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Annual Report for FY 1996

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**ORNL SUPERCONDUCTING TECHNOLOGY PROGRAM
FOR ELECTRIC POWER SYSTEMS**

ANNUAL REPORT FOR FY 1996

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Acronyms and Initialisms

ac	alternating current
ASC	American Superconductor Corporation
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
EBSF	electron beam backscatter patterns
EDS	energy-dispersive spectroscopy
fcc	face-centered cubic
FWHM	Full width half maximum
HTS	high temperature superconductivity/superconductor/superconducting
IBAD	ion-beam-assisted deposition
IBM	International Business Machines
I_c	critical current
IGC	Intermagetics General Corporation
J_c	critical current density
K_c	critical current per unit width of conductor (I_c/w)
ORNL	Oak Ridge National Laboratory
PIT	powder-in-tube
PLD	pulsed-laser deposition
PNZT	lead niobium zirconium titanate
RABiTS	rolling-assisted biaxially textured substrates
RBS	Rutherford Backscattering Spectra
RG&E	Rochester Gas and Electric Company
RTA	rapid thermal annealer
SEM	scanning electron microscopy
SUNY	State University of New York
T_c	critical temperature/transition temperature
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
T_s	sintering temperature
WES	Waukesha Electric Systems
XRD	X-ray diffraction
YSZ	yttria-stabilized zirconia

Executive Summary

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 1996 Annual Program Review held July 31 and August 1, 1996. 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 1996

- Effects of friction and strain rate on the deformation of multifilament BSCCO-2223 powder-in-tube (PIT) tapes have been investigated. In contrast to monofilament tapes, multifilament tapes undergo inhomogeneous deformation when subjected to increased friction and reduction per pass with no noticeable benefits in critical current density (J_c). The different effects of friction on the properties of mono- and multifilament tapes are believed to be caused by the development of “dead zones.” Consequently, although the high temperature superconducting (HTS) core of monofilament tape is densified and can carry high current, only a portion of the filaments in multifilament tape are compacted. That is, a substantial amount of the filaments in tapes deformed under high-friction conditions are weak conductors and do not contribute significantly to J_c . The identification of dead zones in PIT tapes indicates that modifications in deformation conditions and/or tape geometry can be carried out to achieve more homogeneous deformation and densification of the HTS cores.
- A preliminary design review for the HTS transformer project team was held at Waukesha Electric Systems. Recent work has involved calculations and design work for the 1-MVA prototype transformer and supporting tests for alternating current (ac) losses and conductor coatings. Measurements of losses in ac fields can be performed by controlling field magnitude and direction; however, it may be difficult to relate the results to the actual fields seen by the conductor in the transformer. For this reason, a scalable measurement that closely simulates transformer conditions was suggested by Intermagnetics General Corporation (IGC). Oak Ridge National Laboratory (ORNL) staff conducted the measurements at ORNL with the test configuration supplied by IGC. In addition, a practical, commercially available coating for protection of the Bi-2212 tapes was successfully tested.
- A new cooperative research and development agreement (CRADA) was initiated with Southwire Company (Carrollton, Georgia) in October 1995. The funds-in CRADA provides for the development and demonstration of the technology needed for HTS underground transmission cables. Southwire delivered the first bare prototype cable in late October 1995. Four test cables are planned for Phase I of what could be a 5-year, three-phase program. The Phase I project is heavily leveraged by private-sector funding, with Southwire contributing at least \$750,000 of the anticipated \$850,000 total cost.
- The critical current (I_c) vs applied magnetic field has been measured for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (Bi-2212) and $(\text{Tl}_{0.5}\text{Pb}_{0.5})(\text{Sr}_{0.8}\text{Ba}_{0.2})_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Tl-1223) wires for a range of temperatures. I_c is not a single-valued function and can depend on magnetic and thermal history. For the Bi-2212, there was essentially no difference in the I_c for the zero-field-cooled and field-cooled samples, for either decreasing or increasing applied fields. In contrast, the Tl-1223 results exhibit significant hysteresis that may be attributed to behavior of weak-linked grain boundaries that trap magnetic flux. This property of the weak-linked thallium-based conductors may be significant if such conductors are to be used in ac applications.
- The calorimetric technique was used to measure ac losses in a series of high-quality, twisted multifilamentary BSCCO 2223/Ag superconducting tapes produced by American Superconductor Corporation (ASC). The ac losses were correlated to various superconducting properties such as the J_c , the tape aspect ratios, and other parameters to guide ASC toward reducing the ac losses in the next generation of tapes. The ac losses are highly anisotropic with the applied field orientation. This anisotropy leads to a critical twist-pitch relation that depends on the filament aspect ratio rather than simply on the filament diameter. Therefore, most of the ac-coupling losses will be determined by the perpendicular field component exposed to the tapes. Also, the hysteretic losses depend primarily on

the degree of bridging between the individual filaments. We find that the losses are described very well by the critical-state model and that the coupling losses are shown to decrease in wires with twisted filaments.

- Superconducting properties were measured for $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ (Tl-1223) thick films grown on Ag substrates. Thallium-free precursor films of the type $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{Ag}_{0.37}\text{O}_7$ were deposited on both smooth and rough Ag substrates using a spray pyrolysis technique. The film thickness varied between 1 and 3 μm . The surface microstructure of the Ag substrate dictates the growth behavior of Tl-1223 films. The films grown on smooth Ag substrates had local biaxial alignment extending in the plane of the film up to 5 mm. The measured transport J_c s for Tl-1223 films grown on smooth and rough Ag substrates were $\sim 65,000 \text{ A/cm}^2$ and $\sim 37,000 \text{ A/cm}^2$, respectively, at 77 K and zero magnetic field. The films grown on smooth Ag substrates were strongly linked and had good in-field properties with a J_c value of $\sim 10^4 \text{ A/cm}^2$ at 77 K and 0.5 T. This result was obtained with the magnetic field applied perpendicular to the substrate.
- An electrical measurement with direct current (dc) has been completed on the first HTS cable fabricated by the Southwire Company. The cable contained 73 separate tapes in four layers. A copper pipe served as the former. One section of the cable was visibly damaged during fabrication and handling. When tested in liquid nitrogen, the maximum I_c for the undamaged section of the cable was 900 A, exceeding the original goal of 500 A.
- We report superconducting properties of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ (Tl-1223) thick films grown on high-strength substrates. The high-strength substrate was made up of Ag bonded to a suitable metal alloy. Thallium-free precursor films of the type $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{Ag}_{0.37}\text{O}_7$ were deposited on these high-strength substrates using a spray pyrolysis technique. The as-deposited precursor films were heat treated and thallinated in a two-zone furnace. The film thickness was 3 μm . X-ray diffraction (XRD) results showed the presence of *c*-axis-textured Tl-1223 films and some degree of local in-plane texture (colony microstructure). The measured transport J_c s for Tl-1223 films were $\sim 52,000 \text{ A/cm}^2$ at 77 K and zero magnetic field. The microstructures of Tl-1223 films were quite similar to those observed previously for films on polycrystalline yttria-stabilized zirconia (YSZ) substrates.
- A special test coil, fabricated by IGC of Bi-2212 surface-coated wires, was delivered to ORNL in January 1996. The coil was used to help determine the expected ac loss power that will be generated in the full-scale, 1-MVA prototype transformer. ORNL verified that the I_c of the coil was 9.5 A at 77 K. Calorimetric ac loss tests with ac transport current were carried out at several different temperatures, ranging from 4.2 to 50 K. The conductor consists of a 6-mm-wide silver tape surface-coated with BSSCO-2212 and is quite similar to the conductor to be used in the 1-MVA prototype transformer. At the rated operating current of 72 A rms, losses were somewhat above calculated values. We expect that the losses can be reduced considerably with modifications to the coil geometry.
- Epitaxial LaAlO_3 films were grown successfully on SrTiO_3 (100) single crystal substrates. A LaAlO_3 precursor solution was prepared via an all alkoxide sol-gel route. Synthesis of buffer layers and superconductors via sol-gel routes may represent a low-cost, convenient (nonvacuum) way of coating textured metallic substrates. Complete hydrolysis of the solution formed a gel that yielded well-crystallized LaAlO_3 powders when fired in air at 800°C. Epitaxial films of LaAlO_3 were formed during pyrolysis of a solution that was spin-coated on SrTiO_3 (100) single crystal substrates in a rapid thermal annealing furnace. The films were strongly *c*-axis-oriented and had good in-plane texture shown by a ϕ -scan of the (202) plane with full width half maximum (FWHM) = 1.07° .

- The “Teacher’s Guide to Superconductivity for High School Students” has been placed on the World Wide Web. The guide may be accessed by going to the ORNL Superconductivity home page:

<http://www.ornl.gov/HTSC/htsc.html>

- The use of a biaxially textured (001) Ni tape, formed by recrystallization of cold-rolled pure Ni, as an in-plane-aligned substrate material for subsequent HTS film deposition is a possible approach for achieving in-plane-aligned, high- J_c YBa₂Cu₃O₇ films on long-length substrates. The epitaxial growth of a (001)-oriented oxide buffer layer architecture that maintains the sharp crystallographic cube texture of the metal substrate while providing a barrier to chemical interaction of the Ni with the HTS film results in a structure referred to as a Rolling-Assisted, Biaxially Textured Substrate (RABiTS™). We have grown in-plane-aligned, *c*-axis-oriented YBa₂Cu₃O₇ films on thermomechanically rolled textured (001) Ni tapes using pulsed laser deposition with superconducting J_c s, as high as 700,000 A/cm² at 77 K. The superconducting properties of films deposited on the biaxially textured Ni tapes are comparable with those realized for epitaxial YBa₂Cu₃O₇ on single crystal oxide substrates.
- Electrical measurements with both dc and ac currents have been completed on the second HTS cable made by Southwire. This cable is different from the first one in that the tapes on each layer were separated from each other and Kapton tape was used between layers for insulation. Alternating current loss measurements of the first cable and a thermal cycle test were also performed during this period. Analysis of the loss data indicated that the measured loss is governed by the power law behavior of the HTS tape in the resistive transition.
- Two buffer layer architectures for coated conductors were developed on rolled Ni substrates using an electron beam evaporation technique. The first buffer layer architecture consists of an epitaxial laminate of CeO₂/Pd/Ni. The second alternative buffer layer consists of an epitaxial laminate of YSZ/CeO₂/Ni. The CeO₂ films were grown epitaxially on both Pd-buffered Ni and pure Ni substrates. The YSZ films were grown epitaxially on CeO₂-buffered Ni substrates. The crystallographic orientation of the Pd, CeO₂, and YSZ films was (100). We also studied the effect of the CeO₂ layer thickness on rolled-Ni substrates. The CeO₂ layer thickness was found to be critical. The presence of YSZ layers on top of CeO₂ layers seems to alleviate the cracks that are formed underneath. Our scanning electron microscopy (SEM) studies showed that both CeO₂ and YSZ layers were smooth and continuous. The buffer layer architectures that we have developed are useful for the subsequent growth of superconductors such as YBa₂Cu₃O₇ and other high-critical-temperature materials that are chemically and epitaxially compatible with CeO₂ and YSZ buffer layers.
- Electrical measurements with both dc and ac currents have been performed on the third HTS cable made by Southwire. This cable is rated for 2 kA and has been successfully tested to and above the rated current. Two papers were written on the design and test of the cables made during this phase of work and were presented at the 1996 Applied Superconductivity Conference.

Technical Progress in Wire Development

RABITS: AN APPROACH TO HIGH CRITICAL CURRENT DENSITY SUPERCONDUCTING TAPES

[Adapted from David P. Norton et al., "Epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_7$ on Biaxially Textured Nickel (001): An Approach to Superconducting Tapes with High Critical Current Density," *Science* 274, 755–57 (November 1996).]

Since the discovery of high-temperature superconductivity (HTS) in cuprate materials, significant efforts have focused on developing a high-current superconducting wire technology for applications at 77 K.^{1–3} Early in these efforts it was observed that randomly oriented polycrystalline HTS materials have critical current densities (J_c s), $< 500 \text{ A/cm}^2$. In contrast, oriented YBCO thin films grown epitaxially on single crystal oxide substrates, such as (001) SrTiO_3 , exhibit J_c values $> 1 \text{ MA/cm}^2$ at 77 K.⁴ This huge difference between randomly oriented HTS ceramics and single crystal-like epitaxial films is directly related to the misorientation angles at the grain boundaries in polycrystalline materials. Values for J_c across a grain boundary decrease significantly as the misorientation angle increases, with weak-link behavior observed for grain-boundary misorientation angles greater than $\sim 10^\circ$.^{5–13} To achieve high J_c s ($\sim 10^5$ to 10^6 A/cm^2 , 77 K), the crystallographic orientation of the HTS wire or tape must possess a high degree of both in-plane and out-of-plane grain alignment over the conductor's entire length. Preferably, this would be achieved with YBCO because the limits for dissipation-free current at 77 K in an applied magnetic field are most favorable for this material.^{14,15}

One approach to producing a high- J_c HTS tape is to deposit a thick epitaxial film on a substrate material that has a high degree of in-plane and out-of-plane crystallographic texture and can be produced in long lengths. Epitaxial HTS films on single crystal oxides

satisfy the requirements for high J_c , but it is not feasible to produce long lengths of these substrates. Recent efforts have focused on the use of ion-beam-assisted deposition (IBAD) to achieve in-plane alignment of oxide buffer layers on polycrystalline metal substrates for subsequent epitaxial growth of YBCO.^{16–20} Indeed, as shown by Los Alamos National Laboratory and others, a modest degree of in-plane texture for c -axis-oriented YBCO films using IBAD results in a significant increase in J_c , with values ranging from 10^5 to 10^6 A/cm^2 at 77 K.

We report here an approach for achieving in-plane-aligned, high-critical-current (J_c) YBCO films on long-length substrates without IBAD. A biaxially textured (001) Ni tape, formed by recrystallization of cold-rolled pure Ni,^{21,22} is used as the initial, in-plane-aligned substrate. A (001)-oriented oxide buffer layer architecture is then epitaxially grown that maintains the sharp crystallographic cube texture of the metal substrate while providing a barrier to chemical interaction with the Ni. Subsequent growth of YBCO on this structure, referred to as a rolling-assisted, biaxially textured substrate (RABiTS™), results in c -axis-oriented, in-plane-aligned films with J_c s as high as $700,000 \text{ A/cm}^2$ at 77 K. The advantage of this approach over other alternatives, such as IBAD, is in the simplicity of producing the initial in-plane alignment, required for high J_c , by a cold-rolling and annealing process that can easily be scaled to produce arbitrary substrate lengths.

The YBCO/yttria-stabilized ZrO_2 (YSZ)/ CeO_2 layered architecture used to grow in-plane-aligned, high- J_c films on rolled textured (001) Ni is schematically illustrated in Fig. 1.1. The Ni substrates have a relatively sharp cube orientation with a full width half maximum (FWHM) out-of-plane texture $\Delta\theta \sim 6$ to 10° and an in-plane texture $\Delta\theta \sim 6$ to 15° , depending on

Fig. 1.1. An XRD θ - 2θ scan, along with a schematic representation, of a YBCO/YSZ/CeO₂/Ni multilayer structure. The XRD scan shows the out-of-plane (001) orientations of the YBa₂Cu₃O₇ and oxide buffer layers.

the specific rolling and annealing conditions, as well as material purity, with a grain size ranging from ~30 to 100 μm in diameter. The 125- μm -thick Ni substrates were used as-rolled and annealed with no subsequent polishing. The epitaxial oxide buffer layers, along with the *c*-axis-oriented, in-plane-aligned YBCO films, were grown by pulsed laser deposition (PLD) using a KrF excimer laser.

Typically, the epitaxial growth of a (001)-oriented cubic oxide on a (001) Ni surface is inhibited by the formation of (111) NiO at the oxide-metal interface.²³ The Ni substrates were annealed at 900°C in a mixture of 4% H₂ and 96% Ar gas prior to film growth to reduce any NiO on the substrate surface. To further suppress the formation of NiO and to achieve (001)-oriented epitaxy directly on the (001) Ni surface, H₂ gas was introduced into the PLD chamber during the initial stages of CeO₂ growth. Hydrogen is effective in reducing NiO, while having little effect on the CeO₂ film. This (001)-oriented CeO₂ layer provides an oxide template directly on the metal surface for the subsequent epitaxial growth of additional oxide

buffer and HTS layers. We have also developed an alternative approach that utilizes Pd as an epitaxial noble metal interface between the oxide buffer layers and Ni substrate to inhibit the formation of NiO.²²

After the CeO₂ film is deposited, a YSZ layer was grown in situ using PLD. The YSZ layer appears to alleviate cracking of the oxide layers that can occur because of the thermal expansion mismatch between the Ni substrate and the oxides. The CeO₂ and YSZ layers are each ~500 nm thick. A thick (>0.5 μm) YBCO film is then deposited at 780°C in an oxygen pressure of 185 mtorr. After deposition, the films are cooled at 10°C per minute, with the oxygen pressure increased to 700 torr at 400°C.

A θ - 2θ X-ray diffraction (XRD) scan of a YBCO/YSZ/CeO₂ composite structure (Fig. 1.1) reveals that the CeO₂ and YSZ buffer layers, as well as the YBCO layer, are (001)-oriented relative to the surface normal. The intensity ratio of the CeO₂ (111)/(200) peaks is $<10^{-2}$, indicating a very small volume percentage of (111)-oriented oxide. The out-of-plane crystallographic texture for the YBCO, YSZ, CeO₂, and Ni as determined by XRD rocking curves (ϕ -scans) is shown in Fig. 1.2. The rocking curve through the Ni (002) peak shows a significant amount of structure, because of the coarse-grained nature of the rolled textured substrate, yielding an out-of-plane FWHM of ~6°. Subsequent rocking curves through the (002) peaks for the CeO₂ and YSZ layers indicate out-of-plane FWHMs of 5.5 and 5°, respectively. Some structure is also observed in these rocking curves, reflecting the good epitaxial relationship between the oxides and the underlying Ni grains. A significant narrowing in the out-of-plane texture is observed for the YBCO, with the rocking curve through the (005) YBCO peak yielding an out-of-plane FWHM of only 1°. This improvement in the out-of-plane alignment relative to the underlying Ni results from the low (001) surface energy and the anisotropic film growth nature commonly observed for YBCO.⁶ This high degree of out-of-plane

Fig. 1.2. XRD rocking curves and ϕ -scans showing the (a) out-of-plane and (b) in-plane texture of a YBCO/YSZ/CeO₂ multilayer structure on a rolled textured Ni substrate.

texture is important in realizing a high J_c , as it virtually eliminates the [100] tilt boundary contribution to the total grain boundary misorientation angle.

The in-plane crystallographic alignment of the epitaxial YBCO/YSZ/CeO₂/Ni structure, as determined by XRD ϕ -scans through the YBCO (226), YSZ (202), CeO₂ (202), and Ni (222), is also shown in Fig. 1.2. The in-plane FWHM for all of the layers is $\sim 6.8^\circ$, indicating excellent epitaxy of the oxide layers with the biaxially textured metal. If the grain-to-grain misorientation angles are uncorrelated with a normal distribution, $\sim 90\%$ of the Ni grains have in-plane misorientation angles of 7° or less.²⁴ The in-plane (100) CeO₂ and YSZ principal crystallographic axes are rotated 45° relative to the in-plane (100) Ni axis, whereas the a and

b axes of the YBCO are rotated 45° with respect to the YSZ axes, all of which are in agreement with near-coincidence site lattice models.²⁵ From the high-resolution XRD scans, the lattice parameters for the YBCO film are very similar to those reported for fully oxygenated bulk materials, with $a = 3.82$ Å, $b = 3.88$ Å, and $c = 11.691$ Å. The normally cubic CeO₂ and YSZ layers show a slight tetragonal distortion, with the in-plane $a = b = 5.41$ Å, out-of-plane $c = 5.422$ Å for the CeO₂, and $a = b = 5.12$ Å, $c = 5.162$ Å for the YSZ layer. The tetragonal distortion of the oxide buffer layers appears related to the larger thermal expansion coefficient of the Ni substrate relative to these oxides, which tends to place the oxides in compression upon cooling after film growth.

The resistivity, ρ , and J_c values for various samples were measured with a standard four-point contact technique. The superconducting transition temperature, $T_c(R = 0)$, for the YBCO films was typically ~ 88 K. In the a - b plane at 300 K, $\rho \sim 250$ $\mu\text{ohm-cm}$ with a linear resistivity that extrapolates to zero near 0 K, which is consistent with a high-quality, in-plane-aligned YBCO film with little grain-boundary scattering in the normal state. The magnetic field dependence of J_c at 77 K for a 1.4 μm thick YBCO film deposited on a RABiTS tape is shown in Fig. 1.3 with magnetic field, H , applied parallel and perpendicular to the c axis. Using a voltage criteria of 1 $\mu\text{V/cm}$, the J_c of the ~ 3 mm-wide sample was measured on a bridge that was 200- μm wide and 3-mm long patterned by standard photolithography. Similar results have been obtained on 1-mm-wide bridges. At zero field, this YBCO film has a $J_c(77 \text{ K}, H = 0)$ of 575,000 A/cm². We have produced several films with $J_c(77 \text{ K}, H = 0)$ greater than 600,000 A/cm², with the highest value obtained thus far being 700,000 A/cm². These zero-field values are comparable with those obtained by using IBAD¹⁶⁻²⁰ and are within a factor of 4 of those observed for epitaxial YBCO films grown on polished (001) SrTiO₃. The magnetic field dependence of J_c for the film on rolled textured

Fig. 1.3. Magnetic field dependence of J_c , measured at 77 K, is shown for a YBCO/YSZ/CeO₂/rolled textured (001) Ni structure. Also shown is $J_c(H, 77 \text{ K})$ for YBa₂Cu₃O₇ on (001) SrTiO₃, Tl-1223 on polycrystalline YSZ [J. E. Tkaczyk et al., *Appl. Phys. Lett.* **62, 301 (1993)]; and Bi-2223/Ag tape [S. Kobayashi et al., *Physica C* **258**, 336 (1996)].**

Ni is quite similar to that measured for the epitaxial YBCO film on SrTiO₃. In fact, the relative drop of J_c with applied external magnetic field is less for the YBCO film grown on the Ni tape than for the film on (001) SrTiO₃, indicating the presence of additional flux pinning defects in the films grown on the rolled textured Ni. These pinning sites may be associated with growth-induced defect structures²⁶ or low-angle grain boundary pinning or both.^{17,18} For additional comparison, the $J_c(77 \text{ K}, H)$ behavior is also shown for Bi-2223/Ag²⁷ and Tl-1223/YSZ²⁸ tapes.

The temperature dependence of J_c , measured in magnetic fields of 0, 3, and 8 T applied parallel to the YBCO c -axis, is shown in Fig. 1.4. The $J_c(T)$ behavior for the YBCO films on the rolled textured Ni tapes is comparable with that observed for epitaxial films on oxide single crystals, which is consistent with the absence of high-angle grain boundaries in the YBCO film. For comparison, we also show data for conventional low-transition temperature (T_c) superconducting NbTi and Nb₃Sn wires,²⁹ as well for Bi-2212/Ag,³⁰ Bi-2223/Ag,³¹ and

Tl-1223/poly-YSZ²⁸ HTS wires and tapes. Clearly, the performance of the epitaxial YBCO on rolled textured Ni tape is far superior, in terms of J_c , to these other superconducting wire technologies, both for zero-field and high-field applications. In particular, the zero-field J_c of the YBCO on rolled Ni at 77 K is significantly higher than the J_c of state-of-the-art Bi-2223, Bi-2212, or Tl-1223 wires and tapes at 4.2 K. In addition, $J_c(T, H = 8 \text{ T})$ for the YBCO/RABiTS is higher than $J_c(T, H = 0)$ for the Bi-2223/Ag and Tl-1223/YSZ wires in zero field at all temperatures <65 K. At $T < 40 \text{ K}$, $J_c(H)$ for these films is greater than that for conventional low- T_c superconductors, such as NbTi and Nb₃Sn, operating at 4.2 K. Thus the use of rolling textured metal substrates, coupled with the epitaxial growth of appropriate buffer layer architectures and superconducting films, represents a viable means for producing long-length superconducting tapes for high-current, high-field applications at 77 K,

Fig. 1.4. The temperature dependence of J_c , measured at 0, 3, and 8 T, is shown for a YBCO/YSZ/CeO₂/rolled Ni structure. For comparison, data are also shown for Bi-2212/Ag wire [R. Wesche, *Physica C* **246, 186 (1995)]; Bi-2223/Ag tape [P. Haldar et al., *Appl. Phys. Lett.* **61**, 604 (1992)]; Tl-1223/YSZ, NbTi [J. E. Tkaczyk et al., *Appl. Phys. Lett.* **62**, 3031 (1993)]; and Nb₃Sn (D. R. Tilley and J. Tilley, p. 235 in *Superfluidity and Superconductivity*, 3rd ed., IOP Publishing, Bristol, England, 1990).**

particularly if high values of the “engineering” J_c , defined as the I_c per total conductor cross-sectional area (including substrate thickness), can be realized with thinner substrates and/or thicker YBCO films.

References

1. J. W. Ekin, K. Salama, and V. Selvamanickam, *Nature* **350**, 26 (1991).
2. D. T. Shaw, *MRS Bull.* **17**, 39 (1992).
3. E. E. Hellstrom, *MRS Bull.* **17**, 45 (1992).
4. J. M. Phillips, *J. Appl. Phys.* **79**, 1829 (1996).
5. D. Dimos et al., *Phys. Rev. Lett.* **61**, 1653 (1988).
6. D. Dimos, P. Chaudhari, and J. Mannhart, *Phys. Rev. B* **41**, 4038 (1990).
7. D. P. Norton et al., *Appl. Phys. Lett.* **57**, 1164 (1990).
8. Z. G. Ivanov et al., *Appl. Phys. Lett.* **59**, 3030 (1991).
9. R. Gross and B. Mayer, *Physica C* **180**, 235 (1991).
10. M. F. Chisholm and S. J. Pennycook, *Nature* **351**, 47 (1991).
11. M. Kawasaki et al., *Appl. Phys. Lett.* **62**, 417 (1993).
12. E. Sarnelli et al., *Appl. Phys. Lett.* **65**, 362 (1994).
13. S. E. Babcock et al., *Nature* **347**, 167 (1990).
14. D. K. Christen et al., p. 24 in *Superconductivity and its Applications*, Vol. 273, ed. H. S. Kwok, D. T. Shaw, and M. J. Naughton, American Institute of Physics, New York, 1993.
15. M. Rupp, A. Gupta, and C. C. Tsuei, *Appl. Phys. Lett.* **67**, 291 (1995).
16. Y. Iijima et al., *Appl. Phys. Lett.* **60**, 769 (1992).
17. R. P. Reade et al., *Appl. Phys. Lett.* **61**, 2231 (1992).
18. X. D. Wu et al., *Appl. Phys. Lett.* **67**, 2397 (1995).
19. M. Fukutomi et al., *Physica C* **219**, 333 (1994).
20. F. Yang et al., *Physica C* **244**, 299 (1995).
21. H. Makita, S. Hanada, and O. Izumi, *Acta Metall.* **36**, 403 (1988).
22. A. Goyal et al., *Appl. Phys. Lett.* **69**, 1795 (1996).
23. N. N. Khoi, W. W. Smeltzer, and J. D. Embury, *J. Electrochem. Soc.* **122**, 1495 (1975).
24. E. D. Specht et al., *Physica C* **226**, 76 (1994).
25. J. D. Budai, R. T. Young, and B. S. Chao, *Appl. Phys. Lett.* **62**, 1836 (1993).
26. D. H. Lowndes et al., *Phys. Rev. Lett.* **74**, 2355 (1995).
27. S. Kobayashi et al., *Physica C* **258**, 336 (1996).
28. J. E. Tkaczyk et al., *Appl. Phys. Lett.* **62**, 3031 (1993).
29. D. R. Tilley and J. Tilley, *Superfluidity and Superconductivity* (IOP Publishing, Bristol, England, ed. 3, 1990) p. 235.
30. R. Wesche, *Physica C* **246**, 186 (1995).
31. P. Haldar et al., *Appl. Phys. Lett.* **61**, 604 (1992).

SUPERCONDUCTING PROPERTIES OF YBCO DEPOSITS ON RABITS

We have investigated several systematics regarding the superconductive transport properties of YBCO epitaxial deposits on RABITS. A series of superconducting films were deposited by pulsed laser deposition of YBCO onto YSZ/CeO₂-buffered Ni tapes, along with control samples deposited under similar conditions onto single crystal SrTiO₃ substrates. All the samples were short segments of typical length (12–15 mm) and width (~3 mm), with YBCO thicknesses ranging from 1 to 3 μm. In all cases reported here, the RABITS thickness was approximately 126 μm (~125 μm Ni and ~1 μm oxide buffer layer). The focus of the effort was to make a comparative study of the field- and temperature-dependent J_c s among different YBCO/RABITS samples and with properties of the “benchmark” materials

deposited on SrTiO_3 . In addition, a preliminary test of 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.

The samples were prepared for four-terminal transport measurements by sputter deposition of gold or silver current and voltage pads, followed by annealing at 500°C for $\frac{1}{2}$ h, and slow cooling in 1 atm oxygen. The gauge length for the voltage terminals was 4 mm. For some samples, initial measurements of the resistive transition and high temperature J_c were made on the full 3-mm width. To minimize the heating effects at the current contacts and to reduce the overall currents required, thereby extending the measurements to lower temperatures, the samples were subsequently wet-etch patterned to a bridge width of 1 mm. In addition, in some cases pulsed current measurements extended the measurements to the low-field, low-temperature regime. In all cases, the measurements yielded identical results in the regions of overlap, demonstrating that the samples were macroscopically homogeneous and that the measurements were well controlled.

Figure 1.5 shows the magnetic field dependence of J_c at 77 K. The result for a

Fig. 1.5. The magnetic-field-dependent J_c of YBCO/RABiTS compared with other HTS epitaxial thin films that have been deposited on single crystal oxide substrates. Most data are shown for $H||c$, the applications-limiting orientation. The characteristics with $H||ab$ is typical of the strong intrinsic pinning observed for all HTS materials.

1.4- μm -thick YBCO deposit on a RABiTS sample is compared with high- J_c epitaxial layers thinly deposited on single crystal oxide substrates, for several different HTS material classes. In all cases, the films on single crystal substrates have zero-field J_c values in excess of $1 \text{ MA}/\text{cm}^2$. While all the films show excellent, similar characteristics with the field parallel to the film plane ($H||ab$ planes, the so-called “intrinsic pinning” case), Fig. 1.5 emphasizes the characteristics with $H||c$, which is the applications-limiting orientation where the flux pinning is limited by the effects of intrinsic material anisotropy. YBCO is the HTS material of choice for conductor applications, and the high-field properties of YBCO/RABiTS may exceed those of prototype YBCO/ SrTiO_3 films. In fact, the somewhat suppressed $J_c(H=0)$ for YBCO/RABiTS may arise from the high density of crystalline defects produced naturally from the growth process on RABiTS.

Figure 1.6 supports this idea in a comparison of the Rutherford Backscattering Spectra (RBS) for a YBCO/ SrTiO_3 and a YBCO/RABiTS. Analysis of the random spectrum reveals that the YBCO/RABiTS composition is yttrium rich, and slightly barium poor. This result may explain the slightly reduced T_c of 86 to 88 K. Figure 1.6 also shows that the RBS channeling minimum yield $X_{\min} \approx 34\%$ for YBCO/RABiTS compared with $X_{\min} \approx 4\%$ for the YBCO/ SrTiO_3 . Measurements on other YBCO/RABiTS samples indicate that $X_{\min}$ falls in the range of 30 to 50%. The relatively suppressed channeling characteristics of YBCO/RABiTS imply crystalline defects that may be responsible for the enhanced pinning at high vortex densities. Detailed transmission electron microscopy (TEM) characterizations will be required to help confirm these conclusions.

The enhanced flux pinning at high fields for $H||c$ is accompanied by a slight depression of the J_c for $H||ab$. This fact is illustrated in Fig. 1.7, which compares the angular dependence of J_c for a YBCO/RABiTS with a YBCO/ SrTiO_3 as the applied field orientation is

Fig. 1.6. The Rutherford Backscattering Spectra for films of YBCO/RABiTS and YBCO/SrTiO₃. A comparison of the channeling minimum yield $X_{\min}$ shows that the YBCO/RABiTS has more crystalline structural defects.

swept from near $H||c$ to $H||ab$. In this example, for an applied field of 5 T at 77 K, a crossover exists in the value of J_c at intermediate orientation. In addition, the J_c peak near $H||ab$ is less sharp and has additional structure for the YBCO/RABiTS sample. These characteristics are reminiscent of film properties before and after the introduction of columnar flux pinning defects by heavy ion irradiation, where J_c enhancements at high fields for $H||c$ are accompanied by decreases in zero field and for $H||ab$. In this case, one might anticipate that the YBCO/RABiTS materials intrinsically possess

Fig. 1.7. The dependence of J_c on the orientation of the sample in the applied magnetic field of 5 T, comparing YBCO/RABiTS with YBCO/SrTiO₃. The enhanced properties near $H||c$, along with the relatively depressed values near $H||ab$, imply the existence of strong extended pinning defects in the YBCO/RABiTS sample.

some sort of strong-pinning extended defects. Indeed, previous work on YBCO films deposited on vicinal single crystal substrate surfaces has demonstrated enhanced flux pinning and extended "stacking faults" defects propagating upward through the films caused by nucleation and growth at atomic surface steps in the substrates. Again, confirmation of a similar situation must await microstructural analysis.

While the field-dependent J_c levels in YBCO/RABiTS prototypes are adequate to enable new applications in the liquid nitrogen temperature range, the fraction of superconductor in the typical entire structure is presently quite small ($\sim 1 \mu\text{m}/126 \mu\text{m}$, $< 1\%$). One of the important issues to scaleup is obtaining a sufficient level of overall current density, presumably achieved by the combination of both thinner RABiTS and thicker YBCO deposits. To this end, it is important to determine whether good superconducting properties can be retained in thick HTS deposits. In a preliminary study, we have addressed the dependence of J_c on the YBCO deposit thickness. Figure 1.8 shows these results for applied fields of zero and 1 T applied

Fig. 1.8. The dependence of J_c at 77 K on YBCO thickness for a series of YBCO/RABiTS samples. Open symbols are values in self-field, while closed symbols represent J_c in an applied field $H||c = 1$ T. The two represent required J_c levels to satisfy different practical operating criteria. Solid curve: overall engineering current density of 10^4 A/cm². Dashed curve: tape conductor capacity of 10 A/mm width.

parallel to the c axis. Most data are given at 77 K, but some results are presented at 64 K (the temperature of pumped liquid nitrogen just above its solidification point). For YBCO thicknesses of ~ 1 to 3 μm , Fig. 1.8 shows that $J_c(1\text{ T})$ exhibits no systematic thickness dependence with values in the range of ~ 100 to 150 kA/cm² at 64 K. For comparison, the two curves represent J_c values required, assuming the present RABiTS dimensions, to satisfy the two applications criteria of overall $J_c = 1 \times 10^4$ A/cm² (solid line) and $K_c = 10$ A/mm-width (dashed line) for a tape conductor. 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.

Conductor applications will require strain tolerances that permit bending to form coils for components such as magnets and motors. We have conducted initial bend-strain tolerance measurements on two separate samples—one placed in compression and the other in tension.

Measurements were made sequentially by bending and straightening the sample around a specified-diameter mandrel and measuring J_c at 77 K in zero field. The repeated mechanical cycling associated with this technique resulted in a noticeable work hardening of the Ni. The results, along with the effect on the sample resistance R at room temperature, are shown in Fig. 1.9. In compression, J_c degrades rapidly near a strain of 0.5%; the abrupt increase in R at this same strain level indicates the formation of cracks. For the present RABiTS dimensions, this strain level of 0.5% corresponds to a bend diameter of about 2.5 cm. In tension, the degradation onset occurs at smaller strain level but is more gradual. Crack formation is evident at the level of $\sim 0.2\%$. If these preliminary results hold for future configurations having thinner RABiTS and thicker YBCO, there appears to be a basis for optimism that several criteria for real applications can be met. Future developments must focus on issues of reproducibility, long-length demonstrations, rates, and problems presented by the magnetic substrate for applications requiring rapidly changing currents.

SOL-GEL SYNTHESIS OF LaAlO_3 : EPITAXIAL GROWTH OF LaAlO_3 THIN FILMS ON SrTiO_3 (100)

Sol-gel techniques have been developed as viable methods for the fabrication of superconducting¹⁻⁴ and buffer layers⁵⁻⁷ for several reasons. Sol-gel represents a low-cost, nonvacuum process and also presents a convenient way of coating long-length conductors and irregularly shaped substrates. Films of LaAlO_3 are of particular interest as substrates and buffer layers for high temperature superconductors. Critical current densities exceeding 10^6 A/cm² at 77 K have been observed repeatedly from the superconductors $\text{YBa}_2\text{Cu}_3\text{O}_7$ ⁸⁻¹⁰ and $(\text{Tl,Bi})(\text{Sr}_{1.6}\text{Ba}_{0.4})\text{Ca}_2\text{Cu}_3\text{O}_{9.8}$ ¹¹ grown epitaxially on single crystal layers of this material by various deposition

Fig. 1.9. The dependence of J_c for two different YBCO/RABiTS samples on the bend strain produced in both compression and tension. Also shown is the room-temperature normal-state resistance, which serves as an indication of a breakdown by cracking.

techniques. Epitaxial films of the superconductors $(\text{Ti,Pb})(\text{Ba,Sr})_2\text{Ca}_2\text{Cu}_3\text{O}_9$ ¹² and $(\text{Ti,Pb})\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_7$ ¹³ have also been grown on LaAlO_3 . The lattice mismatch

between LaAlO_3 and these superconductors is quite small, and LaAlO_3 offers exceptional chemical stability and is possibly an excellent diffusion barrier. Our interests in LaAlO_3 were to (1) develop a sol-gel route to grow thin films and (2) demonstrate that these films could be processed to give at least preferred orientation but preferably epitaxy. Epitaxial growth of buffer layers on textured surfaces is considered important in the development of practical HTS conductors with high J_c s.^{14,15}

Films of LaAlO_3 have been previously grown via a sol-gel technique on silicon and sapphire single crystal substrates.¹⁶ The chemistry employed in that work is different from the chemistry we used in that, while starting from alkoxides, a chelating agent (acetylacetone) was used to obtain solutions for spin-coating. Fairly complex heat treatments were also employed, but epitaxial growth was not observed. We chose instead to use an all-alkoxide system based on methoxyethoxide complexes in 2-methoxyethanol. This chemistry has been used with success in preparing lead-based ferroelectric films¹⁷ and epitaxial growth of lead niobium zirconium titanate (PNZT) on sapphire.¹⁸ We report here our successful preparation of an all-alkoxide precursor LaAlO_3 solution and the growth of epitaxial LaAlO_3 on SrTiO_3 single crystals.

Experimental

Solution Preparation

The preparation of the LaAlO_3 precursor solution was based on the method used in the sol-gel synthesis of PbTiO_3 and PbZrO_3 .¹⁷ The weighing of solid materials was done in an argon-filled, inert-atmosphere glove box, and the solution preparation was carried out under argon using a modified commercial solvent still (Ace Glass). Aluminum sec-butoxide (Alfa, 95%), lanthanum isopropoxide (Alfa), and 2-methoxyethanol (Alfa, spectrophotometric grade) were used without additional purification. The preparation procedure,

including the formation of the powders and films, is schematically described in a flowchart in Fig. 1.10.

Aluminum sec-butoxide (3.89 g, 15.8 mmol) was refluxed in 50 mL of 2-methoxyethanol. Approximately 30 mL of sec-butanol/ 2-methoxyethanol were distilled from the

isopropoxide (5.03 g, 15.9 mmol) was then added to the refluxing aluminum solution. Approximately 30 mL of isopropanol/ 2-methoxyethanol was distilled off, and the solution was repeatedly rediluted with 30 to 50 mL of fresh 2-methoxyethanol and further distilled for approximately 1.5 h to again ensure exchange by the methoxyethoxide ligand. The final volume of the light yellow solution was adjusted with 2-methoxyethanol to 32 mL to make a 0.5 M LaAlO_3 precursor solution.

Powder Preparation and Analysis

The gel used to prepare powders for differential thermal analysis/ thermogravimetric analysis (DTA/TGA) analysis and XRD was made by adding three times the volume of a 1 M H_2O in 2-methoxyethanol solution to a volume of the precursor solution. This light yellow, transparent gel was decomposed on a hot plate with a portion of the resulting product being used for the DTA/TGA and the remainder being fired between 500 and 800°C in air for 1 to 12 h to determine the crystallization temperature.

DTA/TGA data were obtained in a Sinku-Riko TFD7000 RH instrument. Samples were contained in MgO crucibles and heated in air from room temperature to 900°C and in oxygen from room temperature to 1250°C at a rate of 10°C/min. The XRD pattern of LaAlO_3 powder was collected using a diffractometer (Bragg-Brentano) equipped with a theta-compensating incident-beam divergence slit and a graphite (002) diffracted-beam monochromator. Cu K_α radiation was used.

Coating Procedure and Film Characterization

The solution needed for spin-coating was prepared by partially hydrolyzing a volume of the precursor solution using an equal volume of the 1 M H_2O in 2-methoxyethanol solution. The SrTiO_3 (100) single crystal substrate (Commercial Crystal Laboratories, Inc.) was

Fig. 1.10. Procedure followed to prepare the LaAlO_3 precursor solution, powders, and films.

solution, which was repeatedly rediluted with 30 to 50 mL of fresh 2-methoxyethanol followed by distillation. When the boiling point reached that of 2-methoxyethanol (124°C), after approximately 1.5 h, exchange of sec-butoxide by methoxyethoxide was presumed finished. A stoichiometric amount of lanthanum

ultrasonically cleaned in ethanol for 1 h before being coated. Four coatings of the hydrolyzed precursor solution were applied to the substrate using a spin-coater operated at 2000 rpm for 45 s. Between each coating, the substrate was pyrolyzed in O_2 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 4000 Å.

The same XRD arrangement used to analyze the $LaAlO_3$ powders was used to measure the preferred orientation of $LaAlO_3$ on $SrTiO_3$ (100). Further measurements of the epitaxy of this film were made using a Rigaku rotating-anode X-ray generator equipped with a graphite monochromator selecting $Cu K_\alpha$ radiation and slits defining a 2×2 mm incident beam. A four-circle diffractometer was used to collect pole figures to measure rocking curves of (003) planes of the (001) textured film, which are used to determine the out-of-plane alignment, and to measure ϕ scans of the (202) planes, are used to determine in plane alignment of the film. Electron micrographs of a $LaAlO_3$ film on a $SrTiO_3$ single crystal were taken using a Hitachi S-4100 field emission scanning electron microscope (SEM). The beam voltage used was 15 kV, and the micrographs were taken at several magnifications.

Results and Discussion

The methoxyethoxide solution produced both transparent gels and films with excellent uniformity and coating characteristics. The gels were converted to ceramic powders to study the thermal and structural characteristics of the process as a function of processing temperatures. Based on results of the study of powders, thin films were produced on single crystal substrates to obtain epitaxial films of $LaAlO_3$. The results are described in detail in the following sections.

Effects of Ligand Exchange

The reactivity of the alkoxide ligands with water is what drives the sol-gel process, but this process must be controlled to promote the desired gelling and to avoid precipitation, which can occur during premature hydrolysis. To ensure proper gelation, the reactant metal alkoxides were subjected to ligand-exchange reactions to convert the sec-butoxide and isopropoxide ligands to methoxyethoxide ligands and thus to decrease the moisture sensitivity of the resulting precursor solution. Since the bidentate nature of the methoxyethoxide ligand should "tie up" vacant coordination sites, the rate of hydrolysis should be slowed and thus more readily allow the formation of a gel rather than a precipitate. In addition, the bidentate nature of the methoxyethoxide ligand also allows the more facile formation of mixed-metal alkoxide complexes. Mixed-metal barium and titanium complexes with the methoxyethoxide ligand have been isolated and characterized by X-ray crystallography.¹⁹

Characterization of $LaAlO_3$ Powders

TGA results (Fig. 1.11) indicated that the pyrolyzed gel lost ~30% of its weight while being fired in standing air between room temperature and 900°C, ensuring complete

Fig. 1.11. DTA/TGA analysis of the pyrolyzed gel between room temperature and 900°C in air; scan rate 10°C/min. Thin line: DTA; thick line: TGA.

conversion to LaAlO_3 . DTA results for the pyrolyzed gel are also shown in Fig. 1.11. The main exothermic peaks at ~ 315 and $\sim 750^\circ\text{C}$ were observed; however at this time the identity of these intermediate states is not known. The resulting powder was cooled and run again as a baseline correction. A DTA analysis performed in oxygen yielded a very narrow and sharp exothermic peak at 800°C , suggesting a possible melting event that may be necessary to grow a good epitaxial film.

The XRD patterns of the pyrolyzed gel fired between 500 and 800°C in air are given in Fig. 1.12. Crystallization begins around 600°C with a well-crystallized product resulting from firing at 800°C . LaAlO_3 has a perovskite structure with a 0.2% rhombohedral distortion. Its rhombohedral lattice is described by a hexagonal unit cell with $a = 5.374 \text{ \AA}$ and $c = 13.11 \text{ \AA}$ ²⁰ but can also be indexed on the basis of a simple cubic structure with a lattice parameter $a = 3.790 \text{ \AA}$. The experimental lattice parameter of this well-crystallized, LaAlO_3 product, corrected using Si as an internal standard and indexed as cubic, was calculated to be $a = 3.796 (1) \text{ \AA}$.

Characterization of Epitaxial LaAlO_3 Films

For growing epitaxial films of LaAlO_3 , 800°C in oxygen was chosen as the growth

Fig. 1.12. XRD patterns of the pyrolyzed gel fired between 500 and 800°C . 800°C pattern was indexed based on a simple cubic cell.

temperature because the sharpest exothermic peak was seen at this temperature in the DTA analysis performed in oxygen. As shown in Fig. 1.13, the LaAlO_3 film exhibits c -axis preferred orientation on a SrTiO_3 (100) single crystal substrate. The LaAlO_3 peaks are considered to correspond to (001), (002), and (003) planes in a cubic structure. The figure in the inset is the rocking curve scan of the (003) LaAlO_3 reflection and verifies the good c -axis alignment with the FWHM determined to be 0.87° . Figure 1.14(a) is the ϕ scan made from the (202) plane and indicated that the film had good in plane texture with a FWHM = 1.07° . A typical X-ray pole figure of the cubic (202) reflections [Fig. 1.14(b)] shows a single cube-on-cube epitaxy: $\text{SrTiO}_3(001) \parallel \text{LaAlO}_3(001)_{\text{cubic}}$ and $\text{SrTiO}_3[100] \parallel \text{LaAlO}_3[100]_{\text{cubic}}$. In hexagonal LaAlO_3 coordinates, this is $\text{SrTiO}_3(001) \parallel \text{LaAlO}_3(012)_{\text{hex}}$ and $\text{SrTiO}_3[100] \parallel \text{LaAlO}_3[421]_{\text{hex}}$. A SEM micrograph of a LaAlO_3 on single crystal SrTiO_3 indicates that the grains are small, surface roughness is low, and the film appears to be continuous.

Fig. 1.13. θ - 2θ scan of c -axis-oriented LaAlO_3 on SrTiO_3 (100). S = SrTiO_3 and L = LaAlO_3 . Inset is the rocking curve of the (003) reflection of LaAlO_3 (FWHM = 0.87°).

Fig. 1.14. (a) ϕ scan of the (202) LaAlO_3 reflection (FWHM = 1.07°) and (b) typical X-ray pole figure from LaAlO_3 (202)_{cubic}.

Other Synthesis Efforts

We have investigated other sol-gel routes for preparing LaAlO_3 precursor solutions using lanthanum nitrate hexahydrate or lanthanum acetate as the starting material instead of relatively expensive lanthanum isopropoxide. However, such attempts using these reactants were not particularly successful so far, resulting in either premature hydrolysis (nitrate route) or failure to form a mixed-metal complex (acetate route). We plan to focus now on identifying the proper conditions to grow high- J_c superconductors on these epitaxial LaAlO_3 buffer layers.

Conclusions

A LaAlO_3 precursor solution has been prepared by an all alkoxide sol-gel route. A gel was formed upon complete hydrolysis of the solution and yielded crystalline powders when

pyrolyzed in air beginning around 600°C . The cubic lattice parameter of well-crystallized LaAlO_3 pyrolyzed at 800°C , $a = 0.3796 \pm 0.0001$ nm, agrees quite well with the literature value. Highly c -axis-oriented films of LaAlO_3 [FWHM = 0.87° for the (003) plane] with good in plane texture [FWHM = 1.07° for the (202) plane] have been grown on SrTiO_3 (100) single crystals using a partially hydrolyzed solution and firing in O_2 at 800°C .

References

1. L. Ben-Dor et al., *Physica C* **200**, 418 (1992).
2. M. W. Rupich, Y. P. Liu, and J. Ibechem, *Appl. Phys. Lett.* **60**, 1384 (1992).
3. F. J. Gotor et al., *Physica C* **218**, 429 (1993).
4. M. Paranthaman and D. B. Beach, *J. Am. Ceram. Soc.* **78**, 2551 (1995).
5. G. Guzman, P. Barboux, and J. Perrière, *J. Appl. Phys.* **77**, 635 (1995).
6. F. Wang, A. Uusimäki, and S. Leppävuori, *Appl. Phys. Lett.* **67**, 1692 (1995).
7. U. Selvaraj et al., *Mater. Lett.* **23**, 123 (1995).
8. S. Matsuno, F. Uchikawa and K. Yoshizaki, *Jpn. J. Appl. Phys.* **29**, L947 (1990).
9. A. Mogro-Campero and L. G. Turner, *J. Supercond.* **6**, 37 (1993).
10. P. C. Chou et al., *Physica C* **254**, 93 (1995).
11. Z. F. Ren, C. A. Wang, and J. H. Wang, *Appl. Phys. Lett.* **65**, 237 (1994).
12. D. L. Schulz et al., *Appl. Phys. Lett.* **65**, 2472 (1994).
13. K. E. Myers et al., *Appl. Phys. Lett.* **65**, 490 (1994).
14. D. Dimos et al., *Phys. Rev. Lett.* **61**, 219 (1988).
15. D. Dimos, P. Chaudhari, and J. Mannhart, *Phys. Rev. B* **41**, 4038 (1990).
16. P. Peshev and V. Slavova, *Mater. Res. Bull.* **29**, 255 (1994).

17. K. D. Budd, S. K. Dey and D. A. Payne, *Brit. Ceram. Proc.* **36**, 107 (1985).

18. C. K. Barlingay and S. K. Dey, *Appl. Phys. Lett.* **61**, 1278 (1992).

19. J.-F. Campion et al., *Inorg. Chem.* **30**, 3244 (1991).

20. M. Mizuno et al., *Yugyo Kyokai Shi* **82**, 631 (1974).

GROWTH OF BIAXIALLY TEXTURED BUFFER LAYERS ON ROLLED NI SUBSTRATES BY ELECTRON BEAM EVAPORATION

For conductors developed for high temperature and high-field applications, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (referred to as YBCO) deposits are very promising. Also, Dimos et al.^{1,2} have demonstrated from their YBCO bicrystal studies that high J_c can only be obtained on oriented YBCO films with a high degree of texture both normal to and within the basal plane. Two approaches have been used to deposit biaxially textured YBCO films. The first approach was to grow biaxially textured YSZ buffer layers on polycrystalline Ni-based alloys such as Haynes 230 and Hastelloy C276 through an IBAD process.³⁻⁶ A high J_c of over $1 \times 10^6 \text{ A/cm}^2$ at 75 K and zero field was obtained on 1- μm -thick YBCO films on Ni-based alloys with textured YSZ buffer layers grown by IBAD.⁷ The second approach was developed at Oak Ridge National Laboratory (ORNL) using the RABiTS⁸ concept. Our approach was to use rolling-induced texture to obtain biaxially textured face-centered cubic (fcc) metal strips and to deposit epitaxially on the strips both buffer layers and superconductors to form a conductor. Ni was chosen as the substrate because it readily develops the cube texture and is more oxidation resistant than Cu. Recently, we demonstrated that a J_c of $0.73 \times 10^6 \text{ A/cm}^2$ at 77 K and zero field can be obtained for films with a layer sequence of YBCO/YSZ/ CeO_2 /Ni.⁹ The crystallographic orientations for all the layers were (100). In this architecture, all oxide

layers were grown by PLD. A clear need exists to develop a capability to deposit buffer and superconductor layers by other techniques. These layers must be grown as continuous epitaxial films on Ni. The purpose of the chemical buffer layers is to retard oxidation of Ni, to reduce the lattice mismatch between Ni and YBCO, and to prevent diffusion of Ni into YBCO. Previous studies proved that CeO_2 ,¹⁰⁻¹³ Pd,^{13,14} and YSZ¹⁵ films could be grown epitaxially by vapor-deposition techniques on single crystal substrates. In this paper, we describe our successful development of the growth of buffer layers on rolled Ni substrates using an electron beam evaporation technique. In related work, these buffer layer architectures also have been developed using rf and dc magnetron sputtering; those results are reported separately¹⁶. In this report, the deposition conditions for growing epitaxial Pd, CeO_2 and YSZ films on textured Ni substrates by electron beam evaporation are reported for the first time.

Experimental Results and Discussion

The cube (100) texture in Ni (99.99 %) was produced by cold-rolling to over 90% deformation followed by recrystallization at temperatures ranging from 400 to 1000°C.⁸ The thickness of the textured-Ni substrate used was 125 μm . The deposits were produced without any substrate polishing in an AIRCO Temescal CV-14 system with three electron guns. It was operated by a Temescal FDC-8000 Film Deposition Controller. The films were analyzed by detailed XRD studies. A Philips Model XRG3100 diffractometer with $\text{Cu K}\alpha$ radiation was used to record powder diffraction patterns. For texture analysis, a Rigaku rotating-anode X-ray generator was used, with a graphite monochromator selecting $\text{Cu K}\alpha$ radiation, and slits defining a $2 \times 2 \text{ mm}$ incident beam. A four-circle diffractometer collected pole figures to measure rocking curves (ω scan) of (002) planes of the (001) textured film, which measure out-of-plane alignment. The diffractometer was also used to measure ϕ scans of the (202)

planes. These scans indicate the in-plane alignment of the film. SEM micrographs were taken using a Hitachi S-4100 Field Emission Scanning Electron Microscope. The beam voltage used was 15 kV. The experimental details for the growth of two-buffer-layer architectures on rolled Ni substrates are described in the following sections.

CeO₂/Pd/Ni Architecture

Growth of Pd on Rolled Ni Substrates by Electron Beam Evaporation

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 electron-beam system. After the vacuum had reached 1×10^{-6} torr at room temperature, the substrates were annealed in situ at 400°C for 4 h. The temperature of the substrate was measured using a thermocouple. Then the Pd layer was grown on the textured Ni at temperatures ranging from 100 to 500°C. The typical deposition rate for Pd was between 0.5 and 1.0 nm/s at a pressure of 10^{-6} torr, and the final thickness varied from 200 nm to 1 μ m. The thickness of the film was measured by a quartz crystal monitor during the deposition. The θ -2 θ scan for a 400-nm-thick Pd film deposited on Ni at 500°C showed the presence of a (001)-oriented film. From the ω and ϕ scans for 400-nm-thick Pd films deposited on Ni at 500°C, the FWHM for Ni (002) and Pd (002) obtained were 7.3 and 4.1°, and that of Ni (202) and Pd (202) were 8.8 and 7.4°, respectively. The XRD results show that Pd can be deposited epitaxially on Ni.

Growth of CeO₂ on Pd-buffered Ni Substrates by Electron Beam Evaporation

Initially, biaxially textured Ni substrates were cleaned and Pd films were grown on them as discussed in the previous section. CeO₂ films were then deposited on the Pd-buffered Ni

substrates. After the vacuum in the chamber had reached 1×10^{-6} torr at room temperature, a mixture of 4% H₂ and 96% Ar was introduced until the pressure inside the chamber reached $\sim 10^{-4}$ torr. The gas flow was controlled by a dc-powered piezoelectric valve. The Pd-buffered Ni substrates were then annealed at $\sim 600^\circ\text{C}$ for 30 min at $\sim 10^{-4}$ torr. After the substrates were annealed, the chamber was maintained at a pressure of 2×10^{-5} torr with a mixture of 4% H₂ and 96% Ar. The textured CeO₂ layers were grown on the Pd-buffered Ni at temperatures ranging from 300 to 750°C. The deposition rate for CeO₂ was 0.1 nm/s. The final thickness varied from 50 to 200 nm. Cerium metal was used as the source. The crucibles used were usually graphite. A θ -2 θ scan for a 100-nm-thick CeO₂ film deposited on Pd-buffered Ni at 400°C is shown in Fig. 1.15. The strong CeO₂ (200) lines show the presence of a good out-of-plane texture. The oxygen impurity present in the chamber was apparently enough to oxidize the film to form stoichiometric CeO₂. Figure 1.16 shows the ω and ϕ scans for the same film. The FWHM for Ni (002), Pd (002), and CeO₂ (002) are 6.6, 4.6, and 5.9°, respectively. The rocking curves for Pd and CeO₂ are smooth because these are fine-grained films. By contrast, the Ni substrate is coarse-grained, so its rocking curves consist of many sharp peaks corresponding to individual grains. The FWHM from ϕ scans for Ni (202),

Fig. 1.15. The room-temperature powder XRD for a 100-nm-thick CeO₂ layer deposited on Pd-buffered Ni at 400°C.

Fig. 1.16. The ω and ϕ scans for a 100-nm-thick CeO_2 layer deposited on Pd-buffered Ni at 400°C .

Pd (202), and CeO_2 (202) were 8.3° , 7.8° , and 10.0° , respectively. The XRD results demonstrate that CeO_2 and Pd can be deposited epitaxially on Ni.

YSZ/ CeO_2 /Ni Architecture

Growth of CeO_2 on Rolled Ni Substrates by Electron Beam Evaporation

The electron beam evaporation technique was also used to deposit CeO_2 films directly on Ni. Biaxially textured Ni substrates were mounted on a substrate holder that contained a heater assembly. After the vacuum in the chamber had reached 1×10^{-6} torr at room temperature, a mixture of 4% H_2 and 96% Ar was introduced until the pressure inside the chamber reached ~ 1 torr. The Ni substrates were annealed at $\sim 700^\circ\text{C}$ for 60 min at ~ 1 torr. During CeO_2 deposition, the chamber was maintained at a pressure of 2×10^{-5} torr with a mixture of 4% H_2 and 96% Ar. The textured CeO_2 layers were deposited on the Ni substrates at temperatures ranging from 300 to 750°C . The deposition rate for CeO_2 was 0.1 nm/s, and the final thickness varied from 5 to 150 nm. The XRD results from the θ -2 θ scan as well as from the ω and ϕ scans for 100-nm-thick CeO_2 films deposited on Ni at 600°C revealed good epitaxial texturing. The CeO_2 (002) from the

θ -2 θ scan showed the presence of a good out-of-plane texture. The use of a mixture of 4% H_2 and 96% Ar gas presumably prevents the formation of NiO during the CeO_2 growth. These characterizations show that CeO_2 can be deposited epitaxially on Ni.

Growth of YSZ on CeO_2 -Buffered Ni Substrates by Electron Beam Evaporation

The electron beam evaporation technique was used to deposit YSZ on CeO_2 -buffered Ni substrates. Biaxially textured CeO_2 -buffered Ni substrates were cleaned with methanol and were mounted on a heated substrate holder in the electron-beam system. After the vacuum in the chamber had reached 1×10^{-6} torr at room temperature, a gas mixture of 4% H_2 and 96% Ar was introduced until the pressure inside the chamber reached ~ 1 torr. The CeO_2 -buffered Ni substrates were annealed at $\sim 700^\circ\text{C}$ for 60 min at that pressure. The chamber was then maintained at a pressure of 2×10^{-5} torr with a mixture of 4% H_2 and 96% Ar. The textured YSZ layers were grown on the CeO_2 -buffered Ni substrates at temperatures ranging from 650 to 750°C . The YSZ deposition rate was 0.1 nm/s, and the final thickness varied from 50 to 150 nm. Yttria (10%) stabilized zirconia was used as the source. The θ -2 θ scan is shown in Fig. 1.17 and the ω and ϕ scans are shown in Fig. 1.18. These results were obtained on 100-nm-thick YSZ films grown at 600°C . The strong YSZ (200) and CeO_2 (200) peaks shown in Fig. 1.17 indicate the presence of a good out-of-plane texture. The FWHM for Ni (002), CeO_2 (002), and YSZ (002) were 7.4° , 6.6° , and 6.8° , and that of Ni (202), CeO_2 (202), and YSZ (202) are 9.5° , 8.8° , and 8.5° , respectively. As shown in Fig. 1.19, the CeO_2 (111) and YSZ (202) pole figures demonstrate that the buffer layers are epitaxial with a single orientation. The XRD results show that YSZ can be grown epitaxially on CeO_2 -buffered Ni substrates. To date, our efforts to grow YSZ directly on rolled Ni substrates have produced either randomly oriented YSZ or (111)-oriented films.

Fig. 1.17. The room-temperature powder XRD for a 100-nm-thick YSZ layer deposited on 10-nm-thick CeO_2 -buffered Ni at 600°C.

Thickness Dependence and Crack Formation in CeO_2 Layers

In our studies of CeO_2 layers of various thicknesses deposited on rolled Ni substrates, we found that the as-grown 100-nm-thick CeO_2 layers were cracked whereas 50-nm-thick CeO_2 layers were crack-free. The SEM micrographs that demonstrate these features are shown in Fig. 1.20. After the growth of YSZ on a

50-nm-thick CeO_2 layer, the CeO_2 layers were also cracked but the YSZ layers were crack-free. The presence of YSZ layers on top of CeO_2 layers seems to alleviate the cracks that are formed underneath. The CeO_2 layer thickness was found to be critical. Both CeO_2 and YSZ layers were crack-free for a CeO_2 underlayer thickness of ≤ 10 nm. Our SEM studies showed that both CeO_2 and YSZ layers were smooth and continuous, demonstrating that a very thin layer of CeO_2 is needed to grow textured YSZ layers. Efforts are being made to demonstrate the growth of high- J_c YBCO films on these buffer layers.

Conclusions

We developed two buffer layer architectures on textured-Ni substrates using the electron beam evaporation techniques. The two-buffer layer sequences are $\text{CeO}_2/\text{Pd}/\text{Ni}$ and $\text{YSZ}/\text{CeO}_2/\text{Ni}$. The cube (100) texture in Ni was produced by cold-rolling followed by recrystallization at temperatures ranging from 400 to 1000°C. The CeO_2 layer was deposited epitaxially on both Pd-buffered and textured Ni substrates. The YSZ layer was deposited epitaxially on CeO_2 -buffered Ni substrates. For thicker CeO_2 films on Ni substrates, crack formation was observed. Growth of a 3- to 10-nm-thick CeO_2 layer prevents crack formation and also assists the epitaxial growth of YSZ films.

Fig. 1.18. The ω and ϕ scans for a 100-nm-thick YSZ deposited on 10-nm-thick CeO_2 -buffered Ni at 600°C.

References

1. D. Dimos et al., *Phys. Rev. Lett.* **61**, 219 (1988).
2. D. Dimos, P. Chaudhari, and J. Mannhart, *Phys. Rev. B* **41**, 4038 (1990).

ORNL 97-4192/arb

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Fig. 1.19. The CeO_2 (111) (*top*) and YSZ (202) (*bottom*) pole figures for a 100-nm-thick YSZ layer deposited on 10-nm-thick CeO_2 -buffered Ni at 600°C.

3. Y. Iijima et al., *Appl. Phys. Lett.* **60**, 769 (1992).

4. R. P. Reade et al., *Appl. Phys. Lett.* **61**, 2231 (1992).

Fig. 1.20. The SEM micrographs for (a) 50-nm-thick and (b) 100-nm-thick CeO_2 films deposited directly on rolled Ni substrates. The micrographs were taken at 50-kX magnification.

5. M. Fukutomi et al., *Physica C* **219**, 333 (1994).

6. X. D. Wu et al., *Appl. Phys. Lett.* **65**, 1961 (1994).

7. X. D. Wu et al., *Appl. Phys. Lett.* **67**, 2397 (1995).
8. A. Goyal et al., *Appl. Phys. Lett.* **69**, 1795 (1996).
9. D. P. Norton et al., *Science* **274**, 755–57 (November 1996).
10. X. D. Wu et al., *Appl. Phys. Lett.* **58**, 2165 (1991).
11. M. Maul et al., *J. Appl. Phys.* **74**, 2942 (1993).
12. P. C. McIntyre et al., *J. Electron. Mater.* **24**, 735.
13. Chunyan Tian, Yang Du, and Siu-Wai Chan, *Mater. Res. Soc. Proceedings*, Vol. 355, ed. B. G. Demczyk et al., ISDN 1-55899-256-1 (1995).
14. S. N. Ermolov et al., *IEEE Trans. on Appl. Supercond.* **5**, 1929 (1995).
15. A. Bardal et al., *J. Appl. Phys.* **75**, 2902 (1994) and references therein.
16. Qing He, et al., *Physica C* **275**, 155–61 (1997).

OXFORD CRADA

Oxford Instruments, Inc., and ORNL have a CRADA that involves development of Ag/Bi-2212 conductors for high-field applications. Both dip-coated and powder-in-tube (PIT) conductors are being studied. The ORNL role in the project has involved evaluating batch-to-batch variations in the 2212 powder supplied by a commercial vendor and investigating difficulties encountered during process development.

Processing the Bi-2212 conductors involves partially melting the powders and slow cooling. Reproducible melting behavior is therefore a basic process requirement. Table 1.1 gives melting data for seven lots of commercial powders and nitrate pyrolysis material produced at ORNL. The variables include Ag content, carbon content, cation concentrations, and intra-lot uniformity. The samples were measured in two conditions, as received from the vendor and after a 750/835°C O₂ decarburization heat

treatment. Small (0.1–0.2 g) samples suitable for DTA/TGA were decarburized in flowing oxygen.

The endotherm measurements show that the two Ag-free commercial lots of Bi-2212 are nearly identical and the melting behavior was not altered by the decarburization heat treatment. Results for the Ag-containing powders were more variable, but data on decarburized commercial lots show that Ag lowers the melting temperature by about 15°C. This value is close to the 18° effect obtained by adding Ag₂O to stoichiometric nitrate pyrolysis powder.

With a single exception (lot 5), decarburization produced an increase in melting temperature. It also reduced the inter-lot-variability which is a requirement for the conductor fabrication process. The most serious powder defect identified in this work is the 11°C intra-lot variation observed for lot 3. This lot was inhomogeneous both before and after decarburization. Intra-lot uniformity was considerably better for lots 1 and 4. Cation content also has an effect. The data for five different lots of decarburized Ag-containing powders had a range of 15°C, but part of this variation is caused by differences in the two values for lot 3. This decarburization procedure produces material with a carbon content of 500 to 700 ppm.

The results on melting behavior helped in identifying the source of a problem encountered with Bi-2212/Ag PIT conductors. Before processing, these tapes, which contained decarburized powder from lot 5, were heat treated in vacuum for 2 d at 650°C. This treatment decomposed some 2201 into Bi₆Ca₄O₁₃ but did not prevent blistering during subsequent processing. Heating samples to increasing temperatures showed that the blisters began to form at ~800°C. Powder samples were removed from the Ag sheath and DTA/TGA data were obtained in O₂ at temperatures up to 900°C. These results showed that the onset of melting fell between two values shown in Table 1.1. The samples also experienced a

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Table 1.1. Endotherm temperatures for Bi-2212 powders^a

Powder lot number	Composition (Bi,Sr,Ca,Cu)	Silver (Y/N)	As received (°C)	Remarks	After 750/835°C Oxygen treatment (°C)
1	2.2212	N	883	Average for three runs	884
1	2.2212	N	881	Sample sent to ORNL later	882
2	2.2212	N	883		884
ORNL-Pyrolysis	2212	N	866		868
3	2.2212	Y ^b	854, 883	Average for two runs	864
3	2.2212	Y ^b	867	Sample sent to ORNL later	875
4	2.2212	Y ^b	860, 889	Average, four samples from different locations in lot	868
5	2.2212	Y ^b	878	Confirmed by XRD on two quenched samples	865
6	2.1211.9	Y ^b	846		860
7	2.2211.9	Y ^b	850		861
ORNL-Pyrolysis	2212	Y	848	5 wt % Ag ₂ O	

^aAll data taken in air, using MgO crucibles and heating at 10°C/min. Small (5°) corrections made for apparatus shifts as indicated by BaCO₃ runs.

^bNominally 2212.0.1 Ag.

weight loss of about 0.4% between 700 and 810°. Because the small sample decarburized for the melting study did not lose weight in this temperature range, inadequate decarburization and CO₂ release was suggested. This was confirmed by making measurements in another DTA/TGA that has an attached mass spectrometer. The CO₂ content of the gas phase reached a maximum at ~800°C.

Dip-coated Bi-2212/silver conductors are also being developed for high-field applications. The conductors contain two layers of superconductor and three layers of silver. The Bi-2212 layers are directly exposed at an edge and this is required because the dip-coating process leaves residual organics in the superconductor layers. The residual organics are removed by oxidation at ~350°C. Experience

has shown that removing the organics from coils causes property degradation that is not observed with single conductors. Some coils, heated to temperatures as low as 800°C, showed evidence of extensive melting.

The most obvious difference between a coil and a single conductor is that oxygen can reach the Bi-2212 in the single conductor both through the exposed edge and by diffusion through the outer silver layers. In a tightly wound coil the silver layer route is largely eliminated. To investigate the behavior in a low-oxygen environment, a Bi-2212/organic mixture was exposed to flowing CO₂ in the DTA/TGA apparatus. A thermal event was noted at ~400°C, and the runs were terminated at 840°C. Post-test examination showed that the samples had melted, and XRD revealed that the Bi-2212

had completely decomposed. The decomposition products included elemental Bi and Cu, indicating that the decomposition involved reduction.

This experiment suggested that with a limited supply of oxygen, oxidation of the organics produces some CO, which in turn reduces Bi and Cu to the elemental state. The melting could then be attributed to eutectic formation; the Bi-Ag and Bi-Cu eutectics form at 262°C and 270°C, respectively.

Two methods for avoiding this problem were investigated. Slowly heating samples to 400°C in vacuum removed the organics, and after a second 400°C cycle in air, XRD showed that the product was phase pure Bi-2212. Oxidation at 250°C also removed all of the organics and a lower-temperature oxidation would avoid eutectic formation.

LOCAL TEXTURE, CURRENT FLOW, AND SUPERCONDUCTIVE TRANSPORT PROPERTIES OF TI-1223 DEPOSITS ON PRACTICAL SUBSTRATES

In FY 1996, we extended quantitative investigations of the crystal grain orientations and electrical transport properties of HTS $\text{TiBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ (Ti-1223) deposits on polycrystalline substrates. The results confirm that in these systems current flow comprises percolative networks of strongly coupled material. In the following we describe how superconductive transport properties on different samples, on the same samples at different widths, and on samples with artificially induced strong flux pinning defects confirm the nature of current flow.

It has been demonstrated that Ti-1223 thick films can be synthesized by nitrate-spray pyrolysis of $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ precursors on polycrystalline YSZ or silver, followed by Ti-vapor-phase reaction in a two-zone furnace. These deposits can yield Ti-1223 with J_c s that exhibit strong behavior in magnetic fields,

similar to those of high- J_c epitaxial thin films but with an overall reduced magnitude. The thick films have c -axis texture with (00 ℓ) X-ray rocking curve FWHM of less than 2° but show no long-range in-plane texture using large-area XRD. However, microstructural grain-orientation mapping using electron beam backscattering patterns (EBSP) and X-ray microdiffraction has revealed the presence of local in-plane grain alignment extending over grain colonies of dimensions from 100 μm to 1 mm. These observations have suggested that current transport occurs through a network of percolative paths across adjacent colony boundaries. These paths select the low-angle grain boundaries of the overlapping grain orientation distributions of neighboring colonies.

This type of conduction mechanism should lead to transport properties that are characterized by parallel paths of weak-linked and well-coupled material. In substantial magnetic fields the weak-linked component is quenched, and the properties take on field dependencies that are characteristic of strong material occupying an overall reduced volume fraction. The following experimental results support this view and provide motivation for further development of Ti-1223 thick deposits for conductor applications.

In this work, precursors were deposited on polished polycrystalline YSZ substrates by aerosol spray pyrolysis of nitrate solutions with cation content $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{Ag}_{0.37}$. Typical thicknesses are 3 μm . Ti-1223 is formed by reaction of the precursor films with oxygen/ Ti_2O vapor in a two-zone furnace, with the sample zone maintained at 860°C and the Ti_2O_3 source zone at ~740°C. Reaction times are typically ~1 h, although the reaction occurs very rapidly (within 20 min). Electrical transport measurements were made on short samples (approximately 15 mm long and 8 mm wide). Electrical contact to the Ti-1223 surface was provided by sputtered gold pads. For studies of sample dimension effects, the samples were photolithographically patterned to 3-mm-long

bridges of widths down to $\sim 80 \mu\text{m}$. Measurements of J_c were conducted in fields to 8 T, and J_c was defined at a criterion of $1 \mu\text{V}/\text{cm}$.

Figure 1.21 illustrates the dependence of the transport J_c on magnetic fields oriented parallel to the c axis at 77 K. Data are shown for different Tl-1223/YSZ samples: (1) for two fully epitaxial thin films grown on single crystal LaAlO_3 substrates and (2) for one sample that has been patterned to progressively narrower widths (although the all widths remained large compared with the colony dimensions). The logarithmic scale illustrates the common dependence of J_c on magnetic field; the data in field are similar aside from a multiplicative factor, even among different samples and despite large differences in absolute values. This observation is consistent with current flow occurring in a well-coupled component that occupies a reduced geometrical fraction of the sample. By regarding the epitaxial films with

Fig. 1.21. Field dependence of J_c at 77 K for different Tl-1223 samples and for a sample of different widths. The epitaxial films, deposited on single crystal LaAlO_3 , are $\sim 1 \mu\text{m}$ thick and represents a fully connected benchmarks. The inset shows the same data, with J_c scaled by appropriate multiplicative factors.

$J_c(H=0) > 1 \text{ MA}/\text{cm}^2$ as fully connected benchmarks, one may infer that only 5 to 10% of the Tl-1223/YSZ material is active in a magnetic field, and for that component the $J_c(H)$ characteristics are nearly identical among all samples.

Further confirmation of the strongly coupled, percolative-path model of current flow is provided by the effects of artificially induced flux pinning defects. In previous work, we found that Tl-1223/YSZ samples irradiated parallel to the c axis with energetic heavy ions showed substantial increases in J_c and the irreversibility fields. In this case, it is reasonable that the effects arise from the columnar-defect-induced flux pinning in the well-coupled component and that this component is responsible for virtually all the loss-free current flow in substantial magnetic fields (we know of no mechanism whereby damage will raise the tunneling currents through weak-linked grain boundaries).

An additional test of this current-path model, we investigated the dependence of the apparent J_c on lateral sample dimensions. This effect arises because well-coupled current-path options over long lengths are statistically restricted if sample widths become comparable to or smaller than the colony size. A quantitative analysis of this phenomenon has been conducted through both experiment and numerical modeling. In the former case, the transport $J_c(H)$ s of two Tl-1223/YSZ samples were measured as the samples were patterned to progressively narrower bridge widths, ranging from 8 mm to $75 \mu\text{m}$. The numerical modeling was based on a limiting-current-path analysis applied to the actual colony orientation distribution of one of the samples, measured by X-ray microdiffraction using a $100\text{-}\mu\text{m}$ -diam beam. Current transfer between adjacent colonies was calculated from the observed dependence of J_c on grain misorientation as determined in the epitaxial bicrystal film experiments of Nabatame et al.¹ The model describes the effect as essentially a two-dimensional phenomenon, where c -axis currents

are assumed to be negligible, in contrast to the view of the "brick-wall" model. Figure 1.22 illustrates the ratio of observed J_c to intra-grain J_c for different sample widths, compared with the numerical predictions at zero applied field. The measurements show qualitative agreement but fall somewhat below the numerical predictions. This effect might be explained by the relatively large size of the X-ray beam (comparable to some grain colony dimensions), which may overestimate the intra-colony J_c values within small colonies having a relatively large distribution of grain orientations.

In addition to the decline of J_c at narrow widths, its overall field dependence and the accompanying current-voltage characteristics become qualitatively different. The latter is demonstrated in Fig. 1.23, where the field dependence at 77 K of electric field E on current density J is compared for examples in the two width regimes: $w = 4 \text{ mm} > \text{colony size}$, and $w = 0.2 \text{ mm} \lesssim \text{colony size}$. For the case

Fig. 1.22. The dependence of the apparent J_c on the width of two TI-1223/YSZ samples. The solid curve is a numerical calculation based on a limiting path model of current flow across basal plane tilt boundaries. The calculation assumes a fully connected $J_c = 1 \text{ MA/cm}^2$, consistent with the observed values of epitaxial films.

$w = 4 \text{ mm}$, the $E(J)$ relations are qualitatively similar to those of the epitaxial film (negative curvature and power law at low fields, evolving toward the resistive thermally activated flux flow regime at high fields). For the case $w = 0.2 \text{ mm}$ at low and moderate fields the curves exhibit a constant linear differential resistance as dissipation sets in at currents just above the (low) J_c values. At high fields, the behavior again follows that of intra-grain dissipation. Both these observations are consistent with a picture of parallel conductive channels, one being a well-coupled component and the other being a grain-boundary-limited, weak-link channel. The differences in the overall character of Figs. 1.23(a) and (b) are simply determined by the relative fraction of each component. In Fig. 1.23(b), the dashed line

Fig. 1.23. Dependence of electric field on current density for two sample width regimes. (a) $w = 4 \text{ mm} > \text{grain colony size}$; (b) $w = 0.2 \text{ mm} \lesssim \text{colony size}$.

represents a dominant weak component having a volume resistivity of $\sim 8 \times 10^{-9} \Omega \cdot \text{cm}$.

We have shown that the transport properties of Tl-1223 thick deposits are consistent with the observed grain orientations of the as-formed material on smooth, polycrystalline YSZ surfaces. (Recently, these observations have been extended to Tl-1223 deposits on polycrystalline silver.) The growth characteristics, which produce *c*-axis perpendicular deposits, with large colonies of grains having low-angle in-plane grain boundaries, are necessary for well-coupled current paths. Studies of the dependence of $J_c(H)$ and of the voltage-current characteristics on lateral sample dimensions uphold a picture of percolative, well-coupled current paths through a fraction of the overall sample volume. Although existing J_c values are not high enough to provide practical conductor current levels, large improvements could occur through improved processing for enhanced colony formation, or the epitaxial growth of Tl-1223 on biaxially oriented tapes. These results provide motivation for the further development of Tl-1223 thick deposits for conductor applications.

Reference

1. T. Nabatame et al., *Appl. Phys. Lett.* **65**, 776 (1994).

GROWTH OF $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ SUPERCONDUCTING FILMS WITH LOCAL BIAXIAL ALIGNMENT EXTENDING UP TO 5 MM ON SILVER SUBSTRATES USING A SPRAY PYROLYSIS TECHNIQUE

For the development of long conductors required for high-current electric-power transmission lines, considerable progress has been made using bismuth-based HTS materials through PIT processing. At the same time, the PIT tapes based on $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y-123) and $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ (Tl-1223) superconductors were

usually randomly oriented and characteristically weak-linked. However, recent developments in deposited conductors based on Y-123 and Tl-1223 materials are very promising. For example, the measured J_c of 3- μm -thick Tl-1223 films on polycrystalline YSZ substrates were $3.3 \times 10^5 \text{ A/cm}^2$ at 77 K and zero field, and $>10^4 \text{ A/cm}^2$ at 60 K and 1 T with the magnetic field applied parallel to the *c* axis.^{1,2} Also, a high J_c of more than $1 \times 10^6 \text{ A/cm}^2$ at 75 K and zero field was obtained on 1- μm -thick Y-123 films on Ni-based alloys with IBAD-grown textured YSZ buffer layers.³ Similarly, a high J_c of more than $3.0 \times 10^5 \text{ A/cm}^2$ at 77 K and zero field was recently demonstrated on $>1\text{-}\mu\text{m}$ -thick films on RABiTS samples coated with biaxially textured Pd, CeO_2 , and YSZ buffer layers.⁴ High-quality 1- μm -thick $(\text{Tl,Bi})(\text{Sr}_{1.6}\text{Ba}_{0.4})\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ films were also grown on LaAlO_3 (100) single crystal substrates.⁵ Based on these properties, $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ or $(\text{Tl,M})(\text{Sr}_{1.6}\text{Ba}_{0.4})\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ ($\text{M} = \text{Bi,Pb}$) (both compositions are referred to as Tl-1223) superconductors may have great technological importance for applications over 40 K whereas Y-123 deposited conductors may even be useful at 77 K. However, there is a need for making highly aligned materials because high J_c values with good in-field properties were mostly observed on aligned materials. Hence, we initiated our work on the processing of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ films on metallic substrates using open geometry through a two-step process. In the first step, Tl-free precursor films were deposited by a spray-pyrolysis technique followed by thallination in a two-zone furnace. The spray-pyrolysis equipment is relatively easy to build, and high-density precursor films can be deposited easily. Deposition of high-density deposits is one of the important requirements for making Tl conductors. In this paper, we report our successful development of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ thick films using the spray-pyrolysis technique on Ag substrates. We have grown Tl-1223 films with local biaxial alignment up to 5 mm in the plane of the film on smooth Ag substrates.

Experimental Procedure

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 Ag substrates using the spray pyrolysis technique. The addition of $\text{Ag}_{0.37}$ (5 at. wt %) aided the liquid-phase formation of the Tl-1223 phase. The Ag substrates were either used as received or were obtained by cold-rolling. The typical size of the Ag substrates was 5-mm wide and 1-in. long. Some of the substrates were mechanically polished on a Vibromet 2 using a felt polishing cloth and 0.5- μm grit size diamond paste. The precursor spray solution of Ba, Ca, Cu, and Ag nitrates with a stoichiometry of Ba:Ca:Cu:Ag = 2:2:3:0.37 (5 at. wt % Ag in fully reacted powder) and a molarity of 0.18 based on total cation concentration was prepared by dissolving BaCO_3 , CaCO_3 , CuO and AgNO_3 in conc. HNO_3 and distilled water. The pH of the solution was approximately 1. The spray pyrolysis apparatus was contained in a Plexiglas glove box maintained at ~ 1 atm pressure in a constant flow of dry air. About 10 mL of the spray solution was taken in a glass syringe fitted with a Teflon plunger and a stainless steel needle. Teflon tubing was used to connect the syringe with a stainless steel/Ti ultrasonic spray nozzle. This nozzle was operated at 120 kHz and produced droplets of a median diameter of 18 μm . The nozzle was mounted on a uniaxial translation table that was operated in a bidirectional mode. Substrates were mounted on an Inconel heater block that could heat substrates up to 700°C. The distance between the substrate and the nozzle tip was approximately 1 cm. The temperature of the substrate, the atomization rate of the nozzle, and the travel rate of the nozzle over the substrate were controlled by a computer. The Ag substrates were mounted on the substrate heater block, which was initially maintained at 180°C. After the first coat, the substrate was heated up to 600°C to pyrolyze the film, and was held at 600°C for 5 min and then cooled to 275°C. The lower temperature of 180°C was used for the first coat to increase the

wetting of the film to the substrate. After the second coat at 275°C, the substrate was again heated to 600°C and held at 600°C for 5 min and then cooled back to 275°C. This procedure was repeated until the desired film thickness of ~ 3 μm was obtained. The total deposition time was less than 30 min. During each coat, a 0.75- μm -thick film was deposited. The samples were then transferred into a tube furnace with flowing oxygen. The films were rapidly heated to 500°C at the rate of 200°C/min and then heated to 850°C at the rate of 12°C/min. At that point, the furnace was turned off and the samples were cooled to room temperature under flowing oxygen. The precursor films obtained were smooth and continuous. The powder XRD of the precursor film showed the presence of BaCuO_2 , CaO , and CuO .

Thallination of the precursor films was carried out using a two-zone thallination furnace, composed of a zone containing a Tl source (mostly Tl_2O_3 in a gold boat) and a sample zone in a flowing oxygen atmosphere, similar to that described by DeLuca et al.^{1,2} The sample-zone temperature was raised to 860°C while the source-zone temperature was raised to 600°C. After the sample temperature stabilized at 860°C, the source temperature was increased to a temperature between 725 and 730°C and was maintained at that temperature for 30 min. The partial pressure of thallous oxide (Tl_2O) was calculated to be 1.1×10^{-3} atm at a Tl source temperature of 727°C in 1 atm oxygen. The furnace was then turned off and allowed to cool for a 3- to 4-h period with flowing oxygen. Quenching studies on similar samples have shown that the Tl-1223 phase grows from the substrate through a transient melting. The average thallium uptake was between 0.6 to 0.8 (relative to 1223), as determined from the weight gain of the sample. Previous studies have shown that a slight thallium deficiency is required to form single-phase Tl-1223.^{1,2} The resulting $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{7-y}$ films were black and highly reflective. The film thickness was varied between 1 and 3 μm .

The films were analyzed by detailed XRD studies. A Philips Model XRG3100 diffractometer with Cu K_α radiation was used to record the powder diffraction pattern. A Rigaku rotating anode X-ray generator was used for ω and ϕ scans, with a graphite monochromator selecting Cu K_α radiation, and slits defining a 2×2 mm incident beam. A four-circle diffractometer was used to orient the [001] textured film for diffraction from (1 0 14) planes. Rotating ϕ analyzes the in-plane alignment of the film. A 1×1 mm beam was used to map local alignment, as described earlier.⁶ The films were further characterized by resistivity and transport J_c measurements using a conventional four-probe technique. Either four spring-loaded pin contacts or four Ag wire contacts were made on top of the film. The current leads were on the ends, and the voltage leads were across the sample with a 0.5-cm separation. Values of transport J_c were calculated using a $1 \mu\text{V}/\text{cm}$ criterion. For resistivity measurements, a constant current of 40 mA was used, and the temperature was varied using a closed-cycle He refrigerator. For J_c measurements, the sample was slowly inserted into a liquid nitrogen container, which was positioned inside a magnet capable of producing a maximum field of 0.6 T. The magnetic field was applied perpendicular to the plane of the substrate.

Fig. 1.24. Room-temperature powder XRD pattern for a 1- μm -thick $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ film grown on a typical Ag substrate. The film shows preferential alignment along the c axis.

Results and Discussion

A typical room-temperature powder XRD pattern for a 1- μm -thick $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ film formed on a Ag substrate is shown in Fig. 1.24. The diffraction pattern is characteristic of a predominantly c -axis-oriented Tl-1223 film. The addition of 5 at. wt % Ag in the precursor yielded a transient liquid phase in the presence of thallous oxide. The Tl-1223 phase has been shown to grow from the substrate up.⁷ The smooth Ag substrate apparently influenced the nucleation and/or kinetics of the Tl-1223 phase development. Atomic force microscope images taken on both smooth (polished) and rough (as-received or cold-rolled) Ag substrates were analyzed. The rough Ag had both smooth surfaces and large scratches along the rolling direction. The average surface roughness for the rough Ag is about 6 nm. The surface after polishing showed few irregularities, but a much smoother aspect (mirror-like finish) than for the rough Ag. The average surface roughness for the smooth Ag is about 2 nm. The Ag substrate had a (421) $\langle 210 \rangle$ biaxial texture. The rocking curves (ω scan) for 1- μm - and 3- μm -thick $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ films grown on smooth and rough Ag substrates, respectively, are shown in Fig. 1.25. The FWHM values for the (0010)

Fig. 1.25. Rocking curves for 1- and 3- μm -thick $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ films grown on both smooth and rough Ag substrates, respectively, for a (0010) c -axis orientation.

c-axis peaks are 1.9° and 13° for Tl-1223 films grown on both smooth and rough Ag substrates. This clearly demonstrates that the smooth surface morphology is necessary for the substrates to achieve appreciable texture in the superconducting films. Thus, the substrate roughness dictates the nature of the films grown on it. The single ϕ scan of the (1 0 14) reflection for a 1- μ m-thick $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ film grown on a smooth Ag substrate is shown in Fig. 1.26. Also, a ϕ -scan contour map of the (1 0 14) reflection along the length of the film using a beam size of 1×1 mm is shown in Fig. 1.27. These results indicate the high degree of local in-plane alignment in the film for distances up to 5 mm. The colony microstructure was proposed earlier to explain similar features of local biaxial texture (the presence of small-angle boundaries) of Tl-1223 films with high current densities on polycrystalline YSZ substrates.^{7,8}

Typical resistive transitions were fairly sharp for Tl-1223 films grown on both smooth and rough Ag substrates. The critical temperature (T_c), varied between 106 and 110 K.

Fig. 1.26. XRD ϕ scan of the (1 0 14) reflection for a 1- μ m-thick $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ film grown on a smooth Ag substrate. The film shows preferential in-plane alignment.

The magnetic field dependence of the J_c for 1- and 3- μ m-thick $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ films grown on smooth and rough Ag substrates, respectively, are shown in Fig. 1.28. The J_c values were 64,700 A/cm² and 37,200 A/cm² at 77 K and zero field for films grown on smooth and rough Ag substrates, respectively. For the film on the smooth Ag substrate, the J_c was measured within a single colony. At 0.5 T and 77 K, with the magnetic field applied perpendicular to the substrate, the J_c values were 9,500 A/cm² and 3,200 A/cm² for films grown on smooth and rough Ag substrates. This in-field behavior clearly shows the presence of high-quality Tl-1223 films on smooth Ag substrates. A typical SEM micrograph of a textured $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ film grown on a smooth Ag substrate is shown in Fig. 1.29. This platelike morphology is similar to those observed previously for films grown on polycrystalline YSZ substrates.²

To conclude, we have demonstrated that $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ thick films grown on smooth Ag substrates by a spray-pyrolysis technique followed by thallination in a two-zone furnace had local biaxial alignment up to 5 mm in the

Fig. 1.27. XRD ϕ scans of the (1 0 14) reflection along the length of the $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ films grown on a smooth Ag substrate using a beam size of 1×1 mm. The film shows local in-plane alignment up to 5 mm.

Fig. 1.28. The in-field dependence of J_c for $H \parallel c$ orientation of 1- and 3- μm -thick $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ films grown on smooth and rough Ag substrates, respectively, at 77 K.

Fig. 1.29. Typical SEM micrograph showing the platelike morphology of the textured $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ films grown on Ag substrates.

plane of the film. High J_c values with good in-field properties were obtained for these films. It is not clear whether large colonies are

desirable from a J_c standpoint; however, the surface morphology of the Ag substrates appears to strongly influence the texture development in the Tl-1223 films.

References

1. J. A. DeLuca et al., *Physica C* **205**, 21 (1993).
2. J. A. DeLuca et al., p. 231 in *Processing of Long Lengths of Superconductors*, ed. by U. Balachandran, E. W. Collings, and A. Goyal, the Minerals, Metals & Materials Society, 1994.
3. X. D. Wu et al., *Appl. Phys. Lett.* **67**, 2397 (1995).
4. A. Goyal et al., *Appl. Phys. Lett.* **69**, 1795 (1996).
5. Z. F. Ren, C. A. Wang, and J. H. Wang, *Appl. Phys. Lett.* **65**, 237 (1994).
6. E. D. Specht et al., *Physica C* **226**, 76 (1994).
7. A. Goyal et al., *Appl. Phys. Lett.* **67**, 2563 (1995).
8. D. M. Kroeger and A. Goyal, *J. of Metals*, **46**, 14 (1994) and references therein.

EFFECT OF Mg-DOPING ON THE PROCESSING AND CURRENT CAPACITY OF Bi-2223 POWDER-IN-TUBE CONDUCTORS

Since the discovery of HTS, extensive research effort has been devoted toward the development of practical HTS conductors. To date, PIT $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Bi-2223) tape is one of only two proven HTS conductors that can be fabricated in long lengths. Unfortunately, even though these PIT tapes can be utilized at 77 K under self-field condition, the HTS becomes nonsuperconducting in the presence of a moderate magnetic field (0.5 T). Therefore, to expand the range of applications of these tapes, ways need to be developed to improved flux pinning in these materials.

It has been shown in the melt-textured $Y_1Ba_2Cu_3O_7$ HTS system that flux pinning can be enhanced through the incorporation of inclusions.¹ Even though the exact mechanism of flux pinning in this HTS is still unclear, it is generally accepted that the size of the inclusions must be submicron and that the dislocation density should be high. Because of the similarities between various HTS cuprates, the same beneficial effects should also be found in the Bi-2223 HTS as long as the inclusions do not react adversely with the compound. We reported last year on our effort in the investigation of Mg doping of Bi-2223 aerosol precursor powders. The initial study revealed that in sintered Bi-2223 with Mg doping, MgO particles of 50 to 200 nm were homogeneously distributed throughout the sintered HTS. In addition, the HTS/MgO interfacial regions contain a high density of dislocations, which is favorable for enhancement in flux pinning. Moreover, ac susceptibility measurements showed that there is little or no degradation in the superconducting transition temperature for up to about 10% of MgO doping.

Although no degradation was measured, energy-dispersive spectroscopy (EDS) results showed that the MgO particles contain a small amount of copper. This indicates that unless the dissolved Cu is compensated for, a possibility of degradation exists in the superconducting properties as a result of the tendency to form low-copper-content secondary phases rather than the HTS Bi-2223 phase. In this study, aerosol precursor powders with various degrees of Cu compensation were prepared, and PIT Mg-doped Bi-2223 conductors were fabricated. We will report on the effect of Mg-doping on PIT processing parameters and current capacity. In addition, the microstructure and inhomogeneous MgO distribution within the conductor are presented, and potential solutions to this problem are discussed.

Experimental

Aerosol precursors of 5 vol. % Mg-doped Bi-2223 ($Mg_{0.77}$) with various amount of Cu compensation were prepared and are listed in Table 1.2. These powders were packed into Ag tubes, which were then swaged and drawn into wires of about 1 mm overall diameter. Following the initial drawing process, these wires were rolled by smooth rolls to about 200 μ m overall thickness at 6 μ m reduction per pass. After initial deformation, the monofilamentary tapes were subjected to the following thermomechanical treatment: HT1 = 12 h, P1, HT2 = 12 h, P2, HT3 = 26 h, P3, HT4 = 50 h with heat treatments (HT) carried out at 810, 818, 825, and 832°C in 7.5% oxygen—92.5% argon, and pressing (P) performed at 1.5 GPa between polished steel platens with 5-min holding time. Critical current density measurements were performed on fully processed tapes using the 1- μ V/cm criterion. After the J_c measurements, longitudinal cross sections of selected tapes were polished and were examined by SEM.

Results and Discussion

Variations in J_c with processing temperature of undoped and Mg-doped Bi-2223 with various amount of Cu compensation are shown in Figs. 1.30 through 1.33. It can be seen from

Table 1.2. Amount of Mg-doping and Cu-compensation in the $Bi_2Sr_2Ca_2Cu_xMg_yO_y$ aerosol precursor powders examined in this study

Sample	Composition	Cu (x)	Mg (y)
EX46	Nominal ICP	—	—
EX47	Nominal ICP	3.15 3.07	0.77 0.59
EX48	Nominal ICP	3.20 3.10	0.77 0.75
EX47	Nominal ICP	3.30 3.12	0.77 0.74

Fig. 1.30. Variation in J_c with processing temperature of undoped (EX46) PIT Bi-2223 conductors.

Fig. 1.32. Variation in J_c with processing temperature of Mg-doped (EX48) PIT Bi-2223 conductors.

Fig. 1.31. Variation in J_c with processing temperature of Mg-doped (EX47) PIT Bi-2223 conductors.

Fig. 1.33. Variation in J_c with processing temperature of Mg-doped (EX49) PIT Bi-2223 conductors.

Fig. 1.30 that the J_c of undoped Bi-2223 conductors (EX46) initially increases with sintering temperature (T_s), reaching a maximum value of 27,100 A/cm² at $T_s = 825^\circ\text{C}$, and decreases as the sintering temperature is further increased. Both the existence of an optimum processing temperature and the value of this temperature under a 7.5% oxygen processing atmosphere are in excellent agreement with previous studies. On the other hand, Figs. 1.31, 1.32, and 1.33 show that the J_c of Mg-doped Bi-2223 conductors increase monotonically with

processing temperature, and the optimum processing temperature has not been reached at T_s of 832°C . This increase in processing temperature is analogous to that of Bi-2212 with MgO inclusions, where studies^{2,3} have shown that the optimum processing temperature was increased by 10 to 20°C . The maximum J_c attained by Mg-doped Bi-2223 conductors (EX48) investigated in this study is 28,200 A/cm², a value that is only slightly higher than that of the undoped conductor. Unfortunately, the PIT tapes were exhausted and

Fig. 1.34. Comparison of I_c field dependency of undoped and Mg-doped PIT Bi-2223 conductors.

processing could not be performed at higher temperature to determine the optimum sintering temperature of Mg-doped conductors.

Figure 1.34 shows the magnetic field dependency of I_c of undoped (EX46, 27,100 A/cm²) and Mg-doped (EX48, 28,200 A/cm²) conductors with similar J_c . It can be seen from the normalized I_c comparison that flux pinning has not improved in the Mg-doped PIT. This lack of pinning enhancement may be caused by a number of factors, such as lower T_c , excessive MgO particle size, insufficient doping, or inhomogeneous distribution of MgO inclusions. Transport resistivity measurements and detailed microstructural examination were performed to determine the reason for the lack of flux pinning improvement. Figure 1.35 shows the variations in normalized resistance of undoped and Mg-doped PIT conductors; both the onset and zero-resistance transition temperatures of the two tapes are identical, and the lack of pinning enhancement is not caused by a lowering of T_c through Mg doping.

Figure 1.36 shows a SEM image of the interior of a Mg-doped PIT conductor; the MgO inclusions are less than 1 μ m in diameter with a mean separation distance of about 600 nm. Although the question as to whether sufficient doping is available for pinning cannot be answered, the figure shows that submicron

Fig. 1.35. Variations in normalized resistance of undoped and Mg-doped PIT Bi-2223 conductors.

Fig. 1.36. SEM image of the interior of the HTS core of Mg-doped PIT Bi-2223 conductor.

particles are present within the HTS core, which should provide a high density of dislocation for pinning. On the other hand, detailed examination of the HTS/Ag-sheath interfacial areas revealed that MgO particles are rarely

Fig. 1.37. Bi-2223/Ag sheath interfacial region of Mg-doped PIT conductor. Note the lack of MgO inclusions at the interfacial area.

seen within 4 μm of the interface (Fig. 1.37). Numerous reports have shown that the bulk of the supercurrent in Bi-2223 PIT conductors is typically transported via this well-aligned interfacial region. If this is the case, then the lack of MgO particles within this well-aligned region can certainly lead to zero flux pinning enhancement in the Mg-doped PIT conductors.

The observation that no MgO particle is incorporated within the growing Bi-2223 grains from the HTS/Ag-sheath interface has significant implication in the effort of flux pinning enhancement of Bi-2223 PIT conductors. That is, other types of dopants in the form of inclusions may also be pushed away from the well-aligned interfacial region. The problem of particle pushing has been studied during the solidification of simple systems.⁴⁻⁶ Whether the particles are entrapped within a growing matrix or are simply pushed along the growth front has been shown to depend on the critical velocity of the system, which in turn is affected by numerous factors. Among these are

particle size, interfacial energies, liquid viscosity, relative densities, interface curvature, and thermal conductivity. For example, particle entrapment is favored if the particle size is increased. This, however, is contrary to what is required for pinning enhancement in HTS (i.e., the inclusions have to be as small as possible). Other dominant parameters such as liquid viscosity and interfacial energies may be altered by critically adjusting the characteristics of the liquid phase. One possibility is to dope the precursor powder with Ag, which may alter the viscosity of the liquid as well as provide an abundance of liquid throughout the bulk of the HTS core. Another possibility is by drastically reducing the HTS core thickness such that the liquid phase is not confined to the HTS/Ag-sheath interface but is available throughout the entire core.

Preliminary work on these two potential solutions has been initiated at ORNL. Aerosol precursor powder with 10% Mg and 5% Ag doping was prepared, and was enclosed within a Ag foil in the form of a "folded" tape. In addition, PIT Bi-2223 with 5% Mg doping was carefully rolled to an overall tape thickness of 60 μm . These two tapes were subjected to the following thermomechanical treatment: HT1 = 12 h, P1, HT2 = 88 h with heat treatments (HT) carried out at 837°C in air, and pressing (P) performed between polished steel platens with 5-min holding time (0.2 GPa for folded tape and 1 GPa for PIT tape). Polished longitudinal cross sections of the folded tape with Mg and Ag doping were examined by SEM. Silver inclusions with a particle size of about 1 μm were found to be distributed throughout the HTS core. More importantly, MgO particles could be seen at or near the HTS/Ag-sheath interface (Fig. 1.38). Similarly, MgO particles can be found near the HTS/Ag sheath interface in the PIT with reduced core thickness. Figure 1.39 shows the SEM image of the fracture surface of a peeled PIT tape. This Bi-2223 fracture surface represents a 30° tilted plan view of the HTS roughly 0.2 to 0.5 μm

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Fig. 1.38. Bi-2223/Ag sheath interfacial region of Mg- and Ag-doped Bi-2223 sample. MgO particles can routinely be seen at the interface.

from the HTS/Ag sheath interface. A sizable number of MgO particles ($<0.5 \mu\text{m}$) were found to be embedded within the well-aligned Bi-2223 grains, whereas the holes are believed to be prior locations of MgO particles that were torn away during tape peeling. From these preliminary results, it appears that the problem of lack of MgO particles at the well-aligned HTS/Ag sheath region may be circumvented by a combination of Ag doping and/or fabricating fine-filament PITs (such as that found in multifilamentary conductors). Effort is now under way to fabricate Mg- and Ag-doped fine-filament PITs to examine the microstructural and superconducting characteristics.

References

1. D. F. Lee et al. *Physica C* **202**, 83 (1992).
2. W. Wei et al. *Appl. Supercond. Conf.—IEEE Trans. Supercond.*, to be published.
3. V. V. Lennikov et al., *MRS Spring Mtg.* San Francisco, 1996.

4. D. M. Stefanescu et al., *Met. Trans. A* **19**, 2847 (1988).

5. D. R. Uhlmann et al., *J. Appl. Phys.* **35**, 2986, (1964).

6. G. F. Bolling et al., *J. Crystal Growth* **10**, 56 (1971).

EFFECTS OF INITIAL COLD-WORK CONDITIONS ON THE DEFORMATION AND CURRENT CAPACITY OF MONOFILAMENTARY AND MULTIFILAMENTARY Bi-2223 CONDUCTORS

Among the various processing techniques used in HTS fabrication, the PIT method is currently one of the most promising for applications on an industrial scale. To obtain high J_c in PIT $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Bi-2223) conductors, the tapes have to be subjected to

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Fig. 1.39. Fracture surface of the Bi-2223/Ag sheath interfacial region of a tape that has been rolled to about $60 \mu\text{m}$ thick. MgO particles are embedded within the well-aligned Bi-2223 grains at the interfacial region.

repeated heating and deformation cycles (thermomechanical treatment). While many of the factors affecting the final superconducting properties of the conductors are still not clear, numerous experimental results have shown that thermomechanical treatment leads to the following important characteristics: (1) a high fraction of Bi-2223 phase, (2) a high degree of texture, and (3) a high final density of the HTS core.¹⁻⁵ Even though precise scheduling and mode of deformation utilized in the thermomechanical treatment are extremely important, there is now ample evidence that the final properties of the conductor depend on every fabrication step, from precursor powder selection^{3,6,7} to the cooling rate following the final heat treatment step.^{8,9}

Because final properties strongly depend on previous processing history, deformation conditions and the resultant characteristics of the precursor core even before the initiation of thermomechanical treatment can significantly influence the superconducting characteristics of fully processed Bi-2223 conductors. For example, although the J_c of a Bi-2223 PIT conductor increases with decreasing core thickness, work instability can occur when the initial reduction by cold rolling is large, leading to variations in core layer thickness (sausaging) and an abrupt decrease in J_c .¹⁰ In addition, studies have shown that with an increase in either the initial packing density^{11,12} or the core density by careful cold work,¹² both the final core density and J_c are enhanced. The final density of the tape, which has been shown to be intimately related to current-carrying capability,^{13,14} can be improved by initial deformation despite the occurrence of retrograde densification during heat treatment.

Typically, a Bi-2223 PIT conductor is fabricated by packing precursor powder into a silver tube, which is then swaged, drawn, and rolled at room temperature into tape form. Ideally, it is desirable for the powder-packed Ag tube to deform homogeneously through the various working stages into a tape with uniform

microstructure and properties. However, because of constraint factors such as tool-stock configuration or complexity of the stock shape, plastic deformation is typically inhomogeneous, leading to localized instability and flow that result in nonuniform tape characteristics. Friction has long been known to be one of the most important constraint factors in plastic deformation. An increase in working friction usually leads to effects such as inhomogeneous deformation, increased deformation resistance, and shearing stresses beneath the contact surfaces. Consequently, friction between the tools and the work piece will undoubtedly have a significant effect on the extent of deformation as well as the core homogeneity of PIT tapes. Moreover, the influences of working friction on the deformation of mono- and multifilamentary tapes are not expected to be identical because of the difference in core geometry. We have previously reported on the effects of friction and reduction per pass on the inhomogeneous deformation of mono- and multifilamentary PIT Bi-2223 tapes, and we have shown the existence of dead zones in the conductors. In this report, the current-carrying capability of fully processed tapes will be correlated with initial deformation conditions, and the implication of these conditions on the design and processing of PIT tapes will be discussed.

Experimental Details: Monofilamentary Tapes

In the fabrication of monofilamentary PIT tapes, two precursor powders having different Pb contents with the overall compositions of $\text{Bi}_{1.84}\text{Pb}_{0.32}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_x$ (powder A) and $\text{Bi}_{1.84}\text{Pb}_{0.42}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_x$ (powder B) were produced by an aerosol process. The detailed description of the aerosol process is given elsewhere.¹⁵ After treating these precursor powders at 700°C for 4 h in air to obtain the desired phases, the powders were packed into Ag tubes having a 6.25-mm outer diameter and a 0.75-mm wall thickness. Powder packing was

carried out in a dry box with the aid of a hand press, and the typical packing density was approximately 35% of theoretical. The openings of the Ag tubes were plugged and then closed by swaging, and the wires were drawn to 0.91 mm overall diameter at 50 to 100 μm reduction per pass.

The monofilamentary wires were initially rolled to 245 μm overall thickness at 6 μm reduction in thickness per pass (increasing from 0.7% to 2.4% per pass with successive reductions) using a 4-in.-diam rolling mill with an exit velocity of 25 mm/s. Following initial reduction, deformation by rolling under normal-friction (smooth rolls) and high-friction conditions (roughened rolls; a portion of the roll was roughened by grinding the roll faces with a 60-grit SiC paper) was carried out by deforming the two monofilamentary wires down to about 150 μm overall thickness, again at 6 μm per pass (increasing from 0.7% to 3.8% per pass with successive reductions) with an exit velocity of 25 mm/s (Table 1.3). Sections of the 150- μm -thick tapes were retained for thermomechanical treatment and J_c measurements while the remaining tapes were deformed down to a thickness of approximately 50 μm to detect the onset of work instability.

Experimental Details: Multifilamentary Tapes

The multifilamentary wire used in this investigation was fabricated at American Superconductor Corporation (ASC). The precursor powder was packed into Ag tubes, and the tubes were drawn into monofilamentary wires; 85 of these wires were packed into a Ag tube and then drawn to 1.3 mm diam. Sections of these wires were deformed to approximately 290 μm overall tape thickness between smooth (normal friction) and roughened (increased friction) rolls at 6 μm reduction per pass (increasing from 0.5% to 2.1% per pass with successive reductions). In addition to the different rolling surfaces, deformation was also performed at 20% reduction per pass so that the effect of strain rate on powder flow could be examined. The various deformation conditions of multifilamentary samples investigated in this study are summarized in Table 1.4.

To examine the evolution of precursor core microstructure, small sections were cut from the various mono- and multifilamentary tapes at different stages of rolling and were examined by optical microscopy. At the conclusion of the initial cold-rolling procedure, the overall thickness and width of individual tapes were

Table 1.3. Sample characteristics of monofilamentary Bi-2223 PIT tapes deformed initially by cold rolling

	Sample ID				
	Before	R-A-1,2	R-A-3,4	R-B-1	R-B-2,3
Rolling (rolls/ reduction per pass)	—	Smooth/6 μm	Roughened/6 μm	Smooth/6 μm	Roughened/6 μm
Thickness t (mm)	0.914	0.156	0.158	—	—
Width w (mm)	—	1.56	1.66	—	—
Δt (%)	0	-83.0	-82.7	—	—
Δw (%)	0	70.9	81.3	—	—
$-(\Delta w/\Delta t)$	—	0.85	0.99	—	—
Final $J_c \times 10^3$ (A/cm ²)	—	9.5	18.0	4.5	10.8

measured with the aid of an optical microscope equipped with micrometer-controlled x - y stage. These tapes were then subjected to thermomechanical treatment, and the J_c of each tape was determined at 77 K using the $1\text{-}\mu\text{V}/\text{cm}$ criterion.

Results and Discussion: Monofilamentary Tapes

In the FY 1995 annual report we showed that decreased friction under uniaxial pressing conditions resulted in crack initiation and propagation in monofilamentary tapes. The ideal case would be zero interface velocity for high-friction coefficient. However, as the friction coefficient between Ag sheath and loading fixtures decreases, the ductile Ag at the interface is free to flow. Consequently, the hard and brittle ceramic core of nonuniform density can flow inhomogeneously, and cracks appear perpendicular to the elongation direction at regions of lower density. Under increasing load, the cracks will continue to propagate until the Ag sheath is sheared between the high-density core sections, and any further spreading of the

tape is accomplished by widening of the cracks. In the case of rolling, we have shown that under normal smooth-rolling conditions, sausaging became noticeable when the core thickness was reduced to about $25\text{ }\mu\text{m}$. The appearance of sausaging has been explained by Osamura et al.¹⁰ in terms of work instability, and the core thickness where instability occurs as determined in this study is in excellent agreement with the results of those investigators. Furthermore, when lubrication was provided by a soap coating and there was not front or back tension, deformation of the precursor core was found to be extremely nonuniform and sausaging occurred at an earlier stage where the core thickness was still in excess of $50\text{ }\mu\text{m}$. As the tape thickness was reduced further, the degree of sausaging became progressively worse. In addition, transverse cracks started to appear in the Ag sheath, which corresponded to a periodic appearance of the core.

It appeared that an increase in deformation friction may provide an avenue toward a more homogeneous and denser core in monofilamentary tapes. This is in contrast to traditional rolling of metals and alloys, during

Table 1.4. Sample characteristics of 85-filament Bi-2223 PIT tapes deformed initially by cold rolling

	Sample ID				
	Before	R-C-1	R-C-2	R-C-3	R-C-4
Rolling (rolls/ reduction per pass)	—	Smooth/ $6\text{ }\mu\text{m}$	Smooth/20%	Roughend/ $6\text{ }\mu\text{m}$	Roughened/20%
Thickness t (mm)	1.280	0.288	0.288	0.309	0.282
Width w (mm)	—	2.16	2.37	2.16	2.27
Δt (%)	0	-77.5	-77.5	-75.9	-78.0
Δw (%)	0	68.8	85.2	68.8	77.3
$-(\Delta w/\Delta t)$	—	0.89	1.10	0.91	0.99
FF (before first HT)	—	22.9	17.7	20.2	18.5
FF (after final HT)	—	20.9	13.7	17.3	16.8
Final $J_c \times 10^3$ (A/cm ²)	—	10.3	17.5	11.8	14.7

which lubrication is employed to reduce the power requirement of the machinery and to facilitate metal flow under the action of the load. When the microstructures of the tapes initially deformed between roughened rolls were examined, neither the general appearance of the precursor cores nor the onset of work instability could be distinguished from those deformed between smooth rolls. The only geometrical difference that can be observed is in the greater amount of lateral spread experienced by the tapes deformed between roughened rolls. As seen in Table 1.3, the width of the tape containing powder A deformed between roughened rolls is larger than that of the smooth rolls even though the former tape is not yet as thin as the latter one, a situation which is consistent with an increase in rolling friction.¹⁶

Following initial deformation, the monofilamentary tapes were subjected to the following thermomechanical treatment: HT1 = 25 h, P1, HT2 = 25 h, P2, HT3 = 25 h, P3, HT4 = 50 h with heat treatments (HT) carried out at 825°C in 7.5% oxygen—92.5% argon, and pressing (P) performed at 1.5 Gpa between polished steel platens with a 5-min holding time. Pressing instead of rolling was selected in the thermomechanical treatment to minimize the occurrence of sausaging, which would have invalidated any correlation between initial deformation conditions and final superconducting properties. In addition to the difference in lateral spreading, J_c of the tapes deformed between smooth and roughened rolls were found to differ throughout the thermomechanical treatment. The variation in J_c with accumulated processing time for powders A and B are shown in Figs. 1.40 and 1.41, respectively. Regardless of the tape composition, the J_c s of the tapes that were initially deformed by roughened rolls are consistently higher than those processed by smooth rolling surfaces.

Fig. 1.40. Variation in J_c with total sintering time of monofilamentary Bi-2223 PIT tapes containing powder A initially deformed between smooth and roughened rolls.

Fig. 1.41. Variation in J_c with total sintering time of monofilamentary Bi-2223 PIT tapes containing powder B initially deformed between smooth and roughened rolls.

Results and Discussion: Multifilamentary Tapes

Transverse cross sections of the four sets of multifilamentary tapes at various stages of initial deformation were examined by optical microscopy; Fig. 1.42 shows the filament distribution when these tapes were reduced to a thickness of about 600 μm . It is fortunate that,

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Fig. 1.42. Optical micrographs of the transverse cross sections of multifilamentary Bi-2223 PIT tapes initially deformed by cold rolling to roughly 600 μm under the following conditions: (a) smooth rolls, 6 μm reduction per pass; (b) smooth rolls, 20% reduction per pass; (c) roughened rolls, 6 μm reduction per pass; and (d) roughened rolls, 20% reduction per pass (bar = 200 μm).

after wet polishing with Al_2O_3 and lapping oil, the degree of initial core densification in these non-heat treated multifilamentary tapes can be determined qualitatively: gray areas represent denser precursor material; black areas represent porous cores. This relative difference in powder density combined with individual core geometry provide a means to probe the internal deformation characteristics of Bi-2223 PIT tapes. The contrasts in Fig. 1.42 indicate that the mechanical deformation of these composite tapes is inhomogeneous. Moreover, the degree of inhomogeneity increases with friction (from smooth rolls to roughened rolls) and strain rate (from small to large reduction per pass). In fact, the deformation pattern of these tapes closely resembles that of the “dead metal zones,” or “dead zones” frequently encountered in metal forming. A cross-sectional schematic of the deformation pattern of a cylinder deformed in simple compression under high friction condition is shown in Fig. 1.43. Because of friction between the tools and the work piece, the material adjacent to these areas (region I) remains almost stationary. These dead metal zones undergo little or no deformation, and have been shown to increase in size with increasing friction, although material at the free surface (region III) deforms as a result of axial compression and

Fig. 1.43. Schematic of the transverse cross section of a metal cylinder deformed by simple compression at room temperature under high-friction condition. The cone-shaped dead zones at the top and bottom of the sample are separated from the deformed bulk by narrow regions of high deformation.

secondary hoop tension, resulting in a bulged surface. With increasing frictional constraint, the tensile strain becomes larger while the compressive strain decreases, resulting in increased bulge severity. The most severe deformation is concentrated in regions just outside the dead zones near each contact surface (region II) in the form of shear bands.¹⁷ These shear bands are initiated along the velocity discontinuities of the slip-line (zero-extension-direction) field and typically appear as two complementary bands forming an X-shaped region in the deforming sample.

In deformation by rolling, the main variables that control the process are (1) the friction between the rolls and the sample, (2) the roll diameter, (3) the deformation resistance of the sample, and (4) the presence of front and back tensions.¹⁶ The friction condition is particularly important because it varies with roll diameter, changes the flow stress by increasing the constraint factor, and determines the amount

of front or back tension needed for significant reduction in rolling load.¹⁸ In addition to affecting the other processing variables, friction is important in rolling because it pulls the metal into the rolls, and it influences the magnitude and distribution of the roll pressure. Typically, theoretical as well as experimental analyses of rolling deformation are concerned with the forces acting perpendicular to the rolled surfaces and along the rolling direction (i.e., a plane strain condition is assumed and lateral spreading is ignored). From those investigations, the presence of a friction hill in the rolling direction with its peak location corresponding to the neutral point has been well established.¹⁸ In particular, the friction hills that were developed by deformation between smooth and roughened rolls have been measured.¹⁹ From these results, it is now known that with roughened rolls, the rolling load will be greater, the roll face pressure will be higher, and the neutral point will move toward the entrance of the rolls.

Although deformation along the longitudinal direction is extremely important, different points of a rolled tape will be subjected to the same loading in this direction because these points have to pass through the identical friction-hill profile at various times. Consequently, techniques such as front or back tension can be employed to alter the roll pressure such that the onset of work instability can be delayed. The deformation pattern exhibited in the transverse cross sections of the multifilamentary tapes, however, clearly demonstrates that the plane strain assumption is incorrect in the case of PIT (finite width) rolling because deformation varies from filament to filament. We have already seen from Fig. 1.42 that as either the working friction or the strain rate is increased, areas of limited deformation (i.e., the dead zones) penetrate deeper toward the interior of the tape. Typically, the formation of these dead zones occurs early in the deformation process, and the dead zones tend to not deform at all until the overall reduction is sufficient to bring them into contact. Because

the amount of overall tape reduction is dictated by the roller gap, higher strain in the tapes is localized to within the central portion along the diagonals (region II in Fig. 1.43), and the extent of this flow localization becomes more severe with higher friction because of the larger dead zones. Figure 1.42 clearly shows that under the conditions of increased friction or strain rate, filaments at the central portion of the tapes are highly densified, become thinner, and elongate more in the lateral direction. In contrast, the filaments near the tape surfaces remain thick and porous and are subjected to little or no deformation. Moreover, the filaments at the edges of the tapes experience only limited densification because these regions (region III in Fig. 1.43) are not subjected to direct compression. Instead, the material at the edges spreads and elongates under the influence of a secondary tensile stress system generated by the adjacent elastic material outside the roll gap.¹⁷

The different extent of lateral spreading can also be seen in the overall dimension of the various tapes. As listed in Table 1.4, the lateral spreading of the tapes deformed between both roughened and smooth rolls increases with the reduction per pass. In addition, the width of the tape deformed between roughened rolls at a small reduction per pass is equal to that deformed between smooth rolls even though it has been reduced by a lesser amount along the thickness direction. In other words, lateral spread is greater for the roughened rolls under these deformation conditions. On the other hand, lateral spread of the tape deformed between roughen rolls at a large reduction per pass is less than that of the smooth rolls. One possible reason may be that, at a small reduction per pass, the influence of strain rate on the flow stress and strain hardening of Ag is minimal, and lateral spreading is dominated by the friction effect. In the case of a large reduction per pass, the flow stress of Ag is likely to increase from both strain rate sensitivity and strain hardening. Under this condition, a higher load can be transferred to the powder core

because the deformation is not necessarily localized to the previously ductile Ag. Thus, multifilamentary tapes deformed between smooth rolls at a large reduction per pass should be deformed more homogeneously but to a larger extent because of the limited size of the dead zones. Moreover, longitudinal sections of this tape revealed that the degree of sausaging is much less than expected even though the reduction per pass is large and the filament thickness is less than 10 μm , a value which is lower than the typical onset of work instability. This lower-than-expected sausaging is believed to be caused by a combination of the increased flow stress and strain hardening of the Ag, interaction between the ceramic filaments, and the low rolling speed employed,²⁰ which has been shown to reduce sausaging.

Following the microstructural examination, 30-mm sections of the various multifilamentary tapes were subjected to the following thermomechanical treatment HT1 = 5 h, P1, HT2 = 5 h, P2, HT3 = 40 h, P3, HT4 = 50 h. Critical current densities of these tapes are listed in Table 1.4. The J_c values indicate that unlike monofilamentary tapes, initial deformation of a multifilamentary PIT tape under high-friction conditions does not necessarily result in the best current capacity. Rather, J_c values of multifilamentary PIT tapes depend on the densification and homogeneity of the cores. This information may be elucidated from the changes in the width-to-thickness ratio ($\Delta w/\Delta t$) as well as from the fill factor; a larger ratio and a lower fill factor correspond to better densification. The variation in J_c s with the changes in width-to-thickness ratio is shown in Fig. 1.44. It can be seen from this figure that J_c increases with the absolute ratio value; i.e., J_c increases with the core density. Figure 1.45 shows J_c as functions of fill factor before the initial heat treatment (as deformed) and after the final heat treatment (fully processed). In both cases, the current capacity increases monotonically with decreasing fill factor, again indicating that J_c is enhanced with improved core density. In

Fig. 1.44. Variation in J_c of multifilamentary Bi-2223 PIT tapes with the changes in width-to-thickness ratio.

addition, the consistency of the ordering of fill factors both before and after heat treatment reaffirms that the beneficial effect of high initial core density will remain despite the occurrence of retrograde sintering.

The different responses of mono- and multifilamentary tapes to friction can be explained (disregarding the influence of strain rate) with the aid of dead-zone development as shown in Fig. 1.46. The precursor core in a monofilamentary tape is located within the central region of the tape. Consequently, even though an increase in working friction leads to larger dead zones, substantial portions of these zones of limited deformation are located within the silver sheath. Therefore, the strain is localized to the precursor and results in higher initial core density, which has been shown to lead to high final core density and high J_c .¹² This result is analogous to that of Utsunomiya et al.²¹ who found higher J_c in tapes that were deformed between rolls of larger diameter. In their study, rolling was employed as the deformation process in the thermomechanical treatment. The effect on the partially densified HTS core in their study, however, should be similar to the influence on the unreacted precursor investigated in this study. As pointed out by Dieter,¹⁶ a large roll diameter results in a larger area of contact and therefore greater frictional

Fig. 1.45. Critical current density of multifilamentary Bi-2223 PIT tapes as functions of tape fill factor before initial heat treatment and after final heat treatment.

forces. In contrast, the same investigators reported that monofilamentary tapes rolled with mineral oil as lubricant exhibited higher J_c s than those of unlubricated samples.²¹ This discrepancy may be caused by rolling during thermomechanical treatment in that particular experiment or by the utilization of front tension in their work, a technique that minimizes slipping and moves the neutral point toward the roll entrance.¹⁸ As mentioned previously, increased working friction has the same effect on the neutral point. In deformation by rolling, the stock at the entry side of the neutral point tends to be pushed back out of the rolls, whereas it is extruded from the rolls at increasing speed at the exit side. Consequently, the partially adhered brittle core suffers a reversal of flow direction at the neutral point, which may lead to core fracture at the low-density sections. By moving the neutral point forward or even to the roll entrance, the compression zone is lengthened, and partial separation of the core material may be able to be healed under the longer compression zone of the roll gap.

The core in monofilamentary PIT tape is confined to the central region of the conductor; however, precursor filaments in multifilamentary tapes are distributed throughout the entire cross section. Thus an

Fig. 1.46. Schematic of dead zones within (a) monofilamentary and (b) multifilamentary tapes deformed under high friction condition. The single core in monofilamentary tape is expected to lie outside the dead zones, whereas a significant number of filaments in the multifilamentary tape will be located within the areas of limited deformation.

increase in friction means that a larger number of filaments will reside within the dead zones and will experience only limited deformation. Because these filaments are porous, important characteristics such as phase purity, *c*-axis texture and grain-to-grain connectivity will remain inferior after heat treatment and will not be able to contribute significantly to the current-carrying capability of the tapes. Consequently, deformation under high friction in multifilamentary tapes of the present geometry does not lead to enhancement in J_c . In fact, the highest J_c in the multifilamentary tapes examined in this study is exhibited by the PIT tape initially deformed between smooth rolls at a large reduction per pass. As previously mentioned, a combination of limited dead zones and high strain rate in this tape resulted in the

largest amount of lateral spreading and therefore thin, dense cores and the most homogeneous deformation characteristics. Consequently, most of the filaments in this tape should be able to carry supercurrent resulting in the highest J_c . Interestingly, the J_c s of these multifilamentary PIT samples increase with lateral spreading, as shown in Fig. 1.44. In fact, the highest J_c values are exhibited by the tapes with the largest amount of lateral spreading in both mono- and multifilamentary configurations, which may be a characteristic to strive for in the continuing refinement of the deformation processing of Bi-2223 PIT tapes.

Summary

The effects of initial cold-work conditions on the deformation of Bi-2223 PIT tapes have been studied in this investigation. The results revealed that deformation of PIT conductors by rolling is three-dimensional (plane strain condition is not followed), and the transverse cross sections of the rolled tapes resemble those of samples deformed under a simple compression condition (i.e., dead zones develop). In monofilamentary tapes, the precursor powder core is located in the central region of the tape and is therefore outside the areas of limited deformation. Under high-friction conditions, most of the deformation is sustained by the monocore, which leads to higher core density and enhanced J_c . In contrast, many filaments in multifilamentary tapes are located within the dead zones. Therefore, when the working friction is increased, the dead zones penetrate deeper into the tape and envelop more filaments. Because these filaments sustain little or no deformation, fewer filaments are active in current transport and high friction does not necessarily result in the highest J_c in multifilamentary tapes. Instead, the optimum J_c found for the deformation conditions utilized in this study is by deformation between smooth rolls at a large reduction per pass. It is believed that the combination of reduced dead zones and

increased flow stress result in large but more uniform deformation of the multifilamentary tape.

It is interesting, however, that although only a limited number of filaments are expected to transport supercurrent in the tape deformed under high-friction and large reduction-per-pass conditions, the J_c is only slightly lower than that of the tape with the most homogeneous deformation. This result indicates the importance of high initial core density as well as the benefit of thin filament cores and suggests various strategies that may increase the overall performance of multifilamentary tapes. One possible modification is the utilization of a thick outer sheath so that the filaments are located outside the dead zones under high-friction conditions. By doing so, the higher strain limited to the central region can be experienced by most of the filaments. An opposite approach may involve the utilization of lubricant to limit the dead zone size. This strategy, however, will need to be accompanied by other modifications, such as the imposition of front and back tension to minimize the occurrence of sausaging.

References

1. K. Osamura, S. S. Oh, and S. Ochiai, *Supercond. Sci. Technol.* **3**, 143 (1990).
2. M. Ueyama et al., *Jpn. J. Appl. Phys.* **30**, L1384 (1991).
3. Y. Yamada, G. Obst, and R. Flukiger, *Supercond. Sci. Technol.* **4**, 165 (1991).
4. Y. B. Huang, et al., *Supercond. Sci. Tech.* **7**, 759 (1995).
5. G. Grasso, A. Perin, and R. Flukiger, *Physica C* **250**, 43 (1995).
6. K. H. Sandhage, G. B. Ruketm, Jr., and W. K. Crater, *J. Metals* **43**, 21 (1991).
7. S. E. Dorris et *Physica C* **212**, 66 (1993).
8. D. A. Cardwell, J. W. Cockburn, and R. W. Whatmore, *Supercond. Sci. Technol.* **2**, 132 (1989).
9. J. A. Parrell, D. C. Larbalestier, and S. E. Dorris, *IEEE Trans. Appl. Supercond.* **5**, 1275 (1995).
10. K. Osamura, S. S. Oh, and S. Ochiai, *Supercond. Sci. Technol.* **5**, 1 (1992).
11. N. V. Vo, S. X. Dou, and H. K. Liu, *Physica C* **250**, 139 (1995).
12. M. Satou et al., *Appl. Phys. Lett.* **64**, 640 (1994).
13. J. A. Parrell, S. E. Dorris, and D. C. Larbalestier, *Physica C* **231**, 137 (1994).
14. G. Grasso et al., *Physica C* **241**, 45 (1995).
15. D. M. Kroeger, H. S. Hsu, and J. Brynestad, U.S. Patent 5,395,821.
16. G. E. Dieter, Jr., *Mechanical Metallurgy*, New York, McGraw-Hill, 1961.
17. S. L. Semiatin and J. J. Jonas, *Formability and Workability of Metals: Plastic Instability and Flow Localization*, Metals Park, Ohio, American Society for Metals, 1984.
18. R. N. Parkins, *Mechanical Treatment of Metals*, New York, American Elsevier, 1968.
19. E. C. Larke, *The Rolling of Strip, Sheet and Plate*, London, Chapman and Hall, 1963.
20. B. Zeimetz, A. Pan, and S. X. Dou, *Physica C* **250**, 170 (1995).
21. H. Utsunomiya et al., *Physica C* **250**, 340 (1995).

Technical Progress in Applications Development

INTERMAGNETICS GENERAL/ORNL/ WAUKESHA ELECTRIC SYSTEMS/ROCHESTER GAS AND ELECTRIC COMPANY SUPERCONDUCTING TRANSFORMER PROJECT

This report covers only the nonproprietary ORNL contributions to the HTS Transformer Project for the FY 1996. Other than ORNL, the organizations participating in the project are the Intermagnetics General Corporation (IGC), Waukesha Electric Systems of General Signal Corporation (WES), and the Rochester Gas and Electric Company (RG&E). Rensselaer Polytechnic Institute provides consulting under subcontract to IGC. The objectives of the project are (1) to develop a low-cost, wind-after-react HTS suitable for use in transformers and other ac apparatus; (2) to determine 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. Significant progress in achieving the first two objectives has resulted in the decision to continue into the demonstration phase, which, together with the completion of key experiments, has been the major focus of efforts this year.

In FY 1996, the team

- developed the capability of manufacturing a long-length surface-coated BSCCO-2212 conductor,
- performed several key experiments to establish essential concepts and to obtain experimental design data for the transformer subsystems,
- developed and tested the key components of the system, and
- designed and started construction of the 1-MVA HTS demonstration transformer.

Design and Testing of Subsystems

Core, Tank, and Bushing Subsystem

It is highly desirable to use as many components from existing transformer technology as possible. With this in mind, we decided to determine whether existing transformer tank technology could be applied to the HTS transformer. The resulting design for the 1-MVA demonstration is externally very similar to a full-scale commercial HTS tank and resembles a conventional tank without a heat exchanger. As a part of the development process, a sub-sized tank was built at WES and was successfully tested for weld integrity at ORNL. The core section for the demonstration unit is similar in size to a single phase of the 30-MVA design. This choice was made to allow the use of the core for prototype testing of several coil systems, to gain experience with full-size components, and to allow use of existing core technology at WES. A small core cross section is presently undergoing tests at ORNL for vacuum outgassing performance. In addition, a full-scale bushing is undergoing tests at ORNL.

Cooling and Cold Mass Support Subsystem

ORNL has lead responsibility for the 80 K cold mass, liquid nitrogen, and cooling loop subsystems. Initial design has been completed. Final testing and integration awaits completion of coil and core fabrication.

AC Loss Measurements in Coil Prototypes

Two sets of ac loss tests were performed in the ORNL variable-temperature cryostat on sub-sized transformer coil pairs provided by IGC. The coils were fabricated from IGC's surface-

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coated BSCCO-2212 tape using winding techniques based upon IGC's experience with homopolar motor coils being developed for a related Naval Research Laboratory program. The ac loss measurements were made by measuring the calibrated temperature rise in He cooling gas (15–45 K) that resulted from ac current pulses. Fault-current performance was also successfully completed on one-third height near-design diameter coils at IGC.

TESTS OF THREE PROTOTYPE HIGH TEMPERATURE SUPERCONDUCTING TRANSMISSION CABLES: SOUTHWIRE CRADA

During the initial phase of the CRADA between ORNL and Southwire Co. to develop HTS underground transmission cable, two 500-A-class and one 2000-A-class prototype cables were constructed. The cables and short samples of the Bi-2223/Ag HTS tapes were tested systematically at ORNL.

The cables were tested with both dc and ac currents in liquid nitrogen. Both cables achieved design currents; however, substantial degradation in comparison with the short-sample critical currents (I_c s) was observed. A simple calorimetric technique was used to measure the ac losses of the cables. A method of utilizing the broad resistive transition of the HTS cable was devised to calibrate the ac loss. Different ac-loss behaviors were observed on the insulated and uninsulated cables.

Short Sample Testing

A series of short sample tests were performed on the Bi-2223/Ag HTS tapes acquired by Southwire Co. Seventy eight samples for the winding of the first cable and 11 samples for the winding of the second cable were measured. These 1-in.-long samples were tested in liquid nitrogen with up to 0.5-T magnetic field parallel and perpendicular to the

wide face of the tape. Figure 2.1 shows the measured zero-field short sample I_c s (at the 1- μ V/cm criterion) along the length of the spool used to wind the second cable. Critical current varies significantly (by a factor of two) along the length of the tape. A mean I_c value of 20 A was measured (the end-to-end value was 17 A). Similarly, a mean I_c value of 19 A was measured for the tapes used to wind the first cable (the end-to-end value was 12 A). Apparently, damaged spots on a large spool were apt to be skipped when short samples (about 1-in. long) were taken.

Magnetic fields degrade the Bi-2223/Ag HTS tapes significantly at liquid nitrogen temperatures. At a background field value of 0.01 T, the present tapes showed an average of 10% degradation in I_c with field parallel to the wide face and 50 % degradation with field perpendicular to the wide face of the tape.

Bending tests were performed on selected samples of the HTS tapes. In a series of tests, I-V curves of 3-in.-long samples were measured

Fig. 2.1. Short sample of I_c along the length of the tape for use in cable 2.

before and after being wrapped side-by-side around a 1-in.-diam former. The samples from the lower- I_c spool showed an average degradation of 30%; those from the higher- I_c spool showed an average degradation of 53%.

Bending tests were also performed with samples about 30-cm long by wrapping them

with lay angles of up to 30° . Critical current degradation between 40 and 50% of the 1-in.-long short sample values was observed.

Prototype Cables

Two prototype 500-A-class transmission cables were fabricated by Southwire using the 3.5×0.22 mm HTS tested tapes. The 1.2-m-long cables were made by spirally winding the tapes on a 22-mm (7/8-in.) copper former with lay angles of about 15° .

For the first cable, no insulation was used to electrically separate the tapes. The ends of the tapes on the first layer were soldered onto the former. Successive layers were wound with alternating twist angles, and the ends were soldered to the previous layer. Seventy three tapes were wound in four layers in the first cable. Figure 2.2 shows a picture of the cable assembled and ready to be lowered into the test dewar. The main body of the cable was enclosed

in a micarta pipe filled with wax to establish adiabatic conditions to measure the temperature rise (and thus the ac loss) of the cable.

The second cable was fabricated in a way similar to the first cable, except that Kapton tape was used between layers for insulation. Sixty six HTS tapes was used in the second cable.

The third Southwire cable was wound from similar HTS tapes as were used in cables 1 and 2. The tapes were wound in 10 layers on a 1-in.-diam stainless steel former. Similar to layers in cable 2, the successive layers were insulated from each other with Kapton tape. Two hundred HTS tapes were used in winding this cable.

DC Current Measurements

The electrical tests of the cables were carried out in liquid nitrogen with the HTS cable held upright in a 1.6-m-deep dewar.

DC I-V of Cable 1

Four voltage taps were placed on the cable, separated from each other by about 30 cm, and were labeled as V_1 to V_4 . Figure 2.3 shows the I-V curves of the different sections of the cable and of the whole cable (V_{Tot}). Gradual resistive voltage rise was seen for currents starting at about 400 A. All resistive voltage of the cable came from the midsection (V_{23}) at currents up to 650 A, caused by visible damage near the

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Fig. 2.2. Cable 1 assembled for both dc and ac current tests.

Fig. 2.3. DC I-V curves of cable 1 at the first cooldown.

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middle of the cable. Nevertheless, the overall I_c of 670 A at the $1\text{-}\mu\text{V}/\text{cm}$ criterion is higher than the design value of 500 A.

DC I-V of Cable 2

The layers of cable 2 were insulated from each other with Kapton tape, and separate current leads were brought out for each layer. Thus the cable could be tested as a whole or separately on individual layers. When the cable as a whole was tested, an I_c of 560 A was measured. Notice also that because of the broad resistive transition, both cable 1 and 2 can be operated stably at more than 1 kA.

During the test of the outermost layer of cable 2, the liquid nitrogen bath was pumped to lower temperatures. Figure 2.4 shows the I-V curves of this layer at three different temperatures of the liquid nitrogen bath. The I_c of this layer increased from 149 to 186 A when the bath temperature was lowered from 77 to 69 K. Thus an increase of about 25% in current-carrying capability can be achieved in the cable by operating with subcooled liquid nitrogen (at about 69 K).

DC Test of Cable 3

DC current test of the cable was performed with a 2-kA power supply. Broad and smooth resistive transition of the cable, similar to those

Fig. 2.4. I-V curves of outermost layer of cable 2 at three different bath temperatures.

of the previous two cables, was observed. A critical current of 1630 A was measured at the $1\text{-}\mu\text{V}/\text{cm}$ criterion. At the power supply limit of 2 kA, the cable produced an average resistive voltage of $2.2\text{ }\mu\text{V}/\text{cm}$.

Thermal Cycle of Cable 1

After a few cycles of cooling down and warming up of cable 1 for dc and ac current measurements, a series of continuous thermal cycle tests was performed. An I-V curve was measured, and the cable was pulled out of the liquid nitrogen bath. After it was warmed up to room temperature in air, the sample was lowered back down to the liquid nitrogen bath. Another I-V curve was measured. Figure 2.5 shows a series of these I-V curves at different thermal cycles. Significant degradation was observed on thermal cycling; however, the degradation seems to level off after the fifth cycle. Critical current of the cable decreased from 670 to 460 A after 10 thermal cycles (a 30 % degradation). Power law fitting of the I-V curves between 0.2 to $2\text{ }\mu\text{V}/\text{cm}$ also shows a decrease of n -value from 3.5 to 2.6.

Fig. 2.5. I-E curves of cable 1 on successive thermal cycles.

Comparison of Short Sample and Cable I_c

The measured I_c per tape of cables 1 and 2 averages about 8.8 A. This is significantly lower than the average short sample value of 19.5 A measured on 1-in.-long short samples. As is described in the series of short sample measurements, several mechanisms can contribute to the degradation of the cable I_c . Short sample I_c measurements can be misleading because they can skip bad spots in the long lengths of the tape. Mechanical strain similar to that applied in winding the cable can degrade the I_c by about 50%. This can come from just handling the long lengths of the tape and from the bending applied in the cabling. The magnetic-field degradation by the cable self-field is well known. In addition, thermal-cycling degradation was also observed.

AC Current Measurements

Cables 1 and 2 were tested with 60-Hz ac currents up to 600 A rms. Steady rms voltages were observed at all test currents. A calorimetric technique was adopted to measure the ac loss of the cable at the applied ac currents. As is shown in Fig. 2.2, a micarta pipe filled with wax was used to thermally isolate the cable from the liquid nitrogen bath. A Chromel-Constantan thermocouple was attached to the middle of the cable to measure its temperature rise against liquid nitrogen at the same depth of the bath; temperature rise (ΔT) of up to 0.3 K was observed.

To calibrate ΔT against the power-loss rate, we used the broad resistive transition feature of the HTS cable itself. The cable was charged and held at a dc current above its I_c , where a resistive voltage can be measured. The ΔT of the cable was also measured under this dc current. The dc $E \cdot I$ product gave the average power loss for the measured ΔT . This technique was found to be more responsive than the heater wires tried on cable 1. Because I_c is not uniform along the length of the cable, power generation is not

uniform, but this is true for both dc power and ac loss. Therefore, the calibration technique is a good simulation of the ac loss. In addition, Joule heating at the cable ends did not contribute to the measured temperature rise because the ends of the cable were immersed in liquid nitrogen. This was verified by the observation that in the dc current calibration runs no temperature rise was observed until the current greatly exceeded I_c .

Figure 2.6 shows the measured ac losses of the two cables as a function of the rms current. Also shown in Fig. 2.6 for reference respective dc I-E curves for two cables. Cable 1, which was not insulated, behaved like a cryoresistive conductor, showing power loss at all ac currents. Similar behavior was reported by Gannon et al.¹ Cable 2 which was insulated, showed no measurable ac loss until about 300 A rms, where the cable also started to show measurable dc resistive voltage. An average ac loss of about 0.2 W/m was measured at 400 A rms. Analysis of the loss data indicated that the measured loss is governed by the power law behavior of the HTS tape in the resistive transition.

Fig. 2.6. The ac losses of both cable 1 and 2 in reference to their DC I-E curve. For the ac current, rms current is plotted.

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Cable 3 was also subjected to ac current tests. Currents measuring up to 2.2 kA rms were charged and held for about 10 min. Steady voltage (mostly inductive voltage) was observed over the cable in each case.

Summary

Two prototype 500-A-class HTS cables have been designed, constructed, and tested. Both cables achieved dc critical currents greater than the design value of 500 A. Furthermore, because of the broad resistive transition, they can be operated stably at more than 1 kA. A third cable was tested successfully to >2000 A ac current.

Comparison of the cable I_c and the short sample values indicated a degradation of about 55%. Several mechanisms were identified as the probable cause of the degradation. Mechanical strain from handling the long lengths of the tape and from bending applied in winding the cable is thought to be the biggest source of degradation.

A calorimetric technique was used to measure ac losses of the cables. A scheme of utilizing the broad resistive transition of the HTS cable was successfully used to calibrate the loss rate. Loss measurements made on the cables with 60-Hz ac currents showed that insulation between the tapes is effective in reducing the ac loss of the cable.

Reference

1. J. J. Gannon, Jr., et al., "Performance Summary of a 4,000-A High Temperature Superconducting Cable Conductor Prototype," *IEEE Trans. Appl. Supercond.* **5** (2), 953–56 (1995).

Summary of Technology Partnership Activities

BACKGROUND

ORNL is a key participant in DOE's national effort on electric power applications of 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 33 superconductivity "pilot center" cooperative agreements and 5 cooperative research and development agreements (CRADAs). 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. Spectator firms can participate in this national program by licensing Laboratory spinoff technologies. However, this type of technology partnering is the traditional one-way variety in which the Laboratory invents and private industry applies. In the ORNL program the cooperative development level of technology partnering is emphasized: joint industry-Laboratory 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 RABiTS™ process represents a new way to produce strongly linked YBCO wires using an industry-scaleable 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 1996, and a summary of funds-out cooperative agreements are shown in Tables 3.1 and 3.2 and in Fig. 3.1.

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)				
	1989–1992	1993	1994	1995	1996
Direct scientific and technical ^a	8,431	3,511	3,334	3,434	2,995
Management and outreach	<u>729</u>	<u>294</u>	<u>298</u>	<u>300</u>	<u>310</u>
Subtotal	9,160	3,805	3,632	3,734	3,305
Subcontracts ^b	593	428	496	198	1,290
Funds-out cooperative agreements	<u>2,821</u>	<u>867</u>	<u>821</u>	<u>611</u>	<u>286</u>
Total program	12,574	5,100	4,949	4,543	4,881

^aSee Fig. 3.1 for distribution of funding for Oak Ridge National Laboratory.

^bDetails are provided in separate tables. 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 industry-Laboratory 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 1996 nearly \$1.6 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 program 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 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.

Table 3.2 Superconductivity program
Summary of Cooperative Agreements as of September 30, 1996

Participant	Approved term	Type ^a	Total agreement cost share (\$ × 1000)			Technology area
			By DOE		By industry	
			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 multifilament conductors deposited by metal-organic chemical-vapor deposition
American Magnetics	10/1/96–4/1/97	C	0	0	82.4	Development, design, and fabrication of hybrid HTS leads
American Superconductor	9/1/91–11/15/96	FO	1,139	650	710	Coil fabrication, technical development, and testing
American Superconductor	4/1/89–11/15/96	FI	2,090	0	1,705.4	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-filament 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	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 HTSc material processing
General Electric (SPI) (complete)	12/1/93–11/30/95	NFE	400	0	1,173	Thallium wire development and generator design
General Electric (B1) (complete)	10/1/89–6/30/96	FO	895	520	614	Laser deposition of conductors; thallium-deposited conductors

Table 3.2 (continued)

Participant	Approved term	Type ^a	Total agreement cost share (\$ × 1000)			Technology area
			By DOE		By industry	
			To ORNL	To industry		
General Electric (C1) (complete)	4/1/90–12/31/90	NFE	135	0	140	Thallium HTSc material processing
HiTc 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
Intermagetics General Corporation	10/1/91–9/30/97	FO	1,452	965	731	HTS transformer; BSCCO 2212 tape development
Intermagetics 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
Midwest Superconductivity/ Westinghouse Electric	6/25/96–6/24/98	C	300	0	980 <u>160</u> 1,140	Develop coated-conductor technology
Neocera (complete)	2/1/91–1/31/93	FO	80	111.6	95.7	Laser ablation multitarget deposition
Oxford Instruments	1/94–1/31/97	C	200	0	275	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
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	1,249.2	Transmission cable
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	Deposition via metal-organic chemical-vapor deposition for electronic devices
Superconductive Components, Inc.	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

Table 3.2 (continued)

Participant	Approved term	Type ^a	Total agreement cost share (\$ × 1000)			Technology area
			By DOE		By industry	
			To ORNL	To industry		
University of Wisconsin—Madison (complete)	8/1/92–3/31/96	FO	110	60	150	Aerosol powder synthesis
Westinghouse Electric (complete)	4/1/89–12/31/93	FO	1,200	750	800	Powder scale-up, BSCCO wire fabrication, and leads
Total			11,562	4,645.6	14,213.7	
FY 1996 active subcontracts						
Georgia Institute of Technology	8/21/95–8/20/96			50		TEM examination of HTS
Imtech	10/3/94–9/30/97			163		Superconducting powder synthesis/scale-up
Massachusetts Institute of Technology	4/29/96–4/28/97			110		Stability of HTS conductors and coils
Oak Ridge Institute for Science and Education	10/95–9/96			360		Postdoctoral research fellowships (4.5)
SUNY at Buffalo	11/1/95–5/31/96			25		Supply epitaxial films of thallium-based HTS materials
	10/1/96–9/30/97			30		
Texas Center for Superconductivity at the University of Houston	5/15/95–5/14/97			104		Processing YBCO and BSCCO superconductors for high current leads and conductors (two students)
University of Tennessee	Ongoing			80		Deposited conductor development (three students)
National Institute of Standards and Technology (Interagency Agreement)	9/22/93–7/31/97			395		BSCCO and TBCCO phase diagram support
Energetics, Inc.	4/96–7/96			70		Technical and analytical support
	8/96–7/97			450		

^aNFE = no-funds-exchange; FO = funds-out; FI = funds-in; and C = CRADA.

3-6 Summary of Technology Partnership Activities

Fig. 3.1. ORNL FY 1996 funding allocation by project.

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

- technical, program, 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;
- assistance in the open annual review meeting preparations and contracting;
- collection and dissemination of programmatic information and program-wide assessments;
- assistance in organizing the Superconducting Technology Program workshops (one per year); and
- review of industrial collaboration opportunities through multilaboratory meetings and conference calls.

ORNL works with the other program laboratories to address issues such 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 manufactures. This committee meets twice a year at ORNL, Argonne National Laboratory, or Los Alamos National Laboratory.

PROGRAM MEASURES

Four new cooperative agreements were executed during FY 1996: 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. Twelve new invention disclosures were submitted by ORNL or industrial principal investigators. These are listed in Table 3.3 together with all others for the program.

Table 3.3. Superconducting Technology Program invention disclosures (cumulative through FY 1996)

ID No.	Subject	Submitted by
ESID935-X	Method for Fabricating Continuous Ribbons of High-Temperature Superconductors	V. K. Sikka and C. E. Dunn
ESID1018-X	Improved $Y_1Ba_2Cu_3O_7$ Superconductor	A. D. Marwick and L. Civale (IBM), and J. R. Thompson
ESID964-X	Chemically Compatible Substrate/Jacket Alloy for Oxide Superconductors	D. M. Kroeger, F. A. List, III, and J. Brynestad
ESID1039-X	Method for Preparation of $(Bi-Pb)_2Sr_2Ca_2Cu_3$ Oxide Powders (Patent 5,395,821 issued 3/7/95)	D. M. Kroeger, J. Brynestad, and H. S. Hsu
ESID1040-X	Method for Preparing Superconducting Wires from Oxide Powders	D. M. Kroeger and H. S. Hsu
ESID1058-X	Rolled Current Density, High-Temperature Ribbon Superconductors from Stacked Predeposited Strips	G. A. Whitlow and J. C. Bowker (Westinghouse) and D. M. Kroeger, and F. A. List III
ESID1124-X	Improved, Strain-Tolerant High-Temperature Superconductor (87X-SD925C) ^a	G. A. Whitlow and W. R. Lovic (Westinghouse)
ESID1129-X	An Improved Heat Treatment for Composite Conductors Using $Bi_2Sr_2CaCu_2O_x$ Superconductor Material (87X-SD925C) ^a	J. C. Bowker and G. A. Whitlow (Westinghouse)
ESID1131-X	Method of Forming Superconducting Joints Between Tapes of Oxide Superconductors (87X-SE934V) ^a	R. H. Arendt and K. W. Lay (GE)
ESID1155-X	Method for Fabricating High-Current-Density, Oxide Superconductor Ribbons (HTSPC-001) ^a	V. K. Sikka
ESID1185-X	Bipolar Pulse Field for Magnetic Refrigeration (Patent 5,357,756 issued 10/25/94)	M. S. Lubell
ESID1193-X	Process for Fabricating Continuous Lengths of Superconductor (86X-SD925C) ^a	D. M. Kroeger and F. A. List
ESID1233-X	High-Current-Density, High-Temperature Superconductors by Deformation of High-Density Materials (87X-SD925C) ^a	G. A. Whitlow, W. R. Lovic, and J. C. Bowker (Westinghouse), D. M. Kroeger, and F. A. List (ORNL)
ESID1384-X	Process to Enhance Superconducting Phase Formation, Grain Alignment, and Fracture Properties of High-Temperature Superconductors	V. Selvamanickam and D. M. Kroeger
ESID1450-X	Improved Efficiency High- T_c Superconducting Magnet Lead Materials	R. K. Williams
ESID1467-X	Superconducting Structure and Method for Making Same	R. K. Williams and J. Brynestad

3-8 Summary of Technology Partnership Activities

Table 3.3 (continued)

ID No.	Subject	Submitted by
ESID1471-X	HTS Coil Grading to Compensate for Anisotropic Behavior of HTS Conductor (86X-SK700V) ^a	D. Aized and R. Schwall (American Superconductor)
ESID1511-X	Enhancement of Persistent Currents in High- T_c Superconductors (86X-SF645V) ^a	L. Krusin-Elbaum, A. D. Marwick, and J. F. Ziegler (IBM), J. R. Thompson (ORNL), and P. Lisowski (LANL)
ESID1512-X	Method for Preparation of Textured $\text{YBa}_2\text{Cu}_3\text{O}_x$ Superconductor	V. Selvamanickam, A. Goyal, and D. M. Kroeger
ESID1632-X	Materials and Fabrication Method for Producing High- T_c Superconducting Tapes (ORNL93-0180) ^a	R. K. Williams (ORNL) and K. R. Marken, Jr. (Oxford)
ESID1636-X	Low-Loss Multifilamentary Superconductor for ac Applications	M. S. Lubell
ESID1638-X	Buffer Template for c -Axis Oriented Perovskite Films on Crystalline Metals	David P. Norton and J. D. Budai
ESID1640-X	Method of Fabricating High-Temperature Superconductors with Enhanced "Biaxial" Texture	A. Goyal, E. D. Specht, D. M. Kroeger, D. K. Christen, J. D. Budai, and D. P. Norton
ESID1654-X	A Sol-Gel Process for the Synthesis of Barium-Calcium-Copper-Oxide Superconductor Precursor	M. Paranthaman and D. B. Beach
ESID1676-X	Torsional Texturing of Superconducting Oxide Substrates (86X-SK700V) ^a	C. J. Christopherson, G. N. Riley, and J. Scudiere (American Superconductor)
ESID1687-X	Making a Transposed Cable Out of High-Temperature Superconducting (HTS) Tapes	J. W. Lue
ESID1697-X	Powder-in-Tube and Thick-Film Methods of Fabricating High-Temperature Superconductors Having Enhanced "Biaxial" Texture	A. Goyal and D. M. Kroeger
ESID1770-X	Structures for High- J_c in a Magnetic Field with Arbitrary Orientation (86X-SK700V) ^a	C. J. Christopherson and G. Snitchler (American Superconductor)
ESID1784-X	Method of Preparing Preferentially Oriented, High-Temperature Superconductors by Seeding	D. F. Lee, A. Goyal, and D. M. Kroeger
ESID1802-X	Low Thermal Conductance, High Thermal Capacity Support for High- T_c Superconducting Current Leads	R. K. Williams
ESID1852-X ^b	Method of Fabricating Tl-Containing Conductors	A. Goyal, D. M. Kroeger, and M. Paranthaman
ESID1853-X ^b	Method of Enhancing Intragranular Superconducting Properties by Controlled Addition of Pinning Centers	A. Goyal and D. M. Kroeger

Table 3.3 (continued)

ID No.	Subject	Submitted by
ESID1867-X ^b	Method of Fabricating TI-1223 Precursors	A. Goyal and D. M. Kroeger
ESID1882-X ^b	Method of Forming Biaxially Textured Alloy Articles	A. Goyal
ESID1884-X ^b	A Continuous Winding Machine for a High-Temperature Superconducting Cable (ORNL95-0381)	Robert L. Brown (consultant)
ESID1912-X ^b	Reaction Barrier Materials for High-Temperature Superconductors	R. K. Williams and J. Brynestad (retired)
ESID1916-X ^b	Alkaline Earth Cuprate Substrate Materials	R. K. Williams
ERID5 ^b	Coupling Device for Reducing the Heat Load to a Superconducting Antenna	Edwin C. Jones
ERID18 ^b	High T _c YBCO Superconductor Deposited on Biaxially Textured Pd Coated Ni Substrate	J. D. Budai, D. K. Christen, A. Goyal, Q. He, D. P. Norton, and M. Paranthaman
ERID19 ^b	High T _c YBCO Superconductor Deposited on Biaxially Textured Ni Substrate	J. D. Budai, D. K. Christen, A. Goyal, Q. He, D. P. Norton, and B. C. Sales
ERID25 ^b	Method of Preparing Textured, Strong, Nonmagnetic, Oxidation Resistant Substrate	R. K. Williams
ERID218 ^b	Biaxially Textured MgO on Buffered Ni Substrate	M. Paranthaman, A. Goyal, D. M. Kroeger, and F. A. List
ERID223 ^b	The Growth of Biaxially Textured Buffer Layers on Rolled Nickel Substrates using Sol-Gel Precursor Solutions	S. S. Shoup, M. Paranthaman, D. B. Beach, A. Goyal, and D. M. Kroeger
ERID233 ^b	Continuous Operation Magnetic Separator Utilizing a Novel Magnetic Field Configuration	M. S. Lubell
ERID254C ^b	Method for Winding 60 Hz Transmission Line Power Cables with High Temperature Superconducting Tape Material (CRADA ORNL95-0381)	M. S. Lubell
ERID301C ^b	High Temperature Superconducting (HTS) Cable End Connector (CRADA ORNL95-0381)	J. W. Lue (ORNL), and U. K. Sinha and J. C. Tolbert (Southwire)

^aNumbers in parenthesis are cooperative agreement numbers under which the work was conducted.

^bNew item since last report.

FY 1996 Presentations and Publications

- A. Goyal, D. P. Norton, Q. He, M. Paranthaman, E. D. Specht, J. D. Budai, D. M. Kroeger, D. K. Christen, R. Feenstra, and J. R. Thompson (ORNL), "Fabrication of Biaxially Aligned Polycrystalline HTSC Using a New Process," invited abstract submitted to MRS Fall Meeting, November 27–December 1, 1995, Boston.
- J. W. Lue and M. S. Lubell (ORNL) and D. Aized, J. M. Campbell, and R. E. Schwall (American Superconductor), "Quenches in a High-Temperature Superconducting Tape and Pancake Coil," *Cryogenics* **36**, 379, November 5, 1996.
- J. R. Thompson, D. Paul, Z. L. Wang, D. M. Kroeger, and D. K. Christen, "Thermal Stability and Annealing of Columnar Defects in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8/\text{Ag}$ Superconductor," *Appl. Phys. Lett.* **67**, 1007 (1995).
- Z. F. Ren, C. A. Wang, and J. H. Wang (SUNY Buffalo); D. J. Miller, J. D. Hettinger, and K. E. Gray (ANL); and D. K. Christen (ORNL), "Composition and Phase Development of Epitaxial Superconducting $\text{Ti}_{0.78}\text{Bi}_{0.22}\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_1\text{Cu}_3\text{O}_{9.8}$ Thin Films by Laser Ablation and Post Annealing, submitted to *Physica C*.
- S. P. Tirumala and K. Salama (Univ. Of Houston), and D. M. Kroeger and D. F. Lee (ORNL), "Reaction Kinetics and Thermomechanical Processing of Bi-2223 Tapes Made from Aerosol Precursors of Various Stoichiometry," abstract submitted to MRS 1996 Spring Meeting, April 8–12, San Francisco.
- A. Goyal, D. P. Norton, E. D. Specht, M. Paranthaman, Q. He, P. M. Martin, J. D. Budai, D. M. Kroeger, D. K. Christen, F. A. List, and J. R. Thompson (ORNL), "Fabrication of Biaxially Textured Superconductors Using the RABiTS Process," abstract submitted to MRS 1996 Spring Meeting, April 8–12, San Francisco.
- E. Kadyrov and D. C. Larbalestier (Univ. of Wisconsin) and D. K. Christen (ORNL), "Effect of Heavy-Ion Irradiation on the Critical Current Density of Nb-47 wt % Ti Thin Films," paper submitted to *Appl. Phys. Lett.*
- M. N. Kunchur, D. K. Christen and C. E. Klabunde (ORNL), "Exploring the Dissipative Regime of Superconductors for Practical Current-Lead Applications," *Appl. Phys. Lett.* **67**, 848 (1995).
- Q. He, D. K. Christen, C. E. Klabunde, M. Paranthaman, J. R. Thompson, A. Goyal, and D. M. Kroeger (ORNL); and J. E. Tkaczyk, K. W. Lay, and A. J. Pedraza (GE), "High-Current Superconducting $\text{TiBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ Thick Films on Polycrystalline Ag by Spin Coating," *Appl. Phys. Lett.* **67**, 294 (1995).
- J. E. Tkaczyk, J. A. Sutliff, J. A. DeLuca, P. J. Bednarczyk, and C. L. Briant (GE); Z. L. Wang (Georgia Tech); and A. Goyal, D. M. Kroeger, D. H. Lowndes, and E. D. Specht (ORNL), "Texture and Transport in Spray Pyrolyzed $\text{TiBa}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ Thick Films," *J. Mater. Res.* **10** (9), September 1995.
- J. R. Thompson (ORNL and Univ. of Tennessee), D. K. Christen and M. Paranthaman (ORNL), L. Krusin-Elbaum and A. D. Marwick (IBM), L. Civale (Centro Atomico Bariloche), R. Wheeler (Ohio State Univ.), J. G. Ossandon (Univ. Of Talca), and P. Lisowski and J. Ullmann (LANL), "The Impact of Tailored Defects on Length Scales and Current Conduction in High- T_c Superconductors," paper to be published in *Lecture Notes in Physics*, ed. P. Klamut, J. Klamut, B. Veel, and B. Dabrowski, Springer-Verlag Publishers, Heidelberg, Germany, 1996.

- D. K. Christen, Q. He, M. Paranthaman, C. E. Klabunde, E. D. Specht, R. Feenstra, A. Goyal, F. A. List, and D. M. Kroeger (ORNL); J. E. Tkaczyk and J. A. DeLuca (GE Corporate R&D); and Z. F. Ren, C. A. Wang, and J. H. Wang (SUNY-Buffalo), "Transport Properties of Tl-1223 Deposits for Possible Conductor Applications," invited paper, published in *Proceedings of the 7th U.S.-Japan Workshop on High- T_c Superconductors*, Tsukuba, Japan, National Research Institute for Metals, Oct. 24–25, 1995, New Superconducting Materials Forum and Society for Non-Traditional Technology.
- E. D. Specht and A. Goyal (ORNL), "Percolative Current Transport in 2D and 3D," abstract submitted to the American Physical Society March Meeting, St. Louis, March 18–22, 1996.
- D. M. Kroeger, A. Goyal, and E. D. Specht (ORNL), "Grain Boundary Misorientation Distributions and Percolation in HTS Conductors," published in *Proceedings of the 10th Anniversary HTS Workshop on Physics, Materials & Applications*, Houston, March 12–16, 1996, World Scientific, p. 193.
- S. S. Shoup (ORNL), "Growth of Epitaxial LaAlO_3 and CeO_2 Films Using Sol-Gel Precursors," published in *Proceedings of the 10th Anniversary HTS Workshop on Physics, Materials and Applications*, Houston, March 12–16, 1996, World Scientific, p. 134.
- M. Paranthaman, A. Goyal, F. A. List, E. D. Specht, D. M. Kroeger, Q. He, and D. K. Christen (ORNL) and J. E. Tkaczyk (GE Corporate Research and Development), "Growth of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ Thick Superconducting Films with Extensive Local Biaxial Alignment on Smooth Ag Substrates," abstract submitted to 1996 Applied Superconductivity Conference, Pittsburgh, August 25–30.
- E. C. Jones (ORNL) and D. Aized, J. M. Campbell, G. Snitchler, G. N. Riley, Jr., C. J. Christopherson, R. E. Schwall, and A. P. Malozemoff (American Superconductor), "AC Losses in Three-Meter-Long Unbridged Twisted Multifilamentary $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x/\text{Ag}$ Tapes," abstract submitted to 1996 Applied Superconductivity Conference, Pittsburgh, August 25–30.
- M. S. Walker, D. W. Hazelton, M. T. Gardner, J. R. Rice, D. G. Walker, R. S. Sokolowski, N. J. Ternullo, and C. M. Trautwein (IGC) and F. A. List (ORNL), "Performance of Coils Wound from Reacted Long Lengths of Low-Cost, Surface-Coated BSCCO-2212 Conductor," abstract submitted to 1996 Applied Superconductivity Conference, Pittsburgh, August 25–30.
- S. P. Mehta and J. A. Ebert (Waukesha Electric Systems); M. S. Walker, F. S. Murray, and D. W. Hazelton (IGC); R. C. Longworth (IGC/APD Cryogenics); R. C. Johnson (Rochester Gas and Electric); J. K. Nelson, R. C. Degeneff, and S. J. Salon (Rensselaer); and B. W. McConnell, J. Hsu, and S. W. Schwenterly (ORNL), "Construction of a 1 MVA HTS Demonstration Transformer," abstract submitted to 1996 Applied Superconductivity Conference, Pittsburgh, August 25–30.
- D. K. Christen (ORNL), "Local Texture, Current Flow, and Superconductive Transport Properties of Tl-1223 Deposits on Practical Substrates," invited talk, published in *Proceedings of the 10th Anniversary HTS Workshop on Physics, Materials, and Applications*, Houston, March 12–16, 1996, World Scientific, p. 193.
- A. Goyal, E. D. Specht, D. M. Kroeger (ORNL), "Effect of Texture on Grain Boundary Misorientation Distributions in Polycrystalline High Temperature Superconductors," *Appl. Phys. Lett.* **68** (5), 29 January 1996.
- S. S. Shoup, M. Paranthaman, D. B. Beach, E. D. Specht, and R. K. Williams (ORNL), "Sol-Gel Synthesis of LaAlO_3 : Epitaxial Growth of LaAlO_3 Thin Films on SrTiO_3 (100)," paper submitted to *J. of Mater. Res.*

- R. N. Bhattacharya, P. A. Parilla, D. L. Schulz, R. D. Blaugher, and D. S. Ginley (National Renewable Energy Laboratory) and M. Paranthaman (ORNL), "Thallium Oxide Superconductors via an Electrodeposition Process," abstract submitted to 1996 Applied Superconductivity Conference, Pittsburgh, August 25–30.
- B. W. McConnell (ORNL), R. Johnson (Rochester Gas & Electric), S. P. Mehta (Waukesha Division, General Signal Corporation), and M. S. Walker (Intermagetics General), "Status of Superconductivity Transformer Development," published in *Proceedings of the American Power Conference, Chicago, Illinois, April 9–11, 1996*, APC, Vol. 58, p. 89.
- J. R. Thompson (ORNL and University of Tennessee), L. Krusin-Elbaum and G. Blatter (IBM), L. Civalé (Centro Atomico Bariloche), and D. K. Christen (ORNL), "Dynamics of Vortices Pinned by Columnar Defects in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Crystals," *Czech. J. Phys.* **46**, 1661 (1996).
- A. Goyal (ORNL), "Application of OIM to High Temperature Superconductors," invited paper presented to Frontiers of Electron Microscopy in Materials Science Conference, June 4–7, 1996.
- F. A. List, P. M. Martin, and D. M. Kroeger (ORNL), "An Automated System for Current-Voltage Characterization of Ceramic Superconductors," *Rev. Sci. Instrum.* **67** (9), 187, September 1996.
- M. Paranthaman, A. Goyal, D. P. Norton, F. A. List, E. D. Specht, D. K. Christen, D. M. Kroeger, J. D. Budai, Q. He, D. F. Lee, and P. M. Martin (ORNL), "Development of Biaxially Textured Buffer Layers on Rolled-Ni Substrates for High Current $\text{YBa}_2\text{Cu}_3\text{O}_{x-y}$ Coated Conductors," abstract submitted to 9th International Symposium on Superconductivity (ISS '96), Sapporo, Hokkaido, Japan, October 21–24, 1996.
- A. Goyal, E. D. Specht, and D. M. Kroeger (ORNL), "Importance of Recrystallization Textures and Grain Boundary Character in High Temperature Superconductors," abstract submitted to ReX-96 International Conference on Recrystallization and Related Phenomena, Monterey, Calif., October 21–24, 1996.
- N. H. Hur and J. R. Thompson (ORNL and Univ. of Tennessee) and M. Paranthaman and D. K. Christen (ORNL), "Superconductivity in the Indium-Doped Tl-1223 Phase: $(\text{Tl}_{0.8}\text{In}_{0.2})(\text{Sr}_{0.8}\text{Ba}_{0.2})_2\text{Ca}_2\text{Cu}_3)_{9-8}$," *Physica C* **268**, 266–270 (1997).
- E. D. Specht, A. Goyal, and D. M. Kroeger (ORNL) and A. Mogro-Campero, P. J. Bednarczyk, J. E. Tkaczyk, and J. A. DeLuca (GE Research and Development Center), "Critical Current, Film Thickness, and Grain Alignment for Spray-Pyrolyzed Films of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$," *Physica C* **270** 91–96 (1996).
- A. Goyal, D. P. Norton, J. D. Budai, M. Paranthaman, E. D. Specht, D. M. Kroeger, D. K. Christen, F. A. List, P. M. Martin, C. E. Klabunde, E. Hatfield, and V. K. Sikka (ORNL); Q. He and B. Saffian (Univ. Of Tennessee); and D. F. Lee (Oak Ridge Institute for Science and Education), "Fabrication of High Critical Current Density Superconducting Tapes by Epitaxial Deposition of YBCO Thick Films on Biaxially Textured Metal Substrates," *Appl. Phys. Lett.* **69**, 1795 (1996).
- D. P. Norton, A. Goyal, J. D. Budai, D. K. Christen, D. M. Kroeger, E. D. Specht, M. Paranthaman, C. E. Klabunde, B. C. Sales, and F. A. List (ORNL); Q. He and Bernd Saffian (Univ. Of Tennessee); and D. F. Lee (Oak Ridge Institute for Science and Education), "Epitaxial $\text{YBa}_2\text{Cu}_3\text{O}_7$ (001) Ni: An Approach to High Critical Current Density Superconducting Tapes," *Science* **274**, 755–57, November 1, 1996.
- M. Paranthaman, C. Vallet, F. A. List, A. Goyal, E. D. Specht, D. M. Kroeger, and D. K. Christen (ORNL), "Growth of $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$ Superconducting Films with Local Biaxial Alignment Extending up to 5 mm on Ag Substrates Using a Spray Pyrolysis Technique," *J. Mater. Res.* **12** (3), March 1997 (in press).

- F. A. List and D. M. Kroeger (ORNL) and V. Selvamanickam (IGC), "Hysteresis of the Transport Critical Current of (Tl,Pb)-(Sr,Ba)-Ca-Cu-O and Bi-Sr-Ca-Cu-O Conductors: Effects of Temperature and Magnetic Field," submitted to *Physica C*.
- A. Goyal, D. P. Norton, M. Paranthaman, E. D. Specht, J. D. Budai, D. M. Kroeger, D. K. Christen, F. A. List, and P. M. Martin (ORNL); Q. He and B. Saffian (Univ. Of Tennessee); and D. F. Lee and S. Shoup (Oak Ridge Institute of Science and Education), "Fabrication of High Critical Current Density Superconducting Tapes by Epitaxial Deposition of YBCO Thick Films on Biaxially Textured Metal Substrates," abstract submitted to 9th International Symposium on Superconductivity, Sapporo, Hokkaido, Japan, October 21-24, 1996.
- A. Goyal, E. D. Specht, and D. M. Kroeger (ORNL), "Grain Boundary Networks and Percolative Current Flow in Polycrystalline HTS Conductors," abstract submitted to 9th International Symposium on Superconductivity, Sapporo, Hokkaido, Japan, October 21-24, 1996.
- D. M. Kroeger, D. F. Lee, A. Goyal, and E. D. Specht (ORNL), "Processing and Long-Range Critical Current Transport in High Temperature Superconductors," being published as book chapter in *Proceedings of the First Pan-American Advanced Studies Institute*, Kluwer Academic Publishers.
- A. Goyal, E. D. Specht, D. K. Christen, and D. M. Kroeger (ORNL) and A. Pashitski, A. Polyanskii, and D. C. Larbalestier (University of Wisconsin Applied Superconductivity Center), "Percolative Current Flow in High J_c Polycrystalline High Temperature Superconductors," *J. Metals* **48**, 24-28.
- Q. He (Univ. Of Tennessee) and D. K. Christen, J. D. Budai, E. D. Specht, D. F. Lee, A. Goyal, D. P. Norton, M. Paranthaman, and F. A. List (ORNL), "Deposition of Biaxially Oriented Metal and Oxide Buffer-Layer Films on Textured Ni Tapes: New Substrates for High-Current, High-Temperature Superconductors," *Physica C* **275**, 155-61 (1997).
- Q. Li, G. N. Riley, Jr., R. D. Parella, S. Fleshler, M. W. Rupich, and W. L. Carter (American Superconductor Corporation); J. O. Willis, J. Y. Coulter, and J. F. Bingert (LANL); V. K. Sikka (ORNL); and J. A. Parrell and D. C. Larbalestier (University of Wisconsin), "Progress in Superconducting Performance of Rolled Multifilamentary Bi-2223 HTS Composite Conductors," submitted to *IEEE Trans. Appl. Supercon.*
- J. W. Lue, M. S. Lubell, E. C. Jones, J. A. Demko, D. M. Kroeger, and P. M. Martin (ORNL) and Uday Sinha and R. L. Hughey (Southwire Company), "Test of Two Prototype High-Temperature Superconducting Transmission Cables," paper presented at the 1996 Applied Superconductivity Conference, August 25-30, Pittsburgh, and to be published in conference proceedings by IEEE Transactions on Applied Superconductivity.
- M. S. Walker, D. W. Hazelton, M. T. Gardner, J. A. Rice, D. G. Walker, C. M. Trautwein, N. J. Ternullo, X. Shi, J. M. Weloth, and R. S. Sokolowski (IGC) and F. A. List (ORNL), "Performance of Coils Wound from Long Lengths of Surface-Coated, Reacted, BSCCO-2212 Conductor," paper presented at the 1996 Applied Superconductivity Conference, August 25-30, Pittsburgh, and to be published in conference proceedings by IEEE Transactions on Applied Superconductivity.
- M. Paranthaman, K. A. David, and T. B. Lindemer (ORNL), "Phase Equilibria of the MgO-Cu₂O-CuO System," *Mater. Res. Bull.* **32**, 165-73 (1997).
- J. G. Ossandon and J. R. Thompson (ORNL and Univ. Of Tennessee), "Stability of Supercurrents in BiSrCaCuO (Bi-2212) High- T_c Superconductor with Artificially Created Defects," paper submitted to *Superlattices Microstruct.*

- M. N. Kunchur (U.S. Air Force/Wright Laboratory and University of South Carolina), D. K. Christen (ORNL), and B. I. Ivlev (Landau Institute for Theoretical Physics), "Transport Behavior in Superconductors at Extreme Dissipation Levels," paper submitted to Proceedings of the International Symposium on Advances in Superconductivity: New Materials, Critical Currents, and Devices, held at the Tata Institute of Fundamental Research, Bombay, India, September 1996.
- M. Paranthaman, A. Goyal, F. A. List, E. D. Specht, D. F. Lee, P. M. Martin, Q. He, D. K. Christen, D. P. Norton, J. D. Budai, and D. M. Kroeger (ORNL), "Growth of Biaxially Textured Buffer Layers on Rolled-Ni Substrates by Electron Beam Evaporation," submitted to *Physica C*.
- A. Goyal, D. P. Norton, J. D. Budai, M. Paranthaman, E. D. Specht, D. M. Kroeger, D. K. Christen, Q. He, B. Saffian, F. A. List, D. F. Lee, P. M. Martin, C. E. Klabunde, E. Hatfield, and V. K. Sikka (ORNL), "High Critical Current Density Superconducting Tapes by Epitaxial Deposition of $\text{YBa}_2\text{Cu}_3\text{O}_x$ Thick Films on Biaxially Textured Metals," *Appl. Phys. Lett.* **69** (12), September 16, 1996.
- D. K. Christen, D. P. Norton, A. Goyal, J. D. Budai, Q. He, C. E. Klabunde, D. M. Kroeger, M. Paranthaman, B. Saffian, and E. D. Specht (ORNL), "Biaxially Oriented Metallic Tape Substrates for High-Temperature Superconductors," *Czech. J. Phys.*, **46**, Suppl. S3, 1531 (1996).
- R. A. Hawsey (ORNL) and D. E. Peterson (LANL), "Coated Conductors: The Next Generation of High- T_c Wires," *Superconductor Industry*, 23–29 (Fall 1996).
- A. Goyal, E. D. Specht, and D. M. Kroeger (ORNL), J. E. Tkaczyk, C. L. Briant, and J. A. DeLuca (GE), "Crystallization of Colonies of Locally Aligned Grains During Thallination of Spray-Pyrolyzed $\text{TiBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ Thick Films," *Appl. Phys. Lett.* **67** 2563–65.
- R. A. Hawsey, J. D. Budai, D. K. Christen, H. R. Kerchner, D. P. Norton, D. M. Kroeger, A. Goyal, F. A. List, P. M. Martin, R. K. Williams, D. F. Lee, M. S. Lubell, J. W. Lue, S. W. Schwensterly, M. Paranthaman, B. W. McConnell, Q. He, H. Hsu, D. R. James, E. C. Jones, H. E. McCoy, B. Saffian, S. Shoup, V. K. Sikka, E. D. Specht (ORNL), *ORNL Superconducting Technology Program for Electric Power Systems—Annual Report for FY 1995*, Oak Ridge National Laboratory, ORNL/HTSPC-7, May 1996.
- D. M. Kroeger and M. Paranthaman (ORNL), *Proceedings of the U.S. DOE HTS Wire Development Workshop, January 31–February 1, 1996, Tampa, Fla.*, Oak Ridge National Laboratory, CONF-960188, June 1996.
- L. Krusin-Elbaum (IBM), L. Civale (Centro Atomico Bariloche), J. R. Thompson (ORNL), and C. Feild (IBM), "Accommodation of Vortices to Columnar Defects: Evidence for Large Entropic Reduction of Vortex Localization," *Phys. Rev. B* **53** (17), 11744–50 (May 1, 1996).
- M. Paranthaman and B. C. Chakoumakos (ORNL), "Crystal Chemistry of $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ ($n=1,2,3,4$) Superconductors," *J. Solid State Chem.* **122**, 221–30 (1996).
- S. W. Schwensterly and V. Y. Wildon, *Rotor Instrumentation Study for High-Temperature Superconducting Generators*, Oak Ridge National Laboratory, ORNL/TM-13229, June 1996.

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