color. We also fabricated a rotating copper cylinder with a heating assembly that can be mounted in

the e-beam system. The cylinder is convenient for winding 1.8 m of 1.0-cm-wide Ni tapes, can be rotated from 0 to 360° at ~8 rpm, and can be heated up to 800°C. Using this rotating cylinder, we have recently demonstrated that over 30-cm-long CeO<sub>2</sub>-buffered Ni substrates can be made (see Fig. 1.24). The thickness of the CeO<sub>2</sub> layer was 1000 Å. The film appeared to be blue in color and the thickness appeared to be uniform throughout the sample. Attempts will be made to grow YBCO on these long substrates.

## OXFORD CRADA: Bi-2212 CONDUCTOR DEVELOPMENT

### Conductor Insulation Materials

Dip-coated Bi-2212/Ag conductors are being developed for high-field insert coil applications. Producing the coils by winding followed by subsequent reaction has the advantage of avoiding cracking degradations that occur when prefired conductors are wound into coils. The difficulties with the wind-and-react process involve removing the organic dip-coating compounds and reactions between the liquid phase formed during partial melting and the oxide electrical insulation. Both Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> react rapidly with the liquid formed when Bi-2212 melts, and the reaction products degrade conductor performance and reduce electrical insulation.

Compatibility tests have shown that CaZrO<sub>3</sub>, SrZrO<sub>3</sub>, and BaZrO<sub>3</sub> do not react with the Bi-2212 liquids, and a preliminary evaluation indicates that they may be useful for wind-and-react coils. Coils insulated with low density

ORNL 98-3988/arb



Fig. 1.24. First demonstration of an ~30-cm-long CeO<sub>2</sub>-buffered Ni substrate using a rotating cylinder in the e-beam evaporator. Ni substrate = 5 mil; CeO<sub>2</sub> thickness = 1,000 Å.

$\text{CaZrO}_3$  powder were compared with  $\text{Al}_2\text{O}_3$  paper-insulated coils. Measurements showed the  $\text{CaZrO}_3$  coils had approximately two times higher resistances between conductor turns. Higher density zirconate coils are now being investigated.

### Removal of $\text{CO}_2$ from Silver-Clad BSCCO Conductors

This study was initiated to experimentally determine if it is possible to remove  $\text{CO}_2$  gas from inside Ag-clad BSCCO conductors. Carbonate ions can be accommodated in the BSCCO lattices and the partial melting process step can result in  $\text{CO}_2$  evolution and conductor bubbling. These defects have been observed at carbon levels as low as 600 ppm. The difficulties have been discussed in detail by Hellstrom and Zhang.<sup>1</sup>

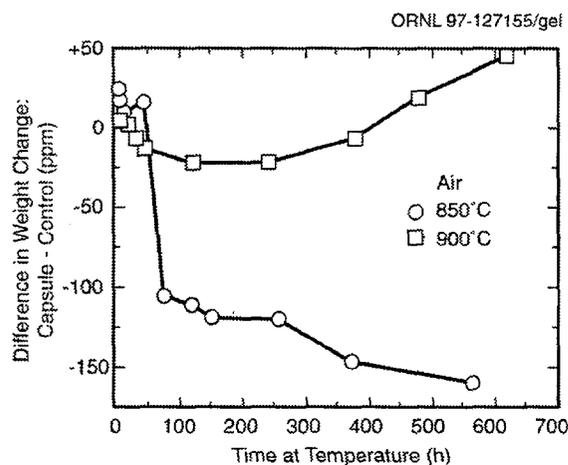
Moisture and excess oxygen can also cause bubble formation, but these species can be removed by vacuum drying and oxygen diffusion through the Ag clad. Evolution of  $\text{CO}_2$  is a more intractable problem because it is mostly retained in the BSCCO lattice until partial melting occurs. Clearly, thorough decarburization of the starting BSCCO powder is the best solution to the problem, but attempts to accomplish this have not always met with success. Another possibility is to develop a heat treatment cycle that would allow the  $\text{CO}_2$  to permeate through the Ag sheath at temperatures just below the partial melting regime. Theoretical considerations indicated that carbon removal by high temperature diffusion was highly unlikely, but the problem is so serious that an experimental test was performed.

The experiments involved heating sealed Ag capsules and controls in flowing He and ambient air at temperatures between 800 and 900°C. The capsules were filled with dried  $\text{CaCO}_3$  and  $\text{SrCO}_3$  and sealed off by e-beam welding. Thermodynamic calculations<sup>2</sup> indicate that at 900°C, the  $\text{CO}_2$  pressures over  $\text{CaCO}_3$  and  $\text{SrCO}_3$  are 1.04 and 0.053 atm. Compounds and test temperatures were matched to avoid

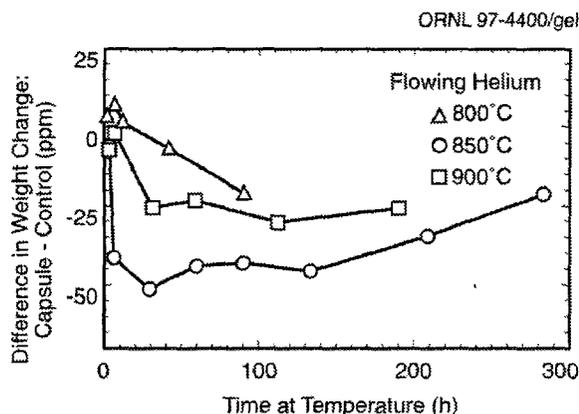
positive internal pressures. The wall thickness of the Ag capsules was 1 mm and the carbonates comprised 7–8% of the mass. All of the Ag components were vacuum annealed for 4 h at 500°C before the capsules were filled and sealed. The balance sensitivity (10  $\mu\text{g}$ ) equals about 4 ppm of the carbonate mass.

The He data are shown in Fig. 1.25 and the air data are shown in Fig. 1.26. On these plots, negative values indicate that the capsules lost more weight than the controls. The step change in the 850°C air data was caused by the capsule sticking to an alumina boat. Processes that might produce a weight change include oxygen pickup, sublimation of Ag, and  $\text{CO}_2$  loss. Results in air and He are similar, indicating that oxygen pickup was not a problem. This also shows that the external oxygen pressure has little effect. Sublimation was significant and maximum weight losses at 900°C were 600–650 ppm. If  $\text{CO}_2$  losses were significant, the capsules would be expected to lose weight more rapidly than the controls, the effect would become stronger at high temperatures, and the differences in capsule and control weights would increase with time. The data show none of these trends, and the maximum weight difference observed corresponds to only about 0.15% of the available  $\text{CO}_2$ .

A negative cannot be proved; but our data show that, for conditions near those encountered



**Fig. 1.25. Differential weight loss for Ag encapsulated carbonates in flowing He.**



**Fig. 1.26. Differential weight loss for Ag encapsulated carbonates in air.**

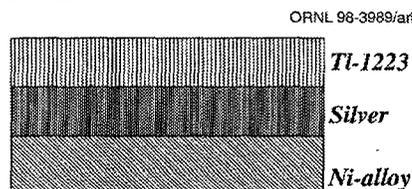
in conductor processing,  $\text{CO}_2$  cannot be removed by diffusion through the cladding. This is consistent with observations that (1)  $\text{CO}_2$  does not react with  $\text{Ag}^3$  and (2) the maximum solubility of carbon in liquid silver is only 22 ppm.<sup>4</sup>

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## GROWTH OF $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ SUPERCONDUCTING FILMS ON HIGH-STRENGTH SUBSTRATES USING A SPRAY PYROLYSIS TECHNIQUE

In continuation of our effort to grow  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$  (Tl-1223) films on metallic substrates using a two-step process, we initiated our work on high-strength oxidation resistant substrates. We have recently developed a technique for bonding Ag to a suitable metal alloy. The typical deposited conductor geometry is shown in Fig. 1.27. The main purpose was to reduce the amount of Ag needed and also to increase the mechanical strength of the substrate. The high-strength substrate also has a smaller thermal expansion mismatch with Tl-1223 as compared with that of Ag and Tl-1223 films. It is also nonmagnetic and has a mechanical strength that is ten times that of pure Ag. The approximate thickness of the high-strength substrate varied from 5 to 10 mil. The typical size of the substrates was 5-mm wide and 1-in. long, and the texture of the substrates was random.



**Fig. 1.27. The deposited conductor geometry of high-strength substrates.**

Initially, thallium-free precursor films with the composition  $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{Ag}_{0.37}\text{O}_7$  were deposited on the high-strength substrate. The precursor films obtained were smooth and continuous. Thallination was carried out using a standard two-zone thallination furnace with a source temperature of  $730^\circ\text{C}$  and a sample temperature of  $860^\circ\text{C}$  for 30 min in flowing oxygen. The resulting  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$  films were black. The film thickness was approximately  $3\ \mu\text{m}$ . X-ray powder diffraction studies showed that the films were highly  $c$ -axis oriented. Values of transport  $J_c$  were calculated

using a  $1 \mu\text{V}/\text{cm}$  criterion. The magnetic field dependence of the  $J_c$  for  $3\text{-}\mu\text{m}$ -thick  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$  films on high-strength substrates is shown in Fig. 1.28. The  $J_c$  values were  $\sim 52,000 \text{ A}/\text{cm}^2$  at  $77 \text{ K}$  and zero field. At  $0.5 \text{ T}$  and  $77 \text{ K}$ , the respective  $J_c$  values were  $9,800 \text{ A}/\text{cm}^2$  and  $4,400 \text{ A}/\text{cm}^2$  for magnetic field applied parallel and perpendicular to the substrate.

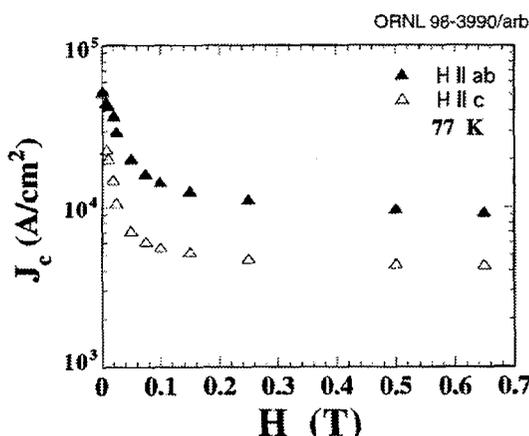


Fig. 1.28. The in-field dependence of  $J_c$  for  $H \parallel ab$  and  $H \parallel c$  orientation of  $3\text{-}\mu\text{m}$ -thick  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$  films grown on high-strength substrates at  $77 \text{ K}$ .

### EPITAXIAL GROWTH OF $\text{BaZrO}_3$ ON SINGLE CRYSTAL OXIDE SUBSTRATES USING SOL-GEL ALKOXIDE PRECURSORS

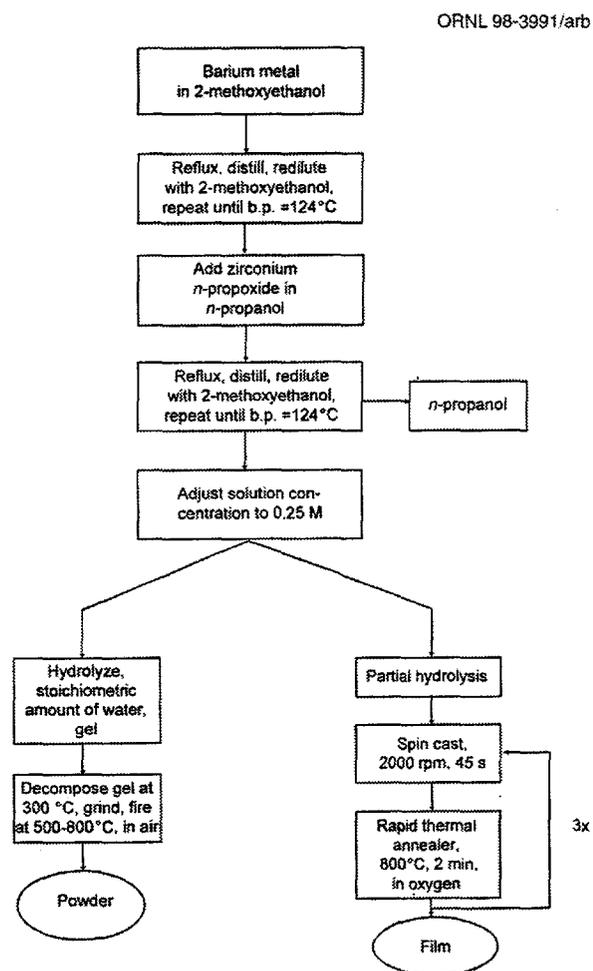
In continuation of our effort to develop a nonvacuum process to produce coated conductors, we used the sol-gel alkoxide precursor route in the present study. Also, this report is mainly focused on the development of sol-gel chemistry for  $\text{BaZrO}_3$  precursors and the feasibility of growing epitaxial thin films on single crystal oxide substrates.  $\text{BaZrO}_3$  has been considered as a potential buffer layer on textured-Ni substrates to grow YBCO coated conductors.  $\text{BaZrO}_3$  has been known to form as an intermediate layer while growing YBCO directly on YSZ layers. Also,  $\text{BaZrO}_3$  is a simple cubic perovskite with a lattice parameter of

$4.193 \text{ \AA}$ . We developed the sol-gel chemistry for  $\text{BaZrO}_3$  precursors and also demonstrated that the  $\text{BaZrO}_3$  films can be grown epitaxially on  $\text{SrTiO}_3$  (100) and  $\text{LaAlO}_3$  (100) substrates.

The starting reagents were weighed in an argon-filled, inert-atmosphere glove box, and the solution preparation was carried out under argon using standard Schlenk-type apparatus. Barium metal (Alfa, 99.99%), zirconium  $n$ -propoxide in  $n$ -propanol (Alfa, 70%), and 2-methoxyethanol (Alfa, spectrophotometric grade) were used without further purification. The flowchart for the preparation of  $\text{BaZrO}_3$  precursors is given in Fig. 1.29.

Barium metal (0.858 g, 6.25 mmol) was allowed to react with 50 mL of 2-methoxyethanol. The barium metal dissolved completely within a few minutes of reflux by evolving hydrogen, and a clear-white barium methoxyethoxide solution was obtained. A stoichiometric amount of zirconium  $n$ -propoxide (2.935 g, 8.96 mmol) was then added to the barium solution. Approximately 25 mL of  $n$ -propanol/2-methoxyethanol were distilled off, and the solution was repeatedly rediluted with 25–30 mL of fresh 2-methoxyethanol and further distilled for approximately 2 h to again ensure complete exchange of propoxide by the methoxyethoxide ligand. The final volume of the yellow-colored solution was adjusted with 2-methoxyethanol to 50 mL to make a 0.25 M  $\text{BaZrO}_3$  precursor solution. A partially hydrolyzed solution suitable for spin-coating was prepared by adding approximately 1 equivalent of water (1M  $\text{H}_2\text{O}$  in 2-methoxyethanol) per cation equivalent. The solution was allowed to age overnight at room temperature prior to the coating process. Part of the starting precursor solutions were fully hydrolyzed, and the resulting gels were dried on a hot plate. The powders thus obtained were used for the differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

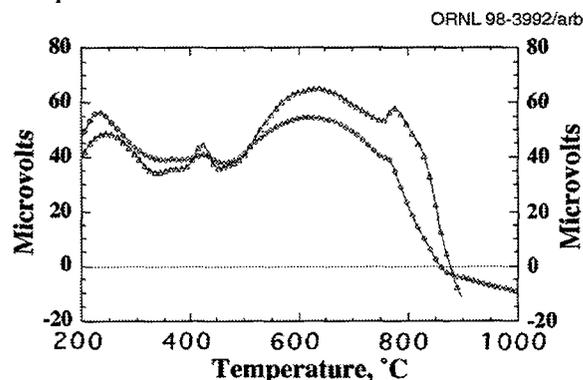
The substrates used for coating in this study were  $\text{SrTiO}_3$  (100),  $\text{LaAlO}_3$  (100), and sapphire (polycrystalline) (Commercial Crystal



**Fig 1.29. Flowchart for the preparation of BaZrO<sub>3</sub> precursors.**

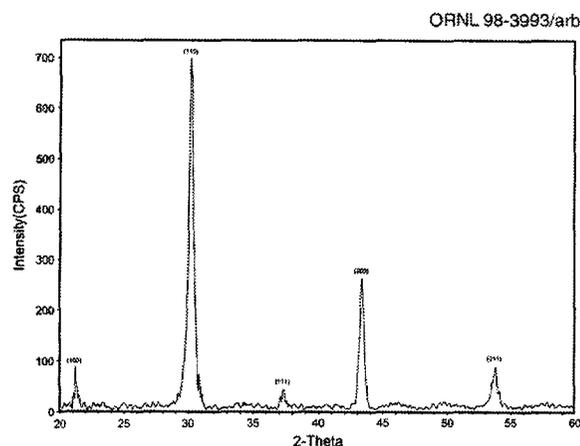
Laboratories, Inc., 1 cm × 1 cm size, ~0.5-cm thick, one side epi-polished). After the substrates were cleaned ultrasonically in ethanol for a few minutes, three coatings of the partially hydrolyzed precursor solution were made using a spin-coater operated at 2000 rpm for 45 s. Between each coating, the substrate was pyrolyzed in oxygen in a rapid thermal annealer (RTA, AG Associates Model 610) at 800°C for 2 min. The total thickness of the resulting film was approximately 300 nm.

The films were analyzed by detailed XRD studies. A Philips Model XRG3100 diffractometer with Cu K<sub>α</sub> radiation was used to record the powder diffraction pattern. A Rigaku rotating anode X-ray generator was used, with a graphite monochromator selecting Cu K<sub>α</sub> radiation and slits defining a 2 × 2 mm incident beam. A four-circle diffractometer was used to collect pole figures to measure rocking curves ( $\omega$  scan) of (002) planes of the (001) textured film, which measure the out-of-plane alignment. The diffractometer was also used to measure  $\phi$  scans of the (101) planes. These scans indicate the in-plane alignment of the film. SEM micrographs were taken using a Hitachi S-4100 field emission SEM. The beam voltage used was 15 kV. The DTA and TGA data were obtained on BaZrO<sub>3</sub> powders in both air and oxygen atmospheres in a Sinku-Riko TFD7000 RH instrument. The DTA scan for the same is shown in Fig. 1.30. The main exothermic event took place between 750 and 800°C in both air and oxygen atmospheres. Hence, the BaZrO<sub>3</sub> films were post-annealed around these temperatures.

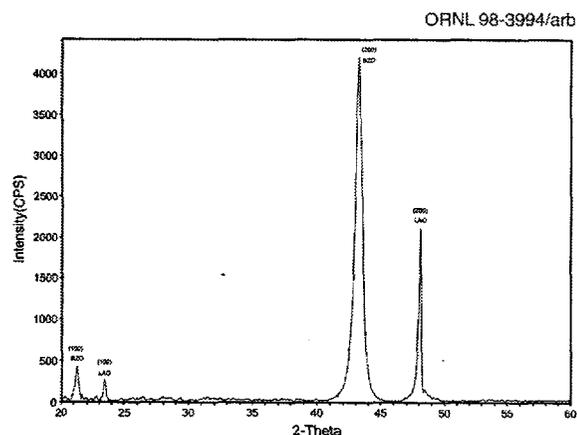


**Fig. 1.30. DTA analysis of the pyrolyzed BaZrO<sub>3</sub> gel in air ( $\Delta$ ) and in oxygen ( $\diamond$ ).** The scan rate used was 10°C/min.

The room temperature powder XRD pattern for 300-nm-thick BaZrO<sub>3</sub> films grown on both sapphire and LaAlO<sub>3</sub> substrates are reported in Figs. 1.31 and 1.32. Figure 1.31 shows the presence of a polycrystalline BaZrO<sub>3</sub> film



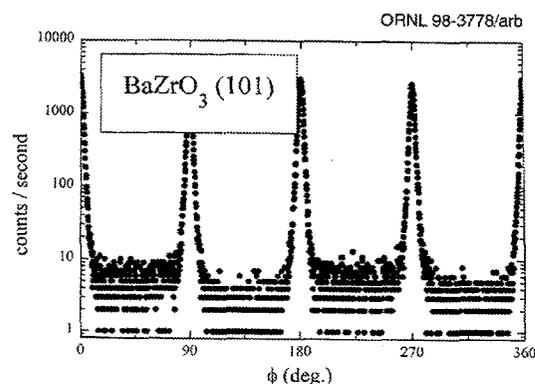
**Fig. 1.31.** The room-temperature powder XRD for 300-nm-thick BaZrO<sub>3</sub> films grown on sapphire substrates.



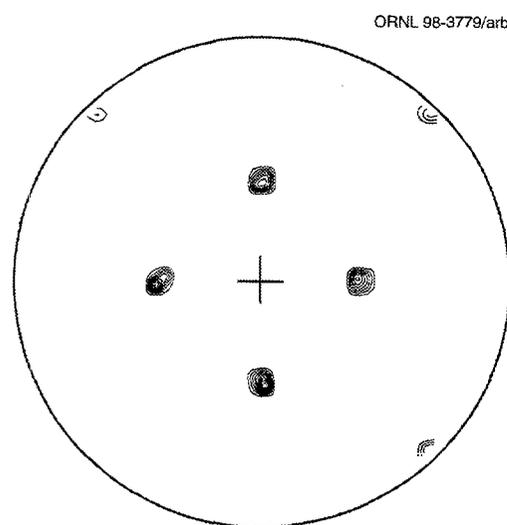
**Fig. 1.32.** The room-temperature powder XRD for 300-nm-thick BaZrO<sub>3</sub> films grown on LaAlO<sub>3</sub> (100) substrates. The film shows the *c*-axis alignment.

whereas Fig. 1.32 indicated the presence of a *c*-axis texture on LaAlO<sub>3</sub> substrates. Similar *c*-axis texture was also obtained on SrTiO<sub>3</sub> substrates. XRD results from the  $\omega$  and  $\phi$  scans for films grown on both SrTiO<sub>3</sub> and LaAlO<sub>3</sub> substrates revealed (100) cube texture. The FWHM values for BaZrO<sub>3</sub> films on SrTiO<sub>3</sub> substrates were 1.8° (out-of-plane epitaxy) and 2.6° (in-plane epitaxy). Similarly, the FWHM values for films grown on LaAlO<sub>3</sub> substrates were 3.1° (out-of-plane) and 5.0° (in-plane). The sharp texture on SrTiO<sub>3</sub> substrates can be

explained in terms of a reduced lattice mismatch. The SrTiO<sub>3</sub> has a lattice mismatch of 6.9% with BaZrO<sub>3</sub> whereas the LaAlO<sub>3</sub> has a mismatch of 9.5% with BaZrO<sub>3</sub>. A typical  $\phi$  scan for a 300-nm-thick BaZrO<sub>3</sub> film grown on a SrTiO<sub>3</sub> substrate is shown in Fig. 1.33. A typical (220) pole figure for a 300-nm-thick BaZrO<sub>3</sub> film grown on a SrTiO<sub>3</sub> substrate is shown in Fig. 1.34. Figures 1.33 and 1.34 indicate the presence of a single cube-on-cube texture. The BaZrO<sub>3</sub> films grown on these substrates were smooth, crack-free, and continuous.



**Fig. 1.33.** A typical  $\phi$  scan featuring the epitaxial nature of BaZrO<sub>3</sub> films on SrTiO<sub>3</sub> (100) substrates.



**Fig. 1.34.** A typical BaZrO<sub>3</sub> (220) pole figure for a 300-nm-thick BaZrO<sub>3</sub> film on SrTiO<sub>3</sub> (100) substrates.

In summary, we developed the sol-gel chemistry for  $\text{BaZrO}_3$  precursors. The precursor solutions were partially hydrolyzed and spin-coated on several substrates. The films were post-annealed in oxygen at  $800^\circ\text{C}$  for a total of 6 min in a rapid thermal annealer. The orientation of the  $\text{BaZrO}_3$  films grown on sapphire substrates were polycrystalline. But the films on  $\text{SrTiO}_3$  and  $\text{LaAlO}_3$  substrates had both out-of-plane and in-plane texture. The  $\text{BaZrO}_3$  films on  $\text{SrTiO}_3$  substrates had a fairly sharp texture as the result of the presence of a reduced lattice mismatch. Thus we demonstrated the epitaxial growth of  $\text{BaZrO}_3$  films on single crystal  $\text{SrTiO}_3$  (100) and  $\text{LaAlO}_3$  (100) substrates using sol-gel alkoxide precursors. The  $\text{BaZrO}_3$  precursors developed in the present work may be used for producing epitaxial buffer layers on RABiTS<sup>TM</sup> for YBCO coated conductors.

### GROWTH OF EPITAXIAL $\text{LaAlO}_3$ FILMS ON $\text{SrTiO}_3$ (100) SUBSTRATES USING A DIP-COATING PROCESS

A dip-coating unit was assembled at ORNL by mounting a translation unit on a support. The dip coater was controlled automatically with a substrate withdrawal velocity of  $\leq 1.0$  m/min. The lanthanum aluminum oxide ( $\text{LaAlO}_3$ ) sol-gel alkoxide precursor solutions were used to dip-coat strontium titanium oxide ( $\text{SrTiO}_3$ ) (100) single crystal substrates. After drying in air, the dip-coated substrates were heat-treated in air at  $800^\circ\text{C}$  for 10 min. The film thickness was  $\sim 100$  nm. The detailed XRD studies indicated the formation of epitaxial  $\text{LaAlO}_3$  films. The room temperature powder XRD pattern for a 100-nm-thick  $\text{LaAlO}_3$  film on  $\text{SrTiO}_3$  (100) substrate showed the presence of a *c*-axis aligned film. XRD results from the  $\omega$  and  $\phi$  scans (as shown in Figs. 1.35 and 1.36) revealed a (100) cube texture. The FWHM values were  $0.2^\circ$  (out-of-plane epitaxy) and  $0.4^\circ$  (in-plane epitaxy). The sharp texture indicates the presence of a highly textured  $\text{LaAlO}_3$  film. A

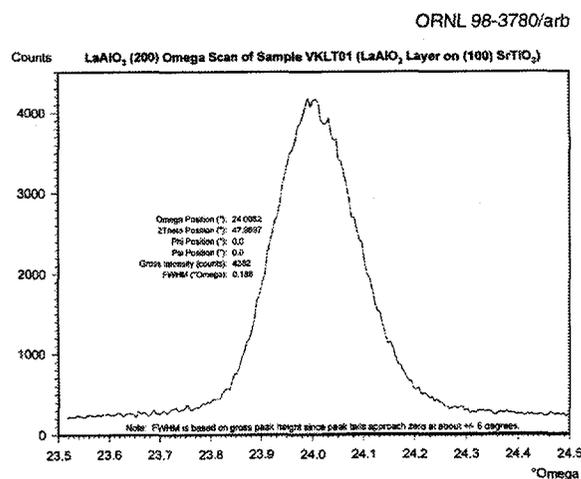


Fig. 1.35. A typical  $\omega$  scan featuring the epitaxial alignment of  $\text{LaAlO}_3$  films on  $\text{SrTiO}_3$  (100) substrates.

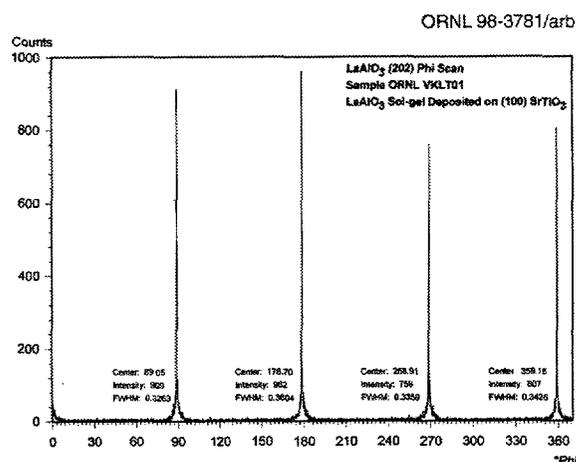


Fig. 1.36. A typical  $\phi$  scan featuring the epitaxial nature of  $\text{LaAlO}_3$  films on  $\text{SrTiO}_3$  (100) substrates.

typical (202) pole figure for a 100-nm-thick  $\text{LaAlO}_3$  film grown on a  $\text{SrTiO}_3$  substrate is shown in Fig. 1.37. Figure 1.37 indicates the presence of a single cube-on-cube texture. Thus we reproduced our initial results on spin-coated films with the dip-coated films.

Fresh  $\text{LaAlO}_3$  precursor solutions were prepared by starting with lanthanum isopropoxide and aluminum sec-butoxide using 2-methoxyethanol as the solvent. The as-prepared solutions were partially hydrolyzed with different degrees of hydrolysis (1:1.0,

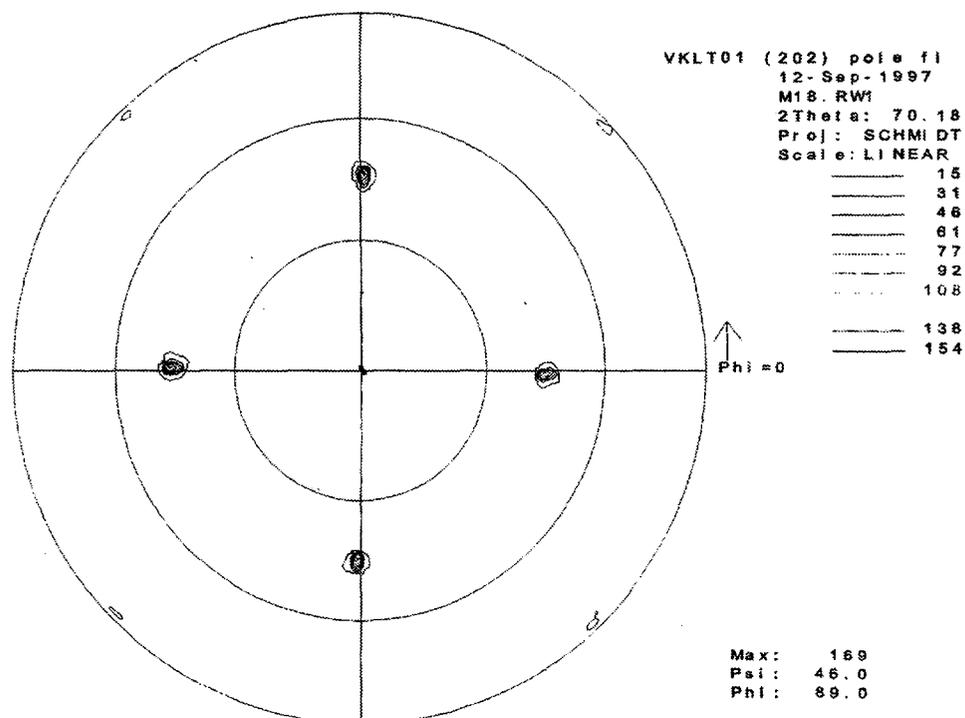


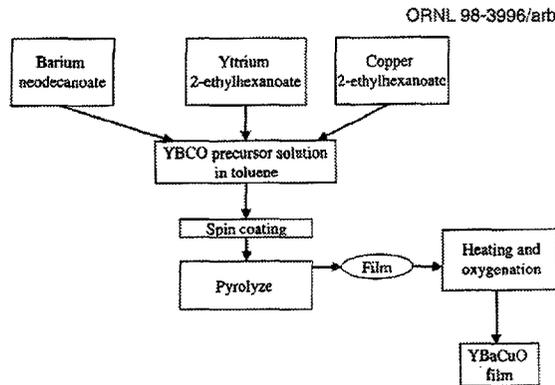
Fig. 1.37. A typical  $\text{LaAlO}_3$  (202) pole figure for a 100-nm-thick  $\text{LaAlO}_3$  film on a  $\text{SrTiO}_3$  (100) substrate.

1:1.2, and 1:1.4 ratio by volume) using 1M  $\text{H}_2\text{O}$  in 2-methoxyethanol. These solutions were dip-coated systematically onto the  $\text{SrTiO}_3$  (100) single crystal substrates to study the effect of various parameters on the film growth. The parameters varied were substrate withdrawal velocity, degree of hydrolysis, aged solutions, annealing time, atmosphere, and temperature. A set of base conditions was kept constant while one parameter at a time was varied. A complex matrix of 20 different sets of growth conditions was used to grow  $\text{LaAlO}_3$  films. This study will help us to identify the conditions needed to coat long length substrates. The films were analyzed in detail by XRD. Some of the films were characterized at the University of Tennessee Space Institute X-ray facility. Efforts are now being made to coat  $\text{LaAlO}_3$  on Ni to see the effect of growth conditions on Ni.

### GROWTH OF EPITAXIAL $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ FILMS ON SINGLE CRYSTAL OXIDE SUBSTRATES USING METAL-ORGANIC DECOMPOSITION PRECURSORS

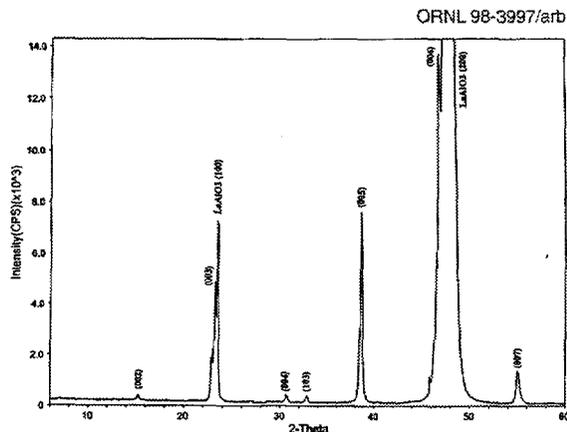
A new metal-organic decomposition (MOD) precursor route for fabricating  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) films was developed in FY 1997. In this process, the starting precursor solution was prepared by dissolving yttrium 2-ethylhexonate, barium neodecaonate, copper 2-ethylhexonate in toluene. The total cation concentration was ~0.14 M. The precursor solution was very viscous. The  $\text{SrTiO}_3$  (100) and  $\text{LaAlO}_3$  (100) single crystals were used as the substrates. The flowchart for the preparation of YBCO film is shown in Fig. 1.38.

The YBCO precursor solutions were spin-coated on  $\text{LaAlO}_3$  substrates at a speed of 2000 rpm for 40 s. A total of five coatings were performed to achieve a thickness of approximately 400 nm. Between each coat, the

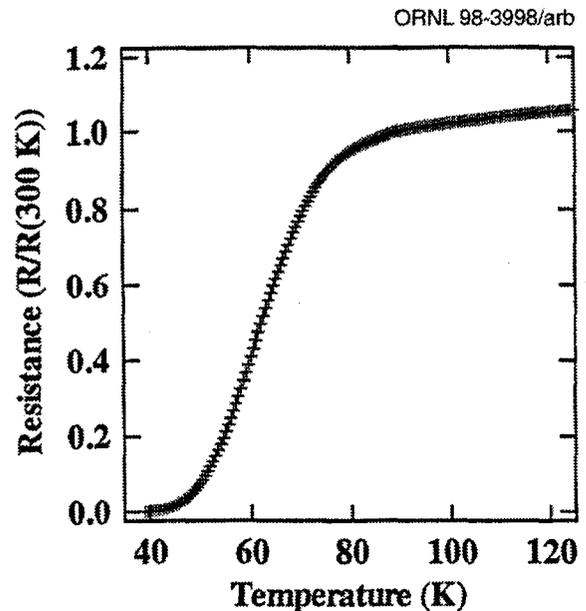


**Fig. 1.38. Flowchart for the preparation of YBCO films.**

films were pyrolyzed at 400°C for 1 h in air. Slow heating rate (2°/min) was essential to get a continuous film. After five coatings, the film was heated again at 400°C for 2 h in 1 atm oxygen to remove all the hydrocarbons and then heat treated at 850°C for 2 h in 2% oxygen. A typical powder XRD pattern for the YBCO film is shown in Fig. 1.39. Figure 1.39 indicates the presence of a *c*-axis aligned YBCO film on LaAlO<sub>3</sub>. Similar results were also obtained for films on SrTiO<sub>3</sub> substrates. On SrTiO<sub>3</sub> substrates, small amounts of *a*-axis oriented YBCO, CuO, and BaCuO<sub>2</sub> impurities were also observed. However, the  $\phi$  scan (102) on the YBCO film on SrTiO<sub>3</sub> indicated the presence of a single cube textured film. The resistance vs temperature plot for the YBCO film on a SrTiO<sub>3</sub> substrate is shown in Fig. 1.40. The film has a

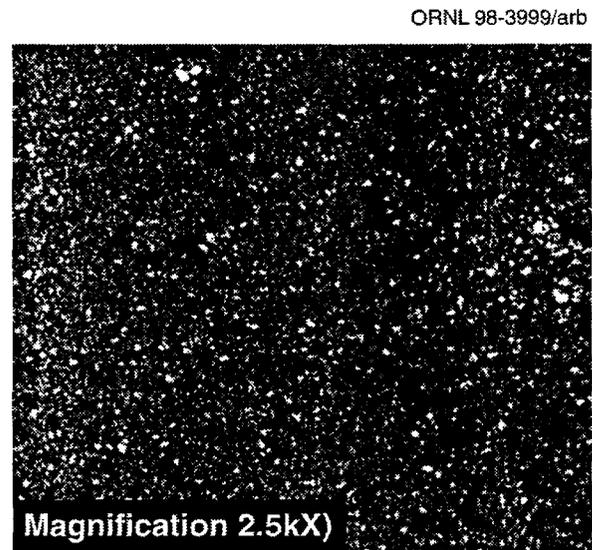


**Fig. 1.39. The powder XRD for a 400-nm-thick YBCO grown on a LaAlO<sub>3</sub> (100) substrate. The film shows the *c*-axis alignment.**



**Fig. 1.40. The resistivity plot for a 400-nm-thick YBCO film grown on a SrTiO<sub>3</sub> (100) substrate.**

very broad transition with a zero resistance of 40 K. The SEM image (as shown in Fig. 1.41) reveals the presence of secondary phases along with the YBCO film. This could be one of the reasons for low critical temperatures ( $T_c$ s).



**Fig. 1.41. The SEM micrograph for a 400-nm-thick YBCO film grown on a SrTiO<sub>3</sub> (100) substrate.**

## THE GROWTH OF EPITAXIAL BUFFER LAYERS ON SINGLE CRYSTAL OXIDE SUBSTRATES USING SOL-GEL ALKOXIDE PRECURSORS

Novel sol-gel precursor solutions of the perovskite-type compounds  $\text{NdAlO}_3$ ,  $\text{GdAlO}_3$ , and  $\text{YAlO}_3$  have been prepared. These compounds are of interest in part because their lattice parameters are smaller than those of the other more traditional buffer layers, such as  $\text{LaAlO}_3$  and  $\text{CeO}_2$ , which may make them better candidates for deposition on Ni when using sol-gel techniques. These aluminate layers also do not have the twinning problems associated with  $\text{LaAlO}_3$ . Epitaxial films of these buffer layers have been grown on single crystal  $\text{SrTiO}_3$  (100) substrates. The solutions were applied to the substrates by spin coating, and then the substrates were pyrolyzed in  $\text{O}_2$  at  $800^\circ\text{C}$  for 2 min in a rapid thermal processor. The thickness of the films was increased by multiple coatings and pyrolysis treatments. Each coating yielded approximately 500–1000 Å of film.

A precursor solution of  $\text{SrTiO}_3$  was made from standard sol-gel procedures using strontium metal and a titanium alkoxide. Epitaxial films of  $\text{SrTiO}_3$  were grown on  $\text{LaAlO}_3$  (100) single crystals by both pyrolysis in a rapid thermal processor at  $600^\circ\text{C}$  in  $\text{O}_2$  for 2 min and by slow heating to  $650^\circ\text{C}$ , annealing for 1 h in air, and slow cooling. Again thickness was increased either by cycles of coatings and pyrolysis treatments in the rapid thermal processor or by drying each coat in air for 10 min at  $300^\circ\text{C}$  before the  $650^\circ\text{C}$  anneal.

Approximately 500 Å resulted from each coating.

The films are strongly  $c$ -axis oriented as indicated by  $\theta$ - $2\theta$  scans, an example of which is seen in Fig. 1.42. The strong  $c$ -axis orientation was affirmed by the rocking curve results of the individual (002) planes, and  $\phi$  scans of the (202) planes, and (111) in the case of  $\text{YAlO}_3$ , confirmed the good in-plane texture. The FWHM values measured from these scans of all the buffer layers are as follows:

$\text{NdAlO}_3$ on $\text{SrTiO}_3$ ,	out-of-plane= $1.5^\circ$ ;
	in-plane= $1.4^\circ$
$\text{GdAlO}_3$ on $\text{SrTiO}_3$ ,	out-of-plane= $1.6^\circ$ ;
	in-plane= $2.1^\circ$
$\text{YAlO}_3$ on $\text{SrTiO}_3$ ,	out-of-plane= $2.8^\circ$ ;
	in-plane= $3.7^\circ$
$\text{SrTiO}_3$ on $\text{LaAlO}_3$ ,	out-of-plane= $1.1^\circ$ ;
	in-plane= $1.6^\circ$

Pole figure analyses revealed that the films exhibit the desired single orientation cube-on-cube epitaxy of  $[100](001)_f || [100](001)_s$ . (See Fig. 1.43.)

ORNL 98-4000/arb

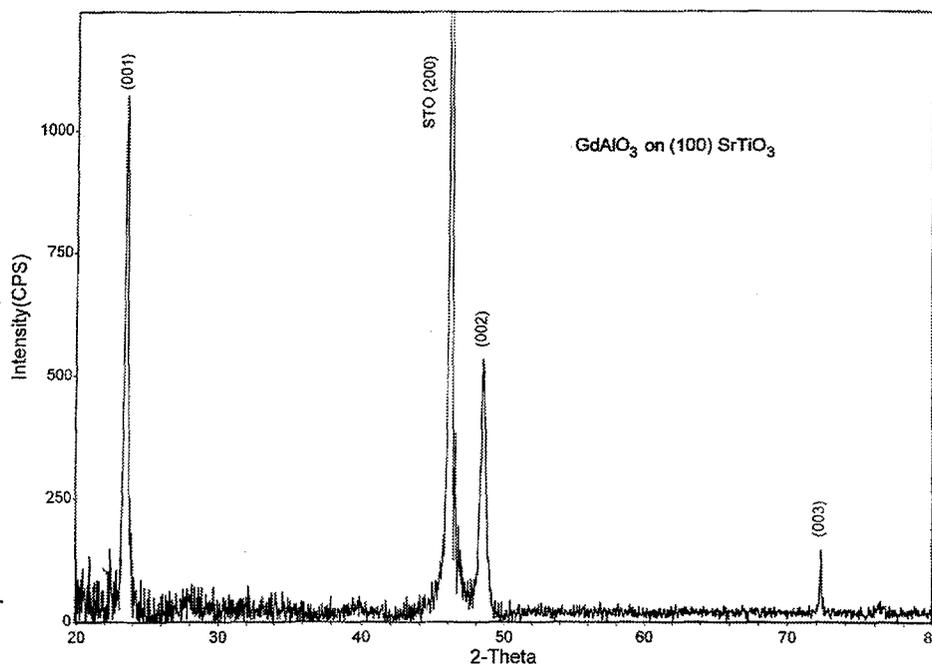


Fig. 1.42.  $\theta$ - $2\theta$  scan of  $\text{GdAlO}_3$  on a  $\text{SrTiO}_3$  (100) single crystal.

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Sol-gel GdAlO<sub>3</sub>/SrTiO<sub>3</sub> grows with  
highly-aligned cube-on-cube epitaxy

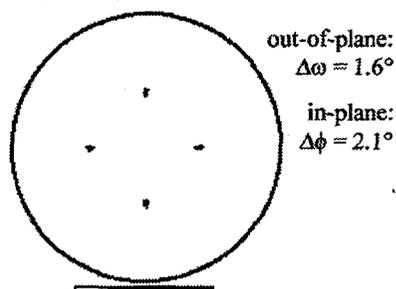


Fig. 1.43. GdAlO<sub>3</sub> (220) pole figure.

### HIGH-RESOLUTION TEM/AEM CHARACTERIZATION OF EPITAXIAL OXIDE MULTILAYERS FABRICATED BY LASER ABLATION ON BIAXIALLY TEXTURED Ni

The success of RABiTST<sup>TM</sup> relies on the successful epitaxial deposition of cube-on-cube or rotated cube-on-cube oriented oxide buffer layers on the {100}<100> textured-Ni substrate. This has been accomplished using two methods. First is by epitaxial deposition of an intervening noble metal layer between the oxide and Ni. The second is by epitaxial deposition of the oxide layers directly on Ni under conditions such that formation of NiO is not thermodynamically expected. YBCO films deposited on such substrates have  $J_c$ s approaching 3 MA/cm<sup>2</sup> at 0 T and 77 K. We report here the results of a detailed microstructural and compositional examination of oxide buffer layers deposited directly on Ni using laser ablation.

#### Experimental Procedure

##### *Fabrication of the YBCO Tapes*

Biaxially textured Ni substrates were formed by consecutive rolling of a polycrystalline, randomly oriented high purity (99.99%) bar to total deformations greater than 95%, followed by recrystallization. Examination

of (111) and (200) pole figures of an as-rolled Ni tape show localization of intensities along the {112}<111> and the {123}<634> orientations along the  $\beta$ -fiber or the skeleton line, consistent with the formation of a sharp copper-type rolling texture. By controlling the surface condition of the work rolls, it was possible to obtain substrates with surfaces with a rms roughness of  $\sim 10$  nm. The substrate was then annealed in situ in a laser ablation chamber at 900°C for 2 h in 4% H<sub>2</sub> in Ar, resulting in the formation of a sharp {100}<100> cube texture. Typical samples showed X-ray  $\omega$ - and  $\phi$ -scans with FWHM of 6° and 7°, respectively. Grain boundary studies of the substrate using electron BKD showed that over 95% of the boundaries had misorientations less than 5°.

Ceramic oxide films were deposited on the biaxially textured Ni substrate using pulsed laser ablation with the substrate held at a constant temperature of 780°C. The multilayer sample studied was of the composition YBCO (1  $\mu$ m)/YSZ (0.2 mm)/(CeO<sub>2</sub>) (0.9  $\mu$ m)/Ni (125  $\mu$ m). (100) epitaxy of CeO<sub>2</sub> was established by performing the initial deposition in 180 mtorr of 4% H<sub>2</sub> in Ar to a thickness of  $\sim 30$  nm. The flow of 4% H<sub>2</sub>-Ar gas was then stopped resulting in a vacuum of 10<sup>-5</sup> torr. An additional layer of  $\sim 50$  nm of CeO<sub>2</sub> was deposited in this vacuum. Oxygen was then introduced into the chamber and the subsequent deposition of CeO<sub>2</sub> was performed in p(O<sub>2</sub>)  $\sim 4 \times 10^{-4}$  torr to a total thickness of 0.9  $\mu$ m. YSZ was deposited on CeO<sub>2</sub> under a p(O<sub>2</sub>)  $\sim 4 \times 10^{-4}$  torr to a thickness of  $\sim 0.2$   $\mu$ m. A 1- $\mu$ m YBCO layer was deposited on the YSZ layer at p(O<sub>2</sub>)  $\sim 180$  mtorr. The sample was first cooled to 200°C at 10°C/min and then furnace cooled to room temperature. Grain boundary studies of the substrate using electron BKD showed that most areas had grain boundary misorientations less than 5°.

##### *Electron Microscopy*

TEM cross-section samples were prepared by coating the YBCO tape with an  $\sim 2$ -mm-thick copper layer using electrodeposition. The

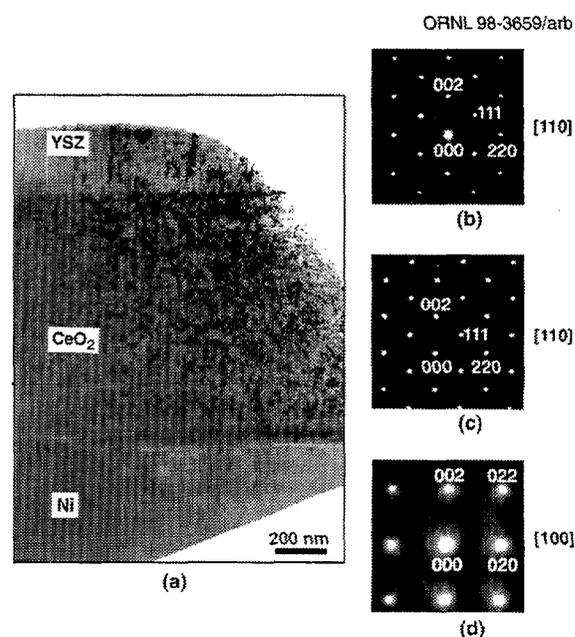
electrodeposition was performed at room temperature using a diluted sulfuric copper solution (90g CuSO<sub>4</sub>, 15 mL H<sub>2</sub>SO<sub>4</sub>, and 475 mL H<sub>2</sub>O). Wrapped in a thick layer of copper, the YBCO tape had enough mechanical integrity to be sliced without delamination at the metal–ceramic interface. TEM foils were then prepared by grinding, polishing, dimpling, and ion milling the 3-mm discs cut from the thin slices. A thin carbon coating was applied to the specimen prior to TEM examination to minimize charging. It should be pointed out that the YBCO is not stable in the sulfuric copper solution whereas all the other layers (Ni, CeO<sub>2</sub>, and YSZ) are stable. Even though not applicable to samples for characterization of the superconducting materials, this is a simple method to prepare cross-sectional samples for studying the multilayer substrate of the superconductor tape (Ni/CeO<sub>2</sub>/YSZ).

Microstructural and microchemical characterizations were performed using both conventional TEM (Philips CM12) and high-resolution analytical electron microscopy (AEM) (Philips CM200). The CM 200 microscope was equipped with a field emission gun (FEG) and an energy dispersive spectrometer (EDS) (Super UTW, Link/Oxford). For high spatial resolution compositional analyses, the microscope was operated in the scanning TEM (STEM) mode with a probe size of 2 nm. Composition profiles across an interface (or a certain region) were collected in the sequential acquisition mode during a single line scan across the interface (or the region) with step sizes of 2–4 nm.

## Results and Discussion

### General Microstructures

The orientation of the individual layers was determined using selected area diffraction (SAD) patterns, as illustrated by Fig. 1.44. First, the specimen was tilted so that in the region shown in Figure 1.44(a), the (100) plane of the Ni substrate, was perpendicular to the electron



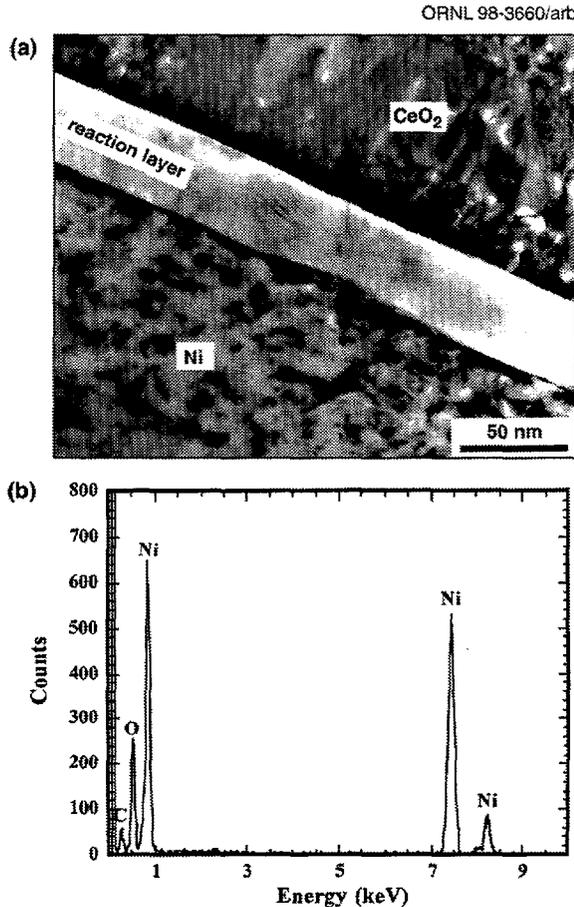
**Fig. 1.44. (a) General interfacial microstructure of the biaxially textured multilayer substrates and SAD patterns collected from (b) the YSZ layer, (c) the adjacent CeO<sub>2</sub>, and (d) the Ni substrate.** The low order reflections are indexed, and the upward drawn direction (i.e., the e-beam direction) is indicated beside each diffraction pattern.

beam as indicated by the SAD patterns in Figure 1.44(d). SAD patterns of the adjacent CeO<sub>2</sub> and YSZ layer were then recorded under such tilt conditions and are shown in Fig. 1.44(c) and (b). Indexing the diffraction patterns showed that the lattice planes perpendicular to the incident beam in the CeO<sub>2</sub> and the YSZ layers were the (110) planes. There was a 45° in-plane rotation between the metal substrate and the oxide layers deposited. The SAD patterns also showed that in all the three layers (Ni, CeO<sub>2</sub>, and YSZ) the [001] axes were perpendicular to the layered structure, consistent with the biaxial nature of the materials.

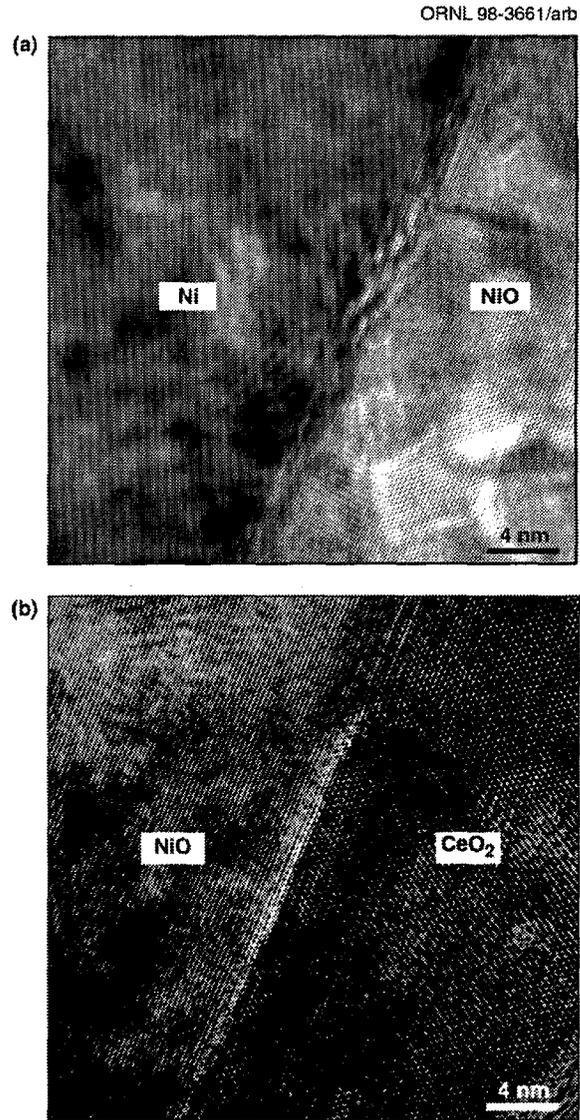
### Ni/CeO<sub>2</sub> Interface

Interfacial reaction was found to occur at the Ni/CeO<sub>2</sub> interface, forming a 10–40-nm-

thick layer as shown in Fig. 1.45(a). This thin reaction layer had a cube-on-cube orientation with the Ni substrate, as revealed by both convergent beam diffraction patterns and high-resolution images. EDS analyses showed that Ni and O were the only elements detected in the interfacial layer [Fig. 1.45(b)]. Therefore, the reaction that occurred at the Ni/CeO<sub>2</sub> interface was oxidation of Ni. The interface between the reaction layer and the Ni substrate was atomically sharp [Fig. 1.46(a)]. However, the thickness of the oxide layer varied along the interface, and the NiO/Ni interface was concave in regions where the oxide was relatively thick, suggesting oxidation propagating from the



**Fig. 1.45. (a) A reaction layer formed at the Ni/CeO<sub>2</sub> interface, and (b) EDS spectrum collected from the reaction layer.**



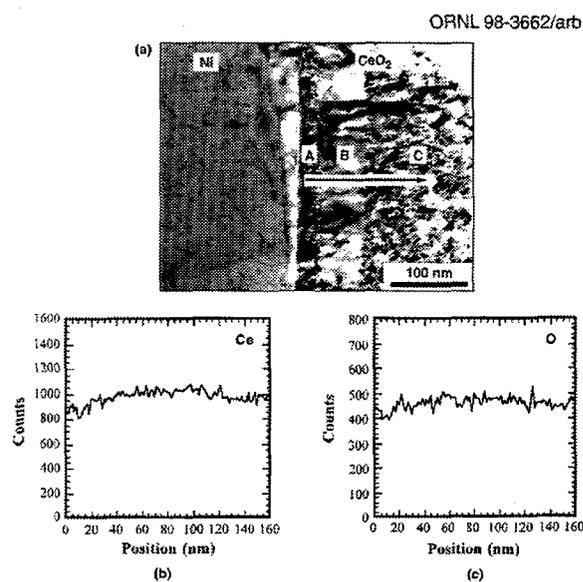
**Fig. 1.46. High-resolution images of (a) the Ni/NiO interface and (b) the NiO/CeO<sub>2</sub> interface.**

NiO/Ni interface into the Ni substrate. The interface between the NiO reaction layer and the CeO<sub>2</sub> buffer layer was sharp and flat, as shown in the high-resolution image in Fig. 1.46(b). A 45° in-plane rotation between the NiO layer and CeO<sub>2</sub> layer was observed. No interdiffusion of Ni and Ce across the interface between the reaction layer and the CeO<sub>2</sub> buffer layer was detected.

It is likely that the NiO layer formed after the initial epitaxy of CeO<sub>2</sub> on Ni because the initial deposition of CeO<sub>2</sub> was performed under oxygen partial pressures at which NiO is unstable. Formation of a Ni oxide layer at the Ni/CeO<sub>2</sub> interface after deposition of the initial CeO<sub>2</sub> layer could occur by solid-state oxygen diffusion through the CeO<sub>2</sub> layer and also by gaseous oxygen diffusion through the cracks in the CeO<sub>2</sub> layer, during the sequential deposition at high temperatures in an oxidizing environment. As mentioned earlier, after the initial deposition under reducing conditions, the CeO<sub>2</sub> film was deposited on the Ni tape at 780°C under increasingly oxidizing conditions to eventually obtain stoichiometric CeO<sub>2</sub>. Furthermore, deposition of the YBCO layer was performed in a background O<sub>2</sub> pressure of 185 mtorr. These deposition conditions presented the possibility of oxygen diffusion to the Ni/CeO<sub>2</sub> interface. Previous studies have also shown that under certain deposition conditions, microcracks can form in the CeO<sub>2</sub> layer because of non-stoichiometry in the oxide layers, lattice mismatch stresses, and residual thermal expansion mismatch stresses between the CeO<sub>2</sub> layer and the Ni substrate. If microcracks form in the CeO<sub>2</sub> layer, diffusion of O<sub>2</sub> along the cracks can be expected, resulting in the preferential formation of NiO at the Ni/CeO<sub>2</sub> interface near the microcracking sites in the CeO<sub>2</sub> layer. This may explain the varying thickness of the NiO layer at the Ni/CeO<sub>2</sub> interface.

### CeO<sub>2</sub> Layer

Three distinct morphologies were observed in the CeO<sub>2</sub> layer. As shown in Fig. 1.47(a), an equiaxed structure (A), ~25 nm thick, was formed during the initial deposition. The equiaxed structure was followed by an ~50-nm columnar structure (B) with the axis of the columns aligned along the [001] axis of CeO<sub>2</sub>. The column spacing was ~20–25 nm. Following the columnar structure was again an equiaxed structure (C) through the rest of the layer. The



**Fig. 1.47. (a) Three distinct morphologies observed in the CeO<sub>2</sub> layer: (A) an equiaxed structure, (B) a columnar structure, and (C) again an equiaxed structure through the rest of the layer; (b) Ce profile along the line-scan across the three different structures from A to C as indicated by the arrow in (a); and (c) O profiles collected along the line-scan across the three different structures from A to C as indicated by the arrow in (a).**

first (A) and second (C) equiaxed structures were similar in appearance. Both contained very high dislocation densities. Conversely, the columnar structure (B) exhibited a very low dislocation density. Each individual column was essentially defect free. Detailed EDS analyses indicated that regions with different morphologies were of the same composition. Shown in Fig. 1.47(b) and (c) are Ce and O profiles recorded during a line scan across the three different structures as indicated in Fig. 1.47(a). No variation in either Ce or O concentration was detected.

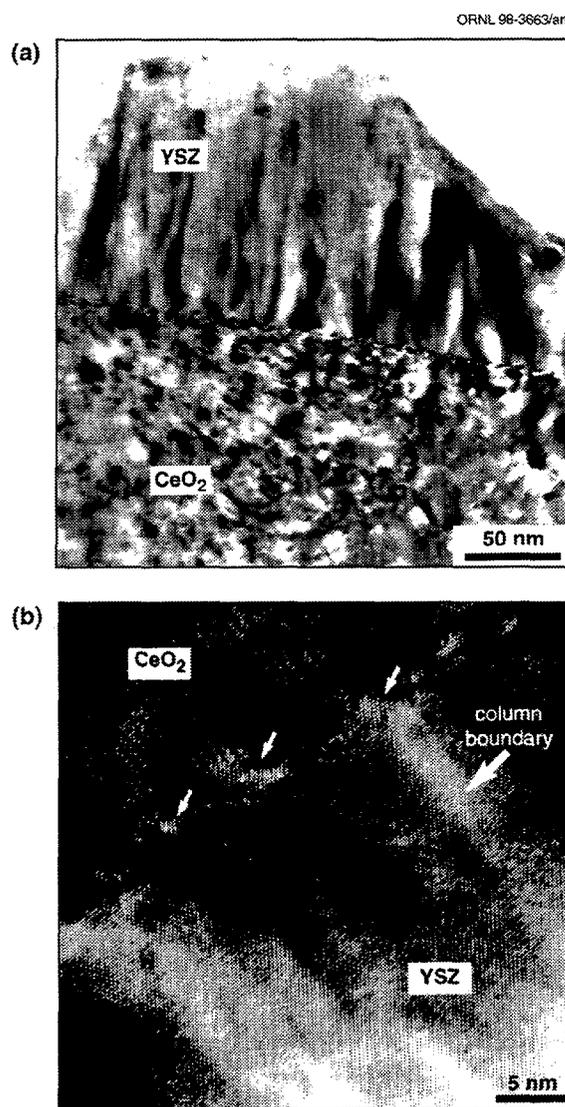
The three distinct morphologies were found to correspond directly to the growth atmosphere during the deposition. The initial deposition of CeO<sub>2</sub> was performed in a forming gas containing H<sub>2</sub> in order to suppress oxidation of Ni. The estimated thickness of this initial layer was 10–30 nm, consistent with layer A observed

in TEM. After the initial deposition, the atmosphere was changed to an oxygen partial pressure of  $10^{-5}$  torr. This change in atmosphere induced the columnar structure (B). The growth atmosphere was finally switched to an oxygen partial pressure of  $4 \times 10^{-4}$  torr, resulting in a change in the growth morphology back to equiaxed.

### ***CeO<sub>2</sub>/YSZ Interface and YSZ Layer***

The interface between the YSZ and CeO<sub>2</sub> layer was free of interfacial reactions, as shown in Fig. 1.48(a). Figure 1.48(b) is a high-resolution image showing lattice fringes extending across the interface. Composition analyses revealed that neither interdiffusion of elements nor interfacial reaction between the CeO<sub>2</sub> and the YSZ phases occurred. Periodic lattice distortions (dislocations) were present at the interface to accommodate the incommensurate lattice planes between the two phases as indicated by the arrow in Fig. 1.48(b). According to high-resolution XRD studies, the normally cubic CeO<sub>2</sub> and YSZ exhibited slightly distorted tetragonal structures due to the residual stresses:  $a = b = 5.41$  Å and  $c = 5.422$  Å for the CeO<sub>2</sub> and  $a = b = 5.12$  Å and  $c = 5.162$  Å for the YSZ. Therefore, the lattice mismatches in both a/b and c directions were 5.7% and 5.0%, respectively. The lattice mismatches corresponded to one dislocation site every ~20 lattice planes, consistent with the high-resolution image in Fig. 1.48(b).

The YSZ layer exhibited a columnar structure with a column spacing of ~40 nm [Fig. 1.48(a)]. The columns aligned along the [001] axis. High-resolution images revealed no orientation variation between the adjacent columns [Fig. 1.48(b)]. The contrast at the column boundaries was simply caused by dislocations originated from the CeO<sub>2</sub>/YSZ interface.



**Fig. 1.48. (a) The interface between the CeO<sub>2</sub> and the YSZ layer and the columnar structure in the YSZ layer; and (b) a high-resolution image showing the periodic dislocations at the CeO<sub>2</sub>/YSZ interface and revealing no orientation variation between adjacent columns in the YSZ.**

## Conclusions

The microstructure of a RABiTS™ comprised of epitaxial multilayers of YSZ (0.2 μm)/CeO<sub>2</sub> (0.9 μm) on a {100}<100> textured Ni (125 μm) template was determined using high-resolution electron microscopy. A reaction layer 10–40 nm thick was observed at the Ni/CeO<sub>2</sub> interface. Detailed microstructural and chemical analyses indicated that the layer was {001} nickel oxide on {001} Ni; however, the NiO layer was discontinuous, suggesting its formation after prior epitaxy of CeO<sub>2</sub> on Ni. Because only cube-on-cube orientation of NiO on Ni was observed, it may be possible to form a continuous layer of cube-oriented NiO by controlled oxidation of Ni as a suitable intermediate buffer layer. The CeO<sub>2</sub> layer was 45° in-plane rotated with respect to the Ni and NiO and was found to consist of three distinct morphologies corresponding to the growth conditions during the deposition. The multilayer studied is most susceptible to microcracking. Because there is a close correlation of the microstructure in the CeO<sub>2</sub> layer to the deposition conditions, it may be possible to

control the morphology of this layer and hence alter the microcracking behavior. Columnar microstructures that in general are more resistant to crack propagation could be formed by performing the majority of CeO<sub>2</sub> deposition in a vacuum of 10<sup>-5</sup> torr. Decreasing the thickness CeO<sub>2</sub> of the layer to below the critical thickness for cracking will also suppress microcrack formation. EDS compositional scans show negligible diffusion of Ni into the CeO<sub>2</sub> layer. Therefore, from the perspective of providing a diffusion barrier to YBCO, only tens of nanometers of CeO<sub>2</sub> are sufficient. Thin CeO<sub>2</sub> layers have been grown by e-beam evaporation of Ce metal on Ni. RABiTS™ with no microcracking in the CeO<sub>2</sub> layer exhibit  $J_c$ s approaching 3 MA/cm<sup>2</sup> at 77 K, 0 T. The YSZ layer exhibits a columnar structure aligned along the [100] axis, with little or no orientation variation between the columns. The interface between the YSZ and CeO<sub>2</sub> layer is atomically sharp and neither interdiffusion of elements nor an interfacial layer was observed. No evidence of microcracking in this layer was observed. Microstructural characteristics of the epitaxial YBCO layer will be reported elsewhere.

# Technical Progress in Applications Development

## **SUPERCONDUCTING TRANSFORMER PROJECT (INTERMAGNETICS GENERAL CORPORATION/ORNL/ WAUKESHA ELECTRIC SYSTEMS/ROCHESTER GAS AND ELECTRIC COMPANY)**

This report covers only the nonproprietary Oak Ridge National Laboratory (ORNL) contributions to the HTS transformer project for FY 1997. Other than ORNL, the organizations participating in the project are the Intermagnetics General Corporation (IGC), Waukesha Electric Systems (WES) of General Signal Corporation, and the Rochester Gas and Electric Company (RG&E). Rensselaer Polytechnic Institute provided consulting under subcontract to IGC. The project objectives are (1) to develop a low-cost, wind-after-react HTS conductor suitable for use in transformers and other ac apparatus; (2) to establish the markets, technical and economic feasibility, and benefits to society of HTS power transformers of medium (30 MVA) to large rating; and (3) to design, build, and test an ~1-MVA single-phase HTS demonstration transformer. During the previous two years of this research effort, significant progress in achieving the first two objectives resulted in the decision to continue into the demonstration phase with construction of the ~1-MVA single-phase HTS demonstration transformer. The construction and test of components have been the major thrusts of the FY 1997 effort. Additional efforts included a more detailed analysis of the commercial design and the 5-MVA alpha prototype that is scheduled to follow the 1-MVA demonstration.

Several key findings of the design studies are presented in an article in the July 1997 issue of the *IEEE Spectrum*. In particular, the finding that HTS transformers can be designed to provide up to 2× overload (albeit with increased refrigeration load) without loss of transformer

life. This enables utilities to buy transformers with lower ratings or to place more capacity in the same location. In contrast, overloading a conventional liquid-filled transformer to 110% rating for only 100 days during a typical 30-year operating period (< 1% of operating time) reduces the life of the unit by 25%. This overload benefit is in addition to the reduced losses and reduced fire and environmental hazard offered by HTS units.

In FY 1997, the team

- constructed the major components needed for a 13.8/6.9-kV, 1-MVA HTS transformer using 30-MVA-scale conductor and core and winding cross sections and initiated final assembly. The major components were
  - 2 km of Bi-2212 tape
  - winding, pretesting, and assembly of the 1-MVA coil set
  - coil instrumentation and sensors
  - HTS cold mass subsystem (namely, the IGC primary and secondary HTS coils, the 77-K radiation shield, support plates, and cryogenic subsystem)
  - core and tank assembly
- updated 30-MVA reference design
- completed preliminary conceptual design of a 5-MVA HTS transformer to power the WES transformer manufacturing plant

### **Construction and Testing of Major Components at ORNL**

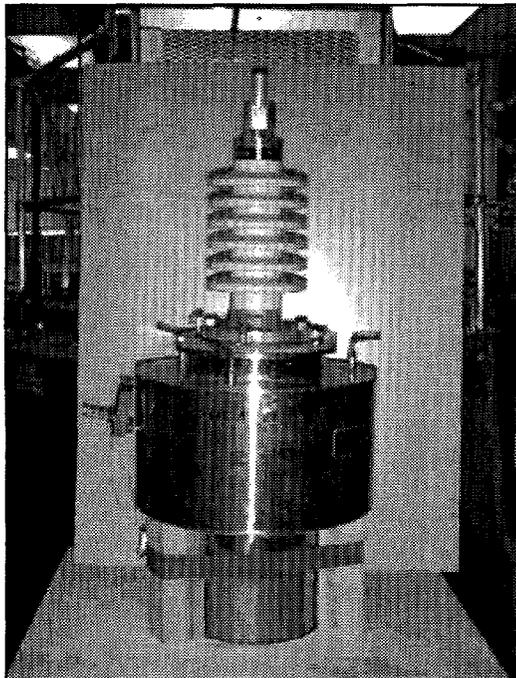
#### ***Bushing Subsystem***

As stated in prior reports, it is desirable to use as many components from existing transformer technology as possible. A test to confirm the ability to use conventional tank and welding technology was initiated in FY 1996,

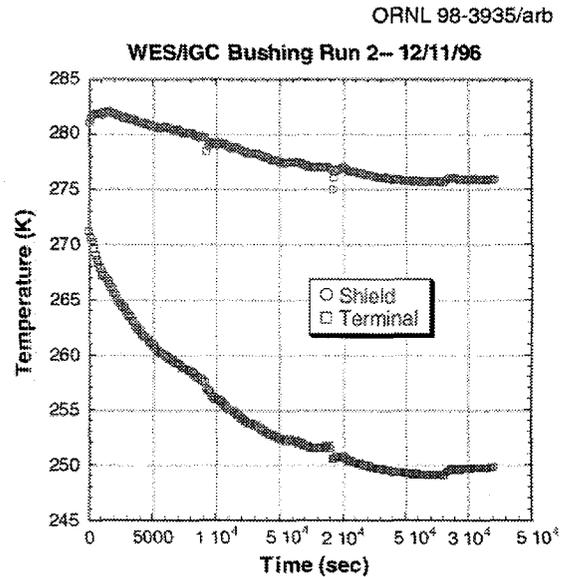
and the tests conducted in FY 1996 established this ability. A full-scale bushing was tested at ORNL to measure the thermal performance of the bushings under simulated operating conditions. The tests were designed to closely simulate the internal liquid nitrogen tank geometry. The test setup is shown in Fig. 2.1. The tests verified that the thermal and materials compatibility performance could be met with conventional bushings and tank. There was no damage to the bushing with temperatures on the terminal of 249 K and on the shield of 276 K (Fig. 2.2).

**Cooling and Cold Mass Support Subsystem**

ORNL had lead responsibility for design and procurement of the 80-K cold mass, liquid nitrogen, and cooling loop subsystems. The bulk of fabrication and assembly are complete on the



**Fig. 2.1. Test setup for measuring the thermal performance of bushings under simulated operating conditions.**



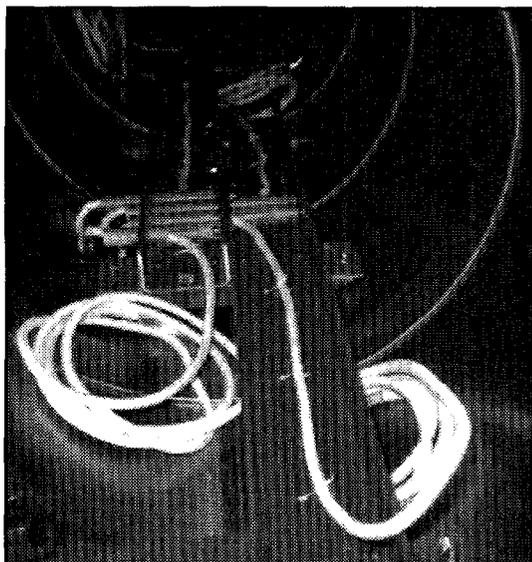
**Fig. 2.2. Tests of conventional bushings show no damage to terminal at 249 K and to shield at 276 K.**

cryogenic portion of the 1-MVA prototype transformer. The main tasks accomplished were

- assembly of the windings onto their upper and lower support plates,
- fabrication of all the interconnecting cooling system piping,
- checkout and repair of all winding sensors,
- design and fabrication of the liquid nitrogen tank high-current feedthrough (Fig. 2.3),
- design and procurement of the cryocooler heat exchanger, and
- design and procurement of the liquid nitrogen shield (Fig. 2.4).

The equipment was shipped to the WES plant in September. The shipment consisted of the high and low voltage superconducting winding assembly with its liquid nitrogen shield and cryogenic support legs, the turbopump and vacuum controls for the vacuum tank, and the cryocooler. The cryocooler, a Cryomech GB-37 unit, had been in storage at ORNL for several years, so its performance was tested and verified. The liquid nitrogen shield was fabricated by an outside vendor to ORNL conceptual designs and specifications and was

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**Fig. 2.3. Liquid nitrogen tank high-current feedthrough.**

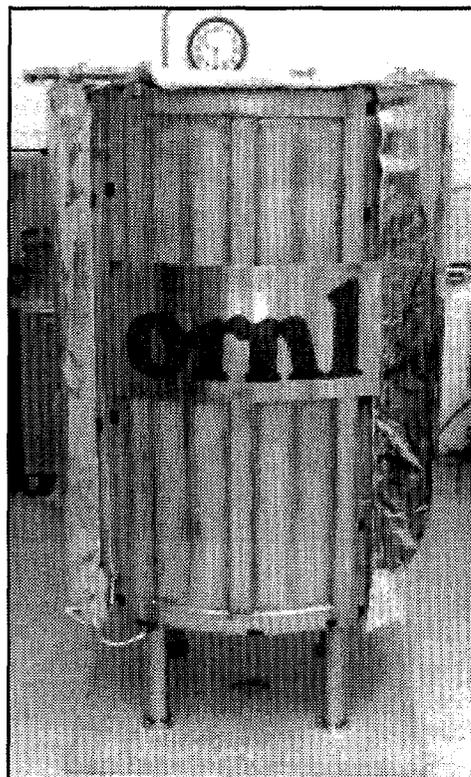
shipped to ORNL for fit-up to the coils. The liquid nitrogen tank was also fabricated externally and shipped directly to WES. The cryocooler heat exchanger and HTS current lead assemblies for the winding were fabricated externally and will be shipped directly to WES.

### Electrical Insulation Systems in Electric Power Equipment

Solid, liquid, and vacuum will be present in all HTS equipment designs. In particular, interfaces between solid/vacuum, liquid/vacuum, and liquid/solid dielectrics under ac and impulse conditions in a cryogenic environment present several unanswered questions. To address some of these issues, ORNL has initiated activities to examine the solid/vacuum and liquid/solid interfaces under the electrical and vacuum conditions appropriate to HTS equipment.

Specifically, three stages of a five-stage (100 kV per stage) impulse generator were set up and an experimental test apparatus was completed. Also a new 150-kV ac power supply with low partial discharge sensitivity has been

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**Fig. 2.4. Liquid nitrogen shield.**

received and will be put into service. A stainless steel vacuum chamber, equipped with a 1-ft high-voltage bushing, was returned to service for conducting surface flashover studies in vacuum. The chamber was cleaned and stainless steel electrodes were installed. The electrodes, with profiled ("Rogowski") edges, provide a plane-plane geometry for either vacuum gap or gap plus dielectric spacer. The bottom electrode is mounted on a linear motion drive with a vacuum feedthrough, permitting an externally controlled variable electrode gap setting. With a 100 L/s turbo molecular pump installed directly onto the vacuum chamber, the system has been pumped down to a pressure of  $2 \times 10^{-7}$  torr, which is more than adequate for testing under conditions that would be encountered for the superconducting systems in which the solid/vacuum dielectric interface is present. Higher pressure in a variety of background

gases can be maintained via a controlled leak. Initial test of the complete system has been performed using disk-shaped spacers, 38 mm in diameter, made of G-11. Three spacer thicknesses, 1, 3, and 5 mm, were made for the initial series of impulse breakdown/flashover tests. Tests with longer spacers are planned. The need for surface flashover studies on solid/liquid nitrogen systems is being examined.

### HTS UNDERGROUND CABLE PROJECT WITH SOUTHWIRE COMPANY

#### Introduction

This report covers only the nonproprietary ORNL contributions to the HTS Underground Cable Project with Southwire Company for FY 1997. During the fiscal year, the project made a transition in the contractual arrangement with Southwire Company from a CRADA to a superconductivity pilot center agreement. For this multiyear joint development project, Southwire will construct a 30.5-m-long, three-phase HTS cable complete with electrical and thermal insulation, outer enclosures, and cable terminations to demonstrate the feasibility of this promising electric utility application. The cable will be installed between two overhead utility towers and will supply 1.25 kA of current at 12.5 kV to the utility and building wire manufacturing plants located at Southwire Company Headquarters in Carrollton, Georgia. The cable will be tested during FY 2000 under real-use situations and will demonstrate Southwire's expertise in HTS cables and confidence that this technology can be supplied to the electric utility industry. To reach this goal, a 5-m-long single-phase

HTS cable rated at 12.5 kV and 1.25 kA was designed during FY 1997 and will be tested at ORNL during FY 1998 in a laboratory environment as a proof-of-design concept.

ORNL has been working with Southwire in two broad areas: (1) providing technical expertise and analyses to assist Southwire in the design of an HTS cable and (2) performing tests of various components using unique laboratory facilities at ORNL in support of the HTS cable design. An HTS cable design process as shown in Fig. 2.5 has evolved and been defined for the 5-m and 30-m HTS cables. Progress and results by ORNL in the development of an HTS cable during FY 1997 are summarized in the following areas:

- short sample testing of HTS tapes
- prototype cables
- electrical dielectric testing
- cable termination
- refrigeration system

#### Short Sample Testing of HTS Tapes

A series of short sample property tests (207 in this reporting period) were performed on the

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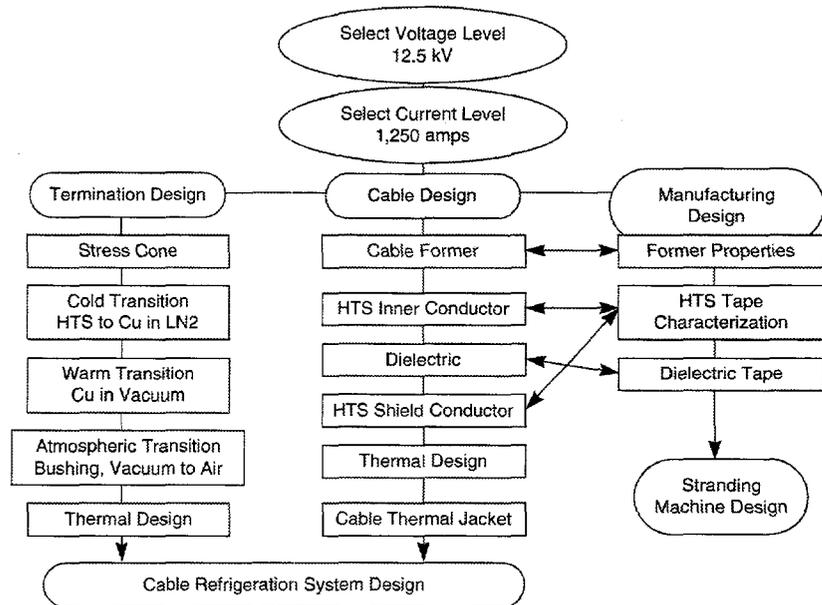


Figure 2.5. HTS cable design process.

Bi-2223/Ag HTS tapes acquired by Southwire. The critical currents ( $I_c$ s) in a background magnetic field ( $I_{cB}$ s) of HTS tapes were measured as functions of thermal cycling, strain, and applied magnetic field.  $I_c$ s were measured first on straight tapes in liquid nitrogen ( $LN_2$ ). After the tapes were warmed in dry air, they were wound on a 1-in.-diameter mandrel at a pitch of  $87^\circ$  (worst case pitch). The tapes were quenched in  $LN_2$  again, and then their  $I_c$ s were measured while in various magnetic fields. The samples were warmed, quenched, and measured repeatedly until four thermal cycles and measurements were completed. The average reduction in  $I_c$  in self-field ( $I_{c0}$ ) between straight and wound sample measurements (first and second cycles) was 29.9%. After four cycles, the measured average reduction of  $I_{c0}$  was 41.1%. The  $I_{cB}$  drop was 15.3% for an applied field (B) of 100 gauss and 50.3% for B of 1000 gauss.

A study of  $I_c$  enhancement was performed after additional manufacturer's processing on HTS tapes acquired by Southwire.  $I_c$  measurements were made to determine the characteristics and integrity of pressed and sintered 1-ft tapes. The tapes were first measured straight in  $LN_2$ , warmed to room temperature, wound on a 1.5-in. mandrel at a pitch of  $30^\circ$ , then quenched into  $LN_2$ . The effect of strain and cycling reduced  $I_c$ s an average of 28.9%.

HTS tapes from three suppliers have been evaluated to determine their performance. Additional  $I_c$  measurements of these tapes were made after they were reprocessed with additional heat treatment steps both with and without pressing.  $I_c$ s were measured straight and then curled at a pitch of  $85.5^\circ$  on a 1-in.-OD mandrel for all three manufacturers' tapes. The

scatter in  $I_c$  measured straight and then wound from each of the suppliers is summarized in Table 2.1.

**Table 2.1. Percentage of scatter in  $I_c$  of suppliers' tapes**

	Company A	Company B	Company C
Straight	34.0	2.1	15.1
Wound	19.6	23.4	34.7

$I_c$ s of these suppliers' tapes were compared with additional heat treatment steps both with and without pressing. In all cases, the additional  $O_2$  heat treatment increased the  $I_c$ s of the tapes.

Ranges of HTS strain tolerances, measured as a function of  $I_c$ , with varying tape pitches on different mandrel diameters have been evaluated. The effect on  $I_c$  from strain developed while winding tapes on different mandrel diameters from 0.50 in. to 1.50 in. was studied. Tape pitches used were  $15^\circ$  and  $30^\circ$ . The larger diameter mandrels had low losses in  $I_c$  from strain on HTSC tapes.  $I_c$  winding angle dependance was measured for two sets of suppliers' tapes. The tapes were wound on a 1-in.-OD thin-walled stainless-steel mandrel at pitches of  $15^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$ ,  $75^\circ$ , and  $90^\circ$  with respect to the mandrel's long axis. Table 2.2 summarizes the percentages of the specification currents.

Effects of cladding for handling, thermal cycling, strain, and shelf life have been explored.  $I_c$ s were measured first for straight samples and then for tapes wound on a 1.5-in.-OD mandrel at a  $30^\circ$  angle from the long axis in  $LN_2$ . There was a 2.6% increase in the mean  $I_c$ s after cycling and winding on the

**Table 2.2. Percentages of vendor-specified (pitch=0) critical currents for suppliers' tapes**

Supplier	Pitch (degrees)					
	15	30	45	60	75	90
Supplier A	113.9	82.5	80.8	63.7	72.1	36.8
Supplier B	95.0	74.4	64.4	65.5	67.8	64.3

mandrel. The cladding enabled the tapes to be handled without damage. Thermal cycling showed no obvious problems.

### Prototype Cables

The testing of 1-m-long, hand-wrapped prototype cables continued in FY 1997.

- All cables contain pairs of oppositely wound HTS tapes with variations in construction techniques.
- Cable 3 was constructed in FY 1996 and tested in FY 1997.
- Cables 4 and 5 were constructed and tested in FY 1997.
- Cables 6, 7, and 8 were constructed; their dc characteristics were measured in FY 1997.

### Prototype Cable Descriptions

The prototype cables are approximately 1-m long and were fabricated by helically winding Ag-sheathed Bi-2223 HTS tapes on a stainless-steel tube former. The prototype cable 3 consists of 10 layers of HTS tapes wound on a 25.4-mm-diam former with Kapton insulation separating each layer. The lay angle for the tapes was  $15^\circ$  in all the layers. In cable 4, the number of layers went back to four (as in cables 1 and 2), but the former diameter had increased to 38.1 mm. This larger diameter former was also used for all later cables.

The prototype cable 5 consisted of four layers of tapes with a lay angle of  $30^\circ$ . This larger lay angle was also used for all later cables. The inner pair of layers had no insulation between the layers, and the outer pair of layers were insulated by Kapton with the individual tapes separated by a thread. This prototype had voltage taps that enabled the voltage across the inner and outer pairs of layers to be measured.

The prototype cables 6 and 7 were made of HTS tapes purchased from a different manufacturer. Cable 6 has two layers of tapes and cable 7 has four layers. The prototype

cable 8 was made of a new batch of HTS tapes made by the same manufacturer that made the tapes for the first five cables.

### Experimental Apparatus and Procedure

A 3-kA dc power supply and a 2-kA ac power supply were used to energize the cables. The voltages from the shunts and voltage taps placed on the prototypes were read using a Keithly 2001 digital multimeter. Data were collected with a Labview 2.2 data acquisition software running on a Macintosh IIfx computer.

For prototype 5, the inner and outer pair of layers of HTS tapes were soldered to separate Cu end plugs at each end of the sample that were electrically insulated from each other. Clamps from the power supply cables could be attached to either or both end plugs of this cable. The main shunt was used to measure the total current supplied to the cable, and two additional shunts were used to measure the currents in the inner and the outer pair.

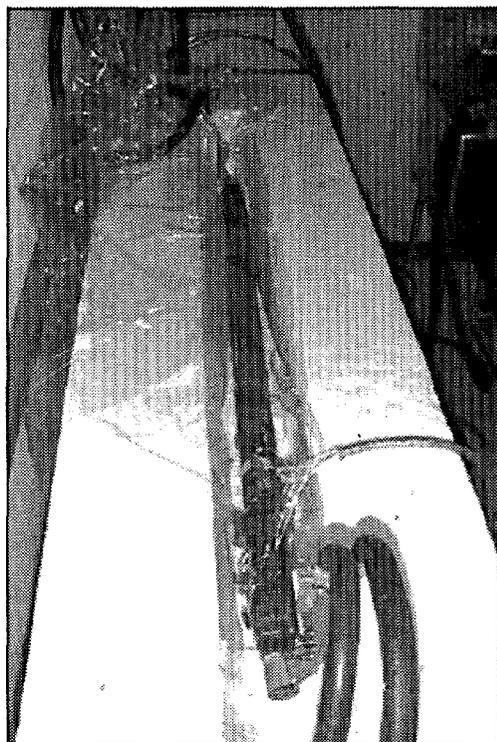
All measurements were made in a  $LN_2$  bath formed by a styrofoam block. Because of the thermal isolation required for ac loss measurements, the prototype cables were enclosed in a micarta or G-10 cylinder filled with wax. Figure 2.6 shows the cable setup for both dc and ac measurements.

### DC Measurements

The dc characteristics were measured for all prototype cables made in FY 1997. All I-V curves show a gradual voltage increase after a certain current, indicative of the broad resistive transition feature of the HTS tapes. The dc  $I_c$  for each cable was obtained using the 1-mV/cm criterion. Table 2.3 summarizes the measured critical currents on the various 1-m prototype cables (including the two cables tested in FY 1996).

The first four cables indicated that the cables made from the first batch of HTS tapes have an average  $I_c$  per tape of 8.6 A in the cable form. The variation in the construction

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**Fig. 2.6. Prototype cable setup for both dc and ac measurements.**

parameters did not make much difference. The HTS used for cable 5 was re-treated by a third party before winding into the cable. This resulted in about a 34% increase in  $I_c$  per tape in the cable form. The 15.4 A  $I_c$  per tape measured

on cable 8 indicated a 79% increase for the second batch tapes as compared to the first batch made by the same manufacturer. As was noted before, prototype cables 6 and 7 were made of HTS tapes purchased from a different manufacturer. This HTS tape has an oxide powder coating on the surface. Rough handling of the tapes to remove the coating for cable 6 may be the reason for the much lower  $I_c$  per tape obtained in this cable as compared with cable 7.

### ***Current Distribution Measurements on Prototype 5***

For prototype cable 5, the measurements were conducted for the conditions where the inner pair, the outer pair, and both pairs of layers were energized. The dc current voltage characteristics for prototype 5 are presented in Figs. 2.7 and 2.8 for the two pairs of layers. For the inner pair, there is a significant change in the characteristics when both pairs of layers carry current. The  $I_c$  drops from around 1000 A when the inner layers alone carry current to around 700 A when both the inner and outer layers carry current. This is attributed to magnetic field effects generated by the outer pair.

The voltage measurements in Fig. 2.8 were for three different HTS tapes in the outer layer. The connected data are for current applied only to the outer pair of tapes. The unconnected data

**Table 2.3. Prototype cable construction parameters and measured  $I_c$ .**

Cable number	Number layers	Number tapes	Lay angle (°)	Former diam. (mm)	dc $I_c$ (A)	$I_c$ per tape (A)
1	4	73	15	22.0	670	9.2
2	4	67	15	22.0	560	8.4
3	10	200	15	25.4	1630	8.2
4	4	112	15	38.1	975	8.7
5	2 + 2	96	30	38.1	1100	11.5
6	2	51	30	38.1	365	7.2
7	4	108	30	38.1	1520	14.1
8	4	104	30	38.1	1605	15.4

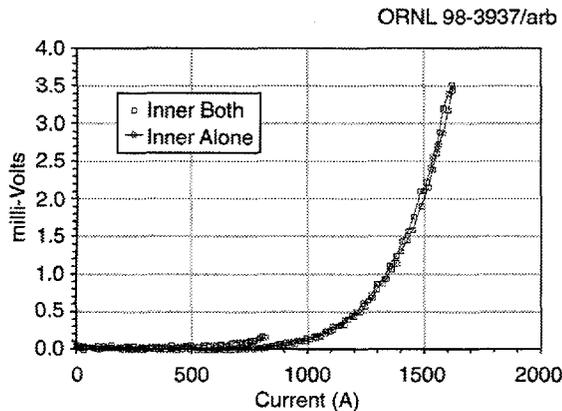


Fig. 2.7. Current voltage characteristics of the inner pair of prototype 5.

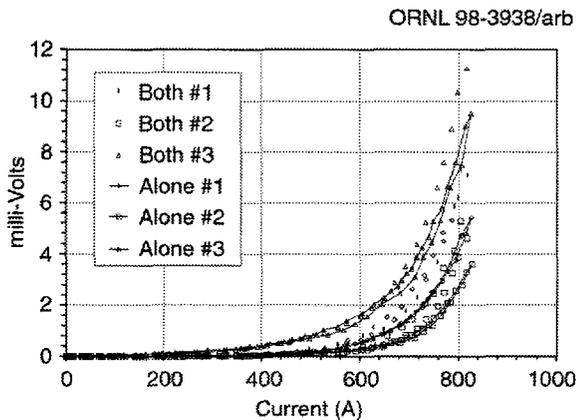


Fig. 2.8. Current voltage characteristics for three voltage taps on the outer pair of prototype 5.

are for both pairs of tapes carrying current. No significant voltage difference was observed between these cases. The different voltages between tapes are caused by variations in the tape characteristics and possible unequal currents in the tapes caused by the different joint contact resistance between the HTS tapes and the copper end plugs.

Current distribution of the inner vs outer pair of this cable was measured with ac as well as dc currents. The results are shown in Fig. 2.9 for both of these conditions. Because the trend did not change with the magnitude of currents, only data of higher dc currents and lower ac currents were shown in this graph. Under dc currents, the ratio of the current flowing through

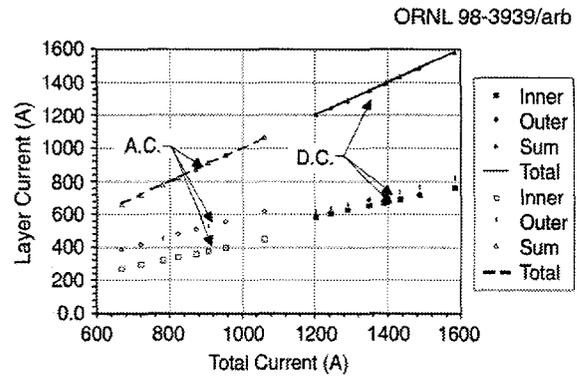


Fig. 2.9. Current distribution in HTS transmission cable prototype 5 under ac and dc conditions.

the outer pair to that flowing through the inner pair should depend only on the series resistance of each loop. Because the measured ratio is close to one (1.04), the series resistance was almost the same for each of the pair.

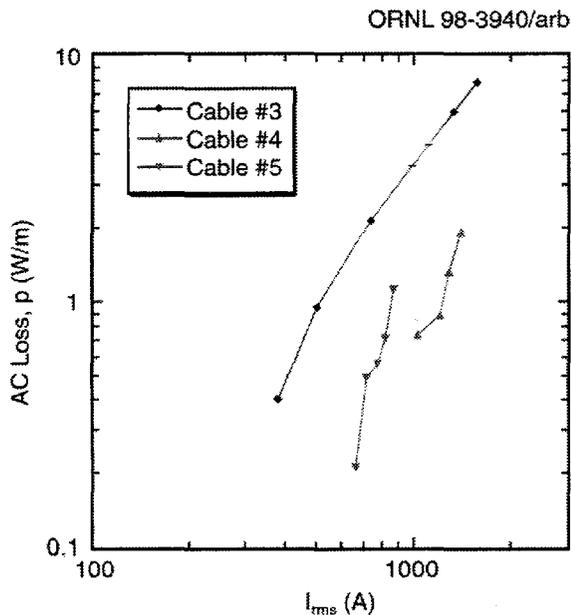
Under ac conditions, the inductive reactance could be important in determining the current distributions. Figure 2.9 shows that the outer layers carry a higher portion of the current under ac. The ratio of the current flowing through the outer pair to that flowing through the inner pair had increased to 1.38. This ratio is also found to be constant over the range of currents tested. Thus the inductances of the different layers of the cable play a significant role in determining the current distribution. Note that the present test setup included extra lead length and thus extra series resistance for the different pairs of the cable. Without this, the inductive effect could be even bigger.

### AC Loss Measurements

A calorimetric technique was used to measure the ac losses in the prototype cables. The cable was enclosed in a micarta or G-10 tube filled with wax to provide a thermal barrier to the surrounding LN<sub>2</sub>. The radial temperature difference of the cable resulting from ac currents was measured relative to the LN<sub>2</sub> bath. The calibration of the cable temperature rise to the power dissipated was accomplished by

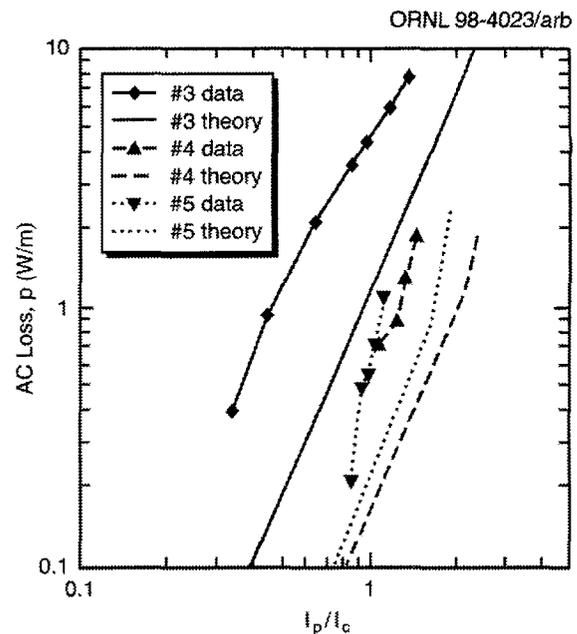
passing dc currents through the cable at values higher than the  $I_c$ . This produces a resistive heating in the sample that results in a temperature rise, and the heating power can be determined from the measured current and voltage.

Figure 2.10 summarizes the ac loss data for cables 3, 4, and 5. Cable 3 had the highest ac loss at all measured currents. Possible causes for this higher than expected loss are (1) the larger number of layers (ten) of this cable than the other cables or (2) the current connection of this cable was made in a way that the current was introduced to the outermost layer of the cable, which aggravates the uneven current distribution.



**Fig. 2.10. Data on ac loss for cables 3, 4, and 5 as a function of the root mean square current.**

To compare the ac loss data with a theory developed by Dresner, we plotted in Fig. 2.11 the loss data together with the theoretical prediction for the three different cables as a function of the peak ac current to the critical current ratio,  $I_p/I_c$ . In this theory, Dresner treated the cable as a cylindrical annulus. He also took into account the broad resistive transition of the HTS tapes such that the cable can be operated



**Fig. 2.11. Comparison of the ac loss data with a theory by Dresner.**

beyond its  $I_c$  as was actually done in the experiments. In this plot it is seen that cables 4 and 5 had about the same ac loss for the same  $I_p/I_c$ . These two sets of data had fair agreement with the theory. No adjustable parameter was used in the theoretical calculation. Cable 3 had a loss rate much higher than the theory for the possible reasons mentioned in the previous paragraph.

### Prototype Cable Summary and Conclusions

Five additional prototype HTS transmission cables were constructed and tested in FY 1997.  $I_c$  measurements of the cables indicated that the cables made from the first batch of HTS tapes had an average  $I_c$  per tape of 8.6 A in the cable form. The variation in the construction parameters did not make much difference. A cable made with retreated tapes resulted in about a 34% increase in  $I_c$  per tape in the cable form. The 15.4 A  $I_c$  per tape measured on cable 8 indicated a 79% increase for the second batch

tapes compared with the first batch made by the same manufacturer.

Current distribution of the inner vs outer pair of prototype cable 5 was measured with ac as well as dc currents. The ratio of the current flowing through the outer pair to that flowing through the inner pair had increased from 1.04 under dc to 1.38 under ac. The inductances of the different layers of the cable play a significant role in determining the current distribution even in these short (1-m-long) cables. The inductive effect causes higher fractions of ac currents to flow in the outer layers.

The ac loss measurements of the prototype cables showed fair agreement with a theory developed by Dresner based on a cylindrical annulus model. Cables that consist of the same number of layers seem to have about the same loss at the same  $I_p/I_c$ s, in spite of the construction parameter differences.

### Electrical Dielectric Testing

The ORNL Dielectrics Group is testing Cryoflex and other (either alternative or reference) materials for their breakdown strengths at ac and impulse voltage stresses. Two test apparatuses have been designed and constructed. One is an apparatus for testing tape samples, typically 1-in. wide in LN<sub>2</sub> at 1 atm pressure. The second apparatus is designed for testing sheet samples in LN<sub>2</sub> at pressures up to 15 atm. The tape tester design is based on IEC standard 243, which describes a method for high voltage (HV) testing of thin tapes and films. The ORNL design as shown in Fig. 2.12 permits testing of these tapes in LN<sub>2</sub> and possibly under tension. Because breakdown measurements are destructive to the material, the tape tester has five sets of electrodes, permitting the measurement of five breakdowns on a single sample.

The sheet testing apparatus utilizes a stainless steel chamber that can be pressurized to 15 atm. A novel dewar was designed and built, allowing HV breakdown experiments in

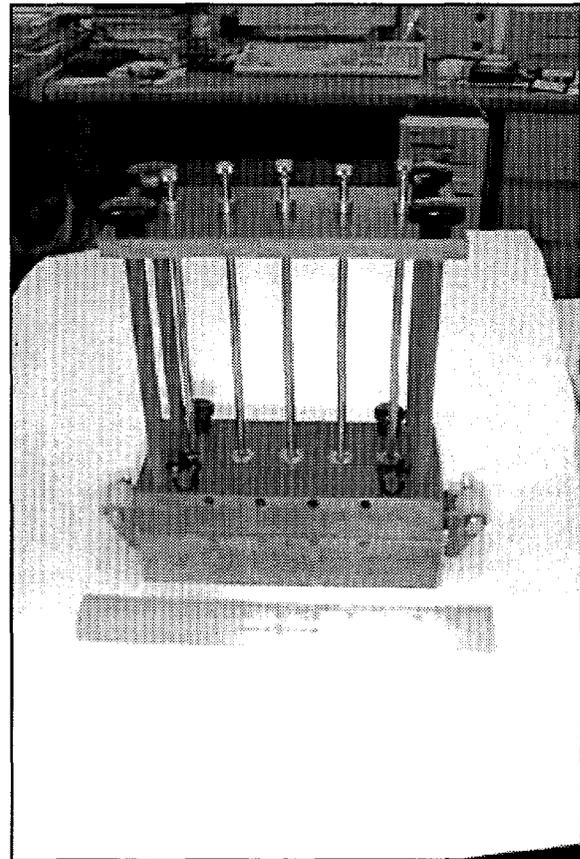
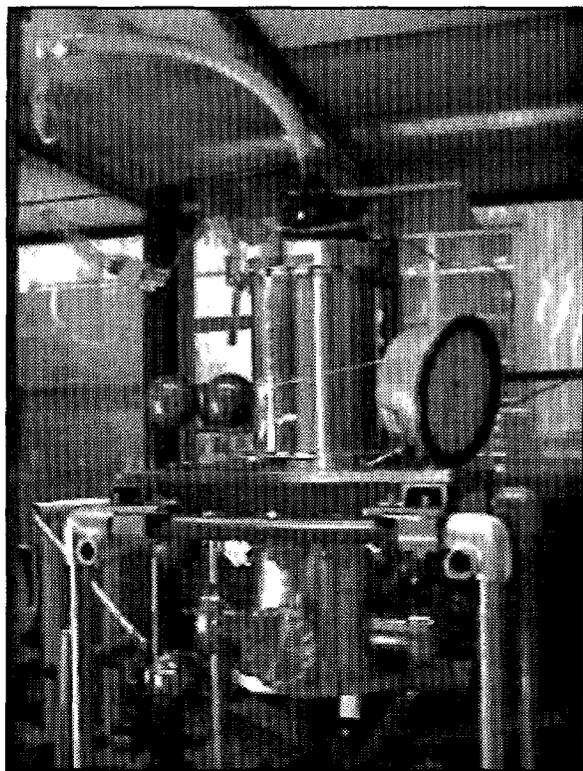


Fig. 2.12. Tape testing apparatus.

LN<sub>2</sub> at high pressure. The design of the dewar is unique in that it avoids the complexity, fabrication time, and cost of a more conventional double- or triple-walled chamber design and is shown in Fig. 2.13.

Much of the effort during this reporting period has been in the design and construction of the testing facilities and in the acquisition and set up of the HV supplies. The supplies includes two HV ac power supplies (100 kV manually controlled, made by American HV Test Systems, and a 150 kV, low noise, 3 pC, with Allen-Bradley programmable logic control, made by Phoenix Technologies) and a Haefely-Trench 500-kV impulse generator. The impulse generator was made operational at 300 kV with voltage rise/fall times of 1.2/50 ms and is shown in Fig. 2.14.

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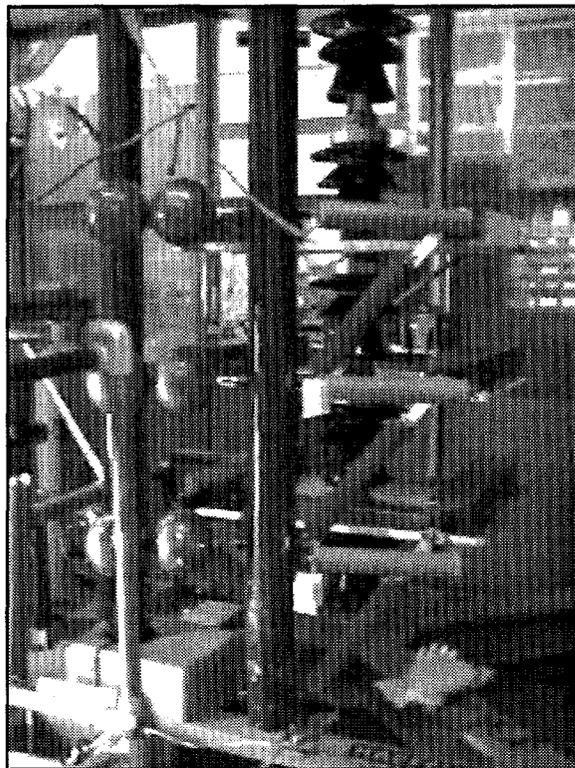


**Fig. 2.13. Sheet testing apparatus utilizes a stainless steel chamber.**

### ***Preliminary Measurements***

Preliminary measurements of tape and sheets have been made to assess the operation of the equipment and to identify problems. Measurements have been made in air,  $\text{LN}_2$  at 1 atm, and one single measurement in  $\text{LN}_2$  at 4 atm. Whereas the primary focus of these studies is the material Cryoflex, other materials have been examined. During the next reporting period, we will obtain systematic impulse breakdown measurements where withstand data (i.e., voltages that the material can withstand without breakdown) are taken at increasing voltages until breakdown occurs (generally resulting in puncture of the material). Planned experiments include measurements on multiple layers of dielectric sheet samples that contain one or more holes to simulate butt gaps,

ORNL 98-4247/arb



**Fig. 2.14. Haefely-Trench 500-kV impulse generator.**

corresponding to the spaces between tape layers in actual cable.

Whereas the data are too preliminary to report breakdown strengths, certain observations have been made. These include partial discharge, surface charging, and puncture. Generally, partial discharge and surface charging observed in air are suppressed in  $\text{LN}_2$ , particularly for Cryoflex. For tapes at atmospheric pressure, both Cryoflex and one of the other dielectric materials studied showed only marginal (if any) improvement in dielectric strength in  $\text{LN}_2$  over that in air. At a pressure of 4 atm in  $\text{LN}_2$ , however, a significantly higher puncture voltage (impulse) was recorded than at 1 atm. Whereas actual breakdown strength data require systematic withstand tests, it appears that higher  $\text{LN}_2$  pressures can be effective in improving the hold off strength of the material.

This is probably the result of the suppression of bubble formation in the liquid.

In preliminary tests on two sheets of Cryoflex in LN<sub>2</sub> at 1 atm, we were able to observe two withstand impulses at around 32 kV and a puncture breakdown at about 47 kV, indicating that the impulse strength is somewhere between these two values; however, none of the values given here can be used for design purposes until systematic experiments can be performed and replicated.

### Model Cable Tests

Model cable tests are planned during the next fiscal year. Design and planning have commenced, including the acquisition of space to set up a new high-bay HV laboratory, to accommodate a 12.5-ft (including bushing) HV high-pressure dewar.

### Cable Termination

The cable termination provides the transition from the HTS conductor at LN<sub>2</sub> temperatures to copper wire at room temperatures. During FY 1997, the design for a 12.5-kV and 1.25-kA HTS cable termination was completed. During the 9-month engineering design, the electrical, mechanical, and thermal properties of components and subsystems of the termination were analyzed by Southwire and ORNL. Approximately 700 h of computer-aided design produced 22 drawings detailing the cable termination design. Purchase orders were placed for the first two cable terminations. Eleven purchase orders to eight different vendors were issued by Southwire. The first two cable terminations will be tested as part of the 5-m cable test during FY 1998. Four additional cable terminations will be built for the 30-m cable facility during FY 1998 and FY 1999.

### Refrigeration System

A cryogenic refrigeration system is required to supply a steady flow of LN<sub>2</sub> at specified

temperatures and pressures that are within the operating ranges of the HTS cable. A cryogenic refrigeration system design has been completed and contains the following components: (1) main LN<sub>2</sub> supply tank, (2) LN<sub>2</sub> supply vacuum jacketed transfer line, (3) surge tank, (4) LN<sub>2</sub> pump, (5) LN<sub>2</sub> subcooler assembly, and (6) subcooler vacuum pumping system. A schematic of the system is provided in Fig. 2.15.

ORNL 98-3941/arb

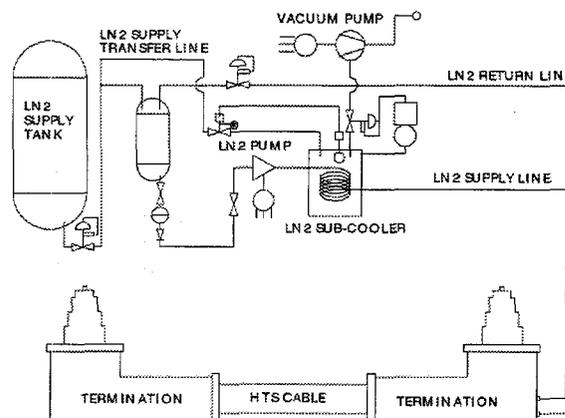


Fig. 2.15. HTS cable cryogenic system.

A skid-mounted cryogenic system that contains the surge tank, pump, subcooler assembly, and vacuum system is being fabricated by Air Products and Chemicals Company, Allentown, Pennsylvania. The LN<sub>2</sub> supply vacuum jacketed transfer line from the main supply tank to the HTS Cable Test Facility already exists at ORNL.

The cryogenic system has been designed to accommodate the different operating states that will exist during operation and testing of the cable. These are defined in the following descriptions:

- Warm—The state when the HTS transmission line is purged and at room temperature conditions.
- Cool-down—The state when the system is configured to gradually bring the HTS cable to operating temperature.

- **Standby**—The state when the HTS transmission cable is accepting LN<sub>2</sub> but the temperatures are too high to permit energizing the cable.
- **Normal**—The state when the HTS transmission cable is cold (i.e., the temperature everywhere along the cable is below the HTS transition temperature) and is ready to be energized.
- **Warm-up**—The state when the system is configured to allow the HTS transmission cable to warm up to room temperature.

### FY 1997 Summary for HTS Underground Cable Project

Significant progress was made during FY 1997 in all aspects of the HTS cable design and component testing. These designs will be tested in FY 1998 with the construction of the 5-m HTS cable test facility.

- **Short Sample Testing of HTS Tapes**—On the basis of a series of short sample property tests (207 in this reporting period) on Bi-2223/Ag HTS tapes acquired by Southwire, the  $I_c$ s were found to be reduced as a result of thermal cycling, strain, and applied magnetic field. These effects can reduce the  $I_c$  by up to 50%. On the basis of measurements of HTS tapes from three manufacturers, differences were found in the  $I_c$ s without strain and with strain. Additionally, the variability of samples from individual manufacturers was also found.
- **Prototype Cables**—Five additional prototype HTS transmission cables were constructed and tested in FY 1997.  $I_c$  measurements of the cables indicated that the cables made from the first batch of HTS tapes had an average  $I_c$  per tape of 8.6 A in the cable form. A cable made of the second batch of tapes indicated a 79% increase in  $I_c$  per tape. Current distribution measurements indicated that the inductances of the different layers of the cable play a significant role in determining the current distribution even in these short (1-m-long) cables. The inductive effect causes higher

fractions of ac currents to flow in the outer layers. The ac loss measurements of the prototype cables showed fair agreement with a theory developed by Dresner based on a cylindrical annulus model.

- **Electrical Dielectric Testing**—Two test apparatuses have been designed and constructed to test breakdown strengths at ac and impulse voltage stresses of Cryoflex. One is an apparatus for testing tape samples, typically 1-in.-wide in LN<sub>2</sub> at 1 atm pressure. The second apparatus is designed for testing sheet samples in liquid at pressures up to 15 atm. Much of the effort during this reporting period has been in the design and construction of the testing facilities and in the acquisition and setup of the HV supplies.

Preliminary measurements of tape and sheets have been made to assess the operation of the equipment and to identify problems. Measurements have been made in air, LN<sub>2</sub> at 1 atm, and one single measurement in liquid at 4 atm. In preliminary tests on two sheets of Cryoflex in LN<sub>2</sub> at 1 atm, we were able to observe two withstand impulses at around 32 kV and a puncture breakdown at about 47 kV, indicating that the impulse strength is somewhere between these two values; however, none of the values given here can be used for design purposes until systematic experiments can be performed and replicated.

- **Cable Termination**—The design for a 12.5 kV and 1.25 kA HTS cable termination was completed. Purchase orders were placed for the first two cable terminations, which will be built and tested in FY 1998.
- **Refrigeration System**—A cryogenic system has been designed to accommodate the different operating states that will exist during operation and testing of the cable. The following five operating states have been defined: warm, cool-down, standby, normal, and warm-up.

# Summary of Technology Partnership Activities

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## BACKGROUND

Oak Ridge National Laboratory (ORNL) is a key participant in DOE's national effort on electric power applications of high temperature superconductivity (HTS). ORNL has formed effective teams that combine the resources of the Laboratory with the entrepreneurial drive of private companies. New technology partnership mechanisms, a feature of the ORNL Superconducting Technology Program for Electric Power Systems since its inception in 1988, have resulted in 39 superconductivity "pilot center" cooperative agreements and 6 cooperative research and development agreements (CRADAs), an increase of 7 in the total number of agreements. In addition, licensing agreements, joint inventions, and joint publications with the private industry partners have ensured that there is technology transfer throughout the program.

Technology partnering on Laboratory-industry teams may occur in several ways. Spinoff technology partnering involves the licensing of patentable Laboratory inventions to industry, continued product or process development to the point of demonstration of precommercial viability, or both. In the ORNL program the cooperative development level of technology partnering is emphasized: joint Laboratory-industry teams work on a problem that (1) requires combined resources and expertise and (2) has a clear objective of precompetitive research and technology development. For the project to succeed, each partner depends on the success of the other.

Most of the cooperative projects with private industry and the Laboratory precompetitive research and development projects are developing key technology in which commercialization of the results is expected to occur after a minimum of 3 to 5 years. Some activities are also of a higher-risk, longer-term nature for which new markets, or a shift of

markets, to embrace HTS are expected if the project succeeds. For example, the ORNL rolling-assisted biaxially textured substrates (RABiTS™) process represents a new way to produce strongly linked YBCO wires using an industry-scalable process. This wire may still be the only option for practical performance levels in high magnetic fields at liquid nitrogen temperatures (65–77 K).

## RELATIONSHIP TO THE DOE MISSION

The ORNL program mission is that of its program sponsor, DOE's Office of Utility Technologies, Superconductivity Program: to develop the technology base necessary for industry to proceed to commercialization of electric energy applications of HTS. HTS will enable new energy-efficient motors, transformers, and transmission lines and will also provide electric power equipment manufacturers with strategic technology for global competitiveness. Electric utilities can defer acquisition of new transmission rights-of-way with successful introduction of superconducting cables. System stability and protection will be enhanced with the introduction of fault current limiters. Distributed utility systems in the future, which will include distributed generation systems, will benefit from the small size and weight of the next generation of electric power equipment.

## FUNDING

DOE funding for the program, subcontracting activities in 1997, and a summary of funds-out cooperative agreements are shown in Tables 3.1 and 3.2.

### 3-2 Summary of Technology Partnership Activities

**Table 3.1. Superconducting Technology Program funding: authorization and outlay by fiscal year**

	New budget authorization/outlay (\$ × 1000)				
	1989–1993	1994	1995	1996	1997
Direct scientific and technical <sup>a</sup>	11,942	3,334	3,434	2,995	3,046
Management and outreach	<u>1,023</u>	<u>298</u>	<u>300</u>	<u>310</u>	<u>310</u>
Subtotal—ORNL	12,965	3,632	3,734	3,305	3,356
Subcontracts <sup>a</sup>	1,021	496	198	1,290	1,021
Funds-out cooperative agreements	<u>3,688</u>	<u>821</u>	<u>611</u>	<u>286</u>	<u>789</u>
Total program	17,674	4,949	4,543	4,881	5,166

<sup>a</sup>Details are provided in separate table. Funds-out cooperative agreements provide partial financial support to U.S. industry for cost-shared cooperative research and development.

## TECHNOLOGY PARTNERSHIP APPROACH

Our interdisciplinary approach uses all resources available at ORNL to meet the program goals for joint Laboratory–industry development of HTS technology for electric power applications. Our superconductivity agreement mechanism interlinks research and development projects with industry and universities that optimize utilization of facilities, expertise, and program resources for the benefit of all participants. This program also coordinates the ORNL activities with the other national laboratories, government agencies, university centers, and industry groups.

Cooperative agreements ensure that technology development is industry-driven. The Office of Science and Technology Partnerships and patent counsel work together to place these agreements. Where appropriate, these efforts are coordinated with projects within ORNL that are funded by the DOE Office of Energy Research, as well as Work for Others and ORNL Director's Research and Development Fund

projects. Effective funds-out to industry is used to supplement industry cost share. In FY 1997, \$1.8 million in funds-out to industry and universities was provided through cooperative agreements and subcontracts. To keep industry involved from the start of the program and to ensure commercialization potential, these technology partnering mechanisms are augmented by CRADAs, user agreements, and licensing activities.

Responsiveness to American industry has high priority in this program. An ORNL ad hoc technical review committee, consisting of a project manager, a scientific coordinator, a manager for conductor development, and a manager for applications development, reviews all inquiries from industry and recommends a project for possible funding. This review ensures that (1) the proposed work fits the program mission, (2) the work is collaborative, (3) there is legitimate commercial interest, and (4) the work is feasible. Substantial private-sector cost share is required on cooperative agreements.

ORNL provides support to the DOE Headquarters (DOE-HQ) Superconductivity

**Table 3.2 Superconductivity Program**  
Summary of Cooperative Agreements as of September 30, 1997

Participant	Approved term	Type <sup>a</sup>	By DOE		By Industry	Technology area
			Total agreement cost share (\$ × 1000)			
			To ORNL	To Industry		
Advanced Fuel Research (complete)	2/1/90-9/30/92	NFE	230	0	442	In situ HTS film deposition monitor
American Magnetics (complete)	8/10/89-8/9/92	NFE	100	0	480	Characterize MOCVD multifilament conductors
American Magnetics	10/1/96-10/1/97	C	0	0	82.4	Development, design, and fabrication of hybrid HTS leads
American Superconductor	9/1/96-8/31/98	FI	150	0	165	
American Superconductor (complete)	9/1/91-11/15/96	FO	1439	800	862	Coil fabrication, technical development, and testing
American Superconductor (complete)	4/1/89-11/15/96	FI	2090	0	1705.4	Fabrication of powder-in-tube wire and tape
Astronautics (complete)	9/1/91-2/28/95	FO	600	450	820	Magnetic refrigeration
CeraNova Corporation (complete)	8/1/93-1/31/95	FO	90	25	75	Melt-processed YBCO wire for leads and coils
Consultec Scientific (complete)	6/1/89-12/31/90	FO	38	45	64	Deposition target device
Corning (complete)	6/1/89-12/31/93	FO	325	275	316	Deposition on flexible ceramic substrates
CPS Superconductor (complete)	4/1/91-3/31/93	NFE	80	0	50	Conductor fabrication—continuous-flament melt-textured YBCO
Dow Corning (I-IIa) (complete)	7/1/90-9/31/91	FO	110	50	67	Thick film deposition
DuPont (complete)	7/1/89-3/31/91	NFE	225	0	250	Thin film devices and bulk applications
Edison Materials Technology Center (complete)	1/2/96-1/1/97	NFE	60	0	100	Develop coil winding technology
Electric Power Research Institute (complete)	7/13/93-7/12/96	C	26	0	215	Variable speed superconducting motors, power electronics, and superconducting magnetic energy storage
Energy Conversion Devices (complete)	5/1/91-3/31/93	NFE	90	0	90	Deposition of conductors
General Electric (A1) (complete)	12/15/88-2/28/89	FI	5	0	45	Thallium HTS <sub>c</sub> material processing
General Electric (SPI) (complete)	12/1/93-11/30/95	NFE	400	0	1173	Thallium wire development and generator design

### 3-4 Summary of Technology Partnership Activities

**Table 3.2 (continued)**

Participant	Approved term	Type <sup>a</sup>	Total agreement cost share (\$ × 1000)				Technology area
			By DOE		By Industry		
			To ORNL	To Industry	To Industry	Industry	
General Electric (B1) (complete)	10/1/89-6/30/96	FO	895	520	614	Laser deposition of conductors; thallium-deposited conductors	
General Electric (C1) (complete)	4/1/90-12/31/90	NFE	135	0	140	Thallium HTSc material processing	
HiTe Superconco (complete)	3/1/90-4/30/91	NFE	40	0	50	Magnetic bearings	
Innovative Materials Technology (complete)	10/1/89-3/31/90	FI	50	0	50	Composite tape fabrication	
Intermagnetics General Corporation	6/15/97-6/14/98	FO	117	125	125	HTS transformer	
Intermagnetics General Corporation	10/1/91-9/30/97	FO	1452	965	731	HTS transformer; BSCCO 2212 tape development	
Intermagnetics General Corporation (complete)	9/1/91-8/31/94	NFE	100	0	100	Thallium powder-in-tube conductor	
IBM (complete)	2/1/90-1/31/93	NFE	255	0	673	Optimize flux pinning via ion-induced defects	
IBM (complete)	2/1/90-5/31/95	FO	201	389	186	Optimize flux pinning via ion-induced defects	
MicroCoating Technologies	9/15/97-9/14/98	FI	0	0	150	Develop coated-conductor technology	
Midwest Superconductivity/Westinghouse Electric	6/25/96-6/24/98	C	300	0	980 160 1140	Develop coated-conductor technology	
Neocera (complete)	2/1/91-1/31/93	FO	80	111.6	95.7	Laser ablation multi-target deposition	
Oxford Instruments	1/94-1/31/99	C	275	0	475	Develop technology for dip-coated BSCCO-2212 wire	
Plastronic, Inc. (complete)	10/22/93-9/30/95	NFE	165	0	225	Apply wire-forming technology to produce BSCCO wire	
Plastronic, Inc.	5/1/97-7/1/98	FI	0	0	120	High-strength, low-ac loss high-temperature superconductor	
Saphikon (complete)	2/1/92-4/30/94	NFE	50	0	492	Deposited conductor fabrication	
Southwire Company	10/3/95-10/5/97	C	201	0	1249.2	Transmission cable	

Table 3.2 (continued)

Participant	Approved term	Type <sup>a</sup>	Total agreement cost share (\$ × 1000)				Technology area
			By DOE		By Industry		
			To ORNL	To Industry	To Industry	Industry	
Southwire Company	2/1/97-1/31/1998	FO	550	500	973	3-phase, 100-ft demonstration cable made with HTS materials	
SUNY-Buffalo (complete)	7/1/89-10/30/92	FO	165	250	255	Laser deposition of conductors	
Stevens Institute of Technology (complete)	1/1/90-5/31/92	FO	90	105	100	MOCVD for electronic devices	
Superconductive Components, Inc. (complete)	3/15/95-3/14/97	NFE	25	0	25	Scale-up of the production of superconducting and precursor powders synthesized by aerosol decomposition method	
Superconductivity, Inc. (complete)	10/1/89-3/31/93	NFE	180	0	133	Magnetic energy storage for end-use applications	
Textron Specialty Materials (complete)	8/1/89-3/31/91	NFE	60	0	45	Deposition of conductors	
3M-Southwire-LANL-ORNL	4/3/97-4/99	C			1375	Development of HTS wire using coated conductor technologies	
Southwire					324		
LANL					1699		
ORNL			600	960 <sup>b</sup>			
University of Wisconsin—Madison (complete)	8/1/92-3/31/96	FO	110	60	150	Aerosol powder synthesis	
Waukesha Electric Systems	6/15/97-6/14/98	FO	117	125	148	HTS transformer	
Westinghouse Electric (complete)	4/1/89-12/31/93	FO	1200	750	800	Powder scale-up, BSCCO wire fabrication, and leads	
<b>FY 1997 active subcontracts</b>							
Imtech	10/3/94-12/31/97			271		Superconducting powder synthesis/scale-up	
Massachusetts Institute of Technology	4/29/96-3/31/98			215		Stability of HTS conductors and coils	
Oak Ridge Institute for Science and Education	Ongoing			360		Postdoctoral research fellowships (4.5)	

3-6 Summary of Technology Partnership Activities

Table 3.2 (continued)

Participant	Approved term	Type <sup>a</sup>	Total agreement cost share (\$ × 1000)		Technology area
			To ORNL	By DOE To Industry	
State University of New York at Buffalo	11/1/95-5/31/96		25		Supply epitaxial films of thallium-based high-temperature superconducting materials
	10/1/96-10/31/97		30		
Texas Center for Superconductivity at the University of Houston	5/15/95-12/31/97		98		Processing YBCO and BSCCO superconductors for high-current leads and conductors (two students)
University of Tennessee	Ongoing		80		Students (3) - Deposited conductor development
National Institute of Standards and Technology (Interagency Agreement)	9/22/93-11/30/98		515		BSCCO and TBCCO phase diagram support
Energetics, Inc.	4/96-7/96		70		Technical and analytical support
	8/96-7/97		450		
	8/97-7/98		350		
Bob Lawrence & Associates	2/17/97-2/16/98		155		Technical and economic benefits assessment and market study
University of Wisconsin	5/1/97-4/30/99		100		TEM and magneto-optic imaging studies on RABiTS™
Marshall O. Pace	4/97-9/97		10		High-voltage breakdown studies on cryogenic insulation
Horatio Rodrigo	5/97-9/97		37		Set up impulse high-voltage generator and conduct vacuum and cryogenic breakdown measurements
Capital equipment	FY 1997		283		Deposited conductor development

<sup>a</sup>NFE = no-funds-exchange; FO = funds-out; FI = funds-in; I=informal; and C = CRADA.

<sup>b</sup>DOE to LANL.

Program for Electric Power Systems by identifying, guiding, and monitoring research and development at ORNL and ORNL subcontractor sites and by performing coordination, analysis, and planning of activities related to the national program.

Some of the various activities performed as part of this task include the following:

- technical, project, and budget guidance;
- project identification and development;
- exploratory research and development;
- support of consultants and subcontracts providing technical, program, or technology partnering support;
- identification, placement, and technical monitoring of subcontractors, review committee members, and workshop guests;
- guidance and support on technology partnering;
- publication of reports and proceedings from workshops;
- identification and initiation of cooperative agreements, interagency agreements (i.e., National Institute of Standards and Technology), and memoranda of understanding;
- distribution of reports to program managers;
- coordination of the Laboratory's Industrial Overview Committee;
- preparation of assessments to address technical, economic, regulatory, and institutional issues in the DOE program;
- coordination of interlaboratory technical team meetings;
- assistance to the DOE-HQ program manager in preparation of the Superconducting Technology Program Annual Operating Plan;
- collection and dissemination of programmatic information and program-wide assessments;
- assistance in organizing the HTS Wire Development Workshop (in partnership with ANL and LANL); and

- review of industrial collaboration opportunities through multilaboratory meetings and conference calls.

ORNL works with the other program laboratories to address such issues as communication among program participants, workshop and meeting implementation, planned competitive solicitations and superconductivity agreements, and coordination of technical and economic assessments.

An Industrial Overview Committee is charged with reviewing program activities and advising Laboratory management as to program progress, policy, and direction. The committee consists of representatives of electric utilities, original equipment manufacturers, and HTS wire manufacturers. This committee meets once a year at ORNL, Argonne National Laboratory (ANL), or Los Alamos National Laboratory (LANL).

## PROGRAM MEASURES

Four new cooperative agreements were executed during FY 1997: American Superconductor Corp., Southwire Company, American Magnetics, and Midwest Superconductivity/Westinghouse. New Statements of Work were negotiated, and agreements were extended with IGC and Oxford Instruments. Ten new invention disclosures were submitted by ORNL or industrial principal investigators. These are listed in Table 3.3.

### 3-8 Summary of Technology Partnership Activities

**Table 3.3. Superconducting Technology Program invention disclosures  
(FY 1997)**

ERID No.	Subject	Submitted by
312	Rolling Methods of Forming Biaxially Textured Articles	A. Goyal
316	Powder Metallurgical Methods of Forming Biaxially Textured Articles	A. Goyal
330	Encapsulated High Temperature Superconductor Bundle	J. W. Lue and M. S. Lubell (ORNL), M. Tomsic (Plastronic)
334	Strengthening High Temperature Superconducting Tapes with Diffusion Bonded Backing	J. W. Lue and M. S. Lubell (ORNL), M. Tomsic (Plastronic)
363	Method of Forming Biaxially Textured Articles	A. Goyal and D. M. Kroeger
366	Method of Forming Biaxially Textured Articles Having Reduced Magnetism	A. Goyal and D. M. Kroeger
367	Method of Forming Biaxially Textured Articles	A. Goyal, D. M. Kroeger, and M. Paranthaman
368	Method of Forming Biaxially Textured Articles	A. Goyal
374	Method of Forming Biaxially Textured Articles by Physical Vapor Deposition	A. Goyal and D. M. Kroeger
375	Biaxially Textured Articles Having Metal Nitride Buffer Layers	A. Goyal and D. M. Kroeger

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