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**OAK RIDGE
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MARTIN MARIETTA

**ORNL Superconducting
Technology Program for
Electric Power Systems**

Annual Report for FY 1994

MASTER

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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

ANNUAL REPORT FOR FY 1994

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Manuscript Completed—October 1994
Date Published—December 1994

Prepared for the
Advanced Utility Concepts Division
Office of Energy Management
Office of Utility Technologies
Office of Energy Efficiency and Renewable Energy
U.S. DEPARTMENT OF ENERGY
(AK 06 00 00 0)

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under contract DE-AC05-84OR21400

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Acronyms and Initialisms

ASC	American Superconductor Corporation
CIP	cold isostatic pressing
CRADA	cooperative research and development agreement
CSL	coincident site lattice
CTE	coefficient of thermal expansion
DOE	U.S. Department of Energy
DOE-HQ	DOE Headquarters
EBSP	electron backscatter diffraction patterns
EDS	energy-dispersive spectroscopy
EM	electromagnetic
EPRI	Electric Power Research Institute
FWHM	full width half maximum
GE	General Electric Corporation
HIP	hot isostatic pressing
HTS	high-temperature superconductivity/superconductor
IBM	International Business Machines
ICP	inductively coupled plasma
IGC	Intermagetics General Corporation
LAMPF	Los Alamos Meson Physics Facility
MP	metallic precursor
MPM	mechanical properties microprobe
NREL	National Renewable Energy Laboratory
ORNL	Oak Ridge National Laboratory
PIT	powder-in-tube
REC	Reliance Electric Company
SCI	Superconductive Components, Inc.
SEM	scanning electron microscopy
SPI	Superconductivity Partnership Initiative
SQUID	superconducting quantum interference device
SUNY	State University of New York
TEM	transmission electron microscopy
TWP	tubular wire process
WNR	Weapons Neutron Research
XRD	X-ray diffraction

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 technology base needed by U.S. industry for commercial development of electric power applications of high-temperature superconductivity. The three major elements of this program are conductor development, applications development, and the Superconductivity Partnership Initiative. This document describes the major research and development activities for this program together with related accomplishments. The technical progress reported was summarized from information prepared for the FY 1994 Annual Program Review held July 19–20, 1994. 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 industrial competitiveness 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 products.

Highlights for Fiscal Year 1994

SIGNIFICANT ACHIEVEMENTS

- Oak Ridge National Laboratory (ORNL) was chosen by the Superconductivity Partnership Initiative generator project team, led by General Electric Corporation (GE), for a major project role.
- In partnership with ORNL and other laboratories, American Superconductor Corporation (ASC) demonstrated the ability to make 600-m lengths of high-temperature superconductor (HTS) wire conducting more than 10,000 A/cm².
- In partnership with ORNL and other laboratories, Intermagnetics General Corporation (IGC) recorded a world-record magnetic field with an HTS coil (2.6 T).
- In collaboration with GE, ORNL discovered a new mechanism for current flow in wires. Such discoveries are needed because current flow is very poorly understood and because currently only 10% of wire cross section carries current.
- *A Teacher's Guide for Superconductivity for High School Students* was completed by Robert Dull, a physics teacher from Largo, Florida, and H. R. Kerchner, an ORNL staff member. This effort was supported by both the Superconductivity Program and the U.S. Department of Energy's (DOE's) Office of Science Education. The guide was reviewed by local schools and science museums and is now available from the National Technical Information Service.
- At the Annual Peer Review of Projects for the Superconductivity Program for Electric Power Systems, an ORNL project, "AC Applications of HTS Wires and Coils," received the highest rating of any project in the entire DOE program. This project was highly acclaimed for its technology-transfer activities and received the highest overall score in that category. In addition to achieving excellent progress in wire and magnet development, this project was cited by the review committee as the "best example of industry/national laboratory collaboration in the entire program."
- As a result of the license by ORNL of superconducting aerosol powder production technology, Superconductive Components, Inc., announced the commercial sale of powders. This was the only new commercial product announcement in the DOE program this fiscal year.
- ORNL completed the first phase of the program's most comprehensive study of the mechanism for current flow in high-temperature superconductors. In two of the three classes of materials studied, reduced weak-link behavior was ascribed to some degree of biaxial alignment between grains, either on a macroscopic scale (tens of millimeters) or on a microscopic scale (<1 mm). ORNL's discovery of a "local order of grains," resulting in long-range percolative current paths through a network of small-angle grain boundaries at colony intersections, provides a working model for the microstructure of practical polycrystalline wires.

NOTABLE ACHIEVEMENTS

- ORNL chaired and developed the agenda in partnership with industry and national laboratories for a highly productive high-temperature superconducting wire development workshop. Hosted by Florida Power Corporation, the workshop was attended by more than 70 participants from industry, universities, and government laboratories. Priority development areas were identified, and additional coordination between DOE, the U.S. Department of Defense, and the U.S. Department of Commerce was discussed.
- ORNL demonstrated a new process for converting Bi-2223 precursor powders to the superconducting phase. The new process can be accomplished in 6 h, compared with the typical 200 to 300 h for processes in use by others. Bi-2223 is the principal powder used to make long superconducting wires.
- ORNL coordinated completion of the program annual operating plan for FY 1994. The plan was completed with input from all active program laboratories.
- Measurements of resistance vs current for thallium deposited on silver, made with a novel, ORNL-developed pulsed-current technique, have shown that the total wire resistance remains a factor of 10 below that of the silver for currents up to 10 times the critical current, even though the superconductor comprises only 1% of the wire cross section. These results (1) suggest important added stability for the thallium-based wires for use as current leads, fault-current limiters, or transmission lines and (2) enhance the prospect of operation above the critical current for brief periods of time with no damage to the structure.
- In collaboration with GE, ORNL demonstrated a reduction in total processing time of more than 20 min (>30%) for fabricating high-critical-current-density thallium wires. ORNL also proved that silver is a necessary component for high current density and determined that a silver content of at least 2% and at most 12% is required.
- ORNL and its industrial partners submitted a record eight new disclosures of possible subject inventions during FY 1994.
- In collaboration with American Superconductor Corporation, ORNL was the first organization to use microhardness as a quantitative measure in the deformation process development of HTS composite wires. The insights gained through this work ultimately led to the fabrication by ASC of the world's longest length of high-performance HTS wire.
- In collaboration with GE, ORNL completed a conceptual design report for a partial helical stator winding for a 100-MVA superconducting generator. This phase of the Superconductivity Partnership Initiative project was completed on schedule and within budget and has been deemed to be of substantial commercial interest to GE.
- In collaboration with the Teacher Research Associates Program, ORNL produced a *Teacher's Guide to Cryogenics and Superconductivity for Middle School Students*. The guide also includes a videotape and instructions for obtaining laboratory demonstration materials.

- “Stability and Protection of Ag/BSCCO Magnets Operated in the 20–40 K Range” [*Cryogenics* 33(9), 900–909 (1993)], a paper by Larry Dresner of ORNL’s Fusion Energy Division, was selected to receive the British Cryogenics Council’s Cryogenics Best Paper Award.

Technical Progress in Wire Development

CRITICAL CURRENTS AND MICROSTRUCTURES OF HIGH-TEMPERATURE SUPERCONDUCTOR MATERIALS

Pulsed Transport Current Studies of Conductors in the Dissipative State

In this project, pulsed currents were used to study the dissipative state of short-segment conductors at current levels well above the critical current (I_c). The objective was to determine the feasibility of transient or steady-state operation in the superconductive dissipative state. The use of pulsed currents enables such studies on short, prototype samples, in which low-resistance current contacts cannot be obtained by current injection over a large contact area (or length). In addition, the short pulse duration limits the total energy input so that experiments can be extended to power-loss levels, where in a dc experiment the internal heating, such as at weak links, might otherwise destroy the sample. This initial, preliminary study involved a comparison of various conductor materials and forms operating in self-field at the temperature of liquid nitrogen (77 K). In this regard, the results may be useful when considering materials and designs for current leads or power transmission lines.

For reliable pulsed-current measurements, the inevitable transient inductive-impedance voltage spikes must decay completely during the pulse duration, leaving only the pseudo-dc voltage characteristics of the superconductor. A key to an effective pulsed-current system is achieving a rapid rise time, followed by a very time-independent current during the pulse. The pulsed-current and detection system used in this project was developed and constructed in house and was specially designed for these types of experiments.

Prototype short conductors were obtained from industrial partners and university collaborators. The samples included melt-processed YBCO rods, TI-1223 and TI-1223/Ag deposits, Bi-2223 monocoil and multiple-core tapes, and YBCO epitaxial films for baseline comparisons. The various contributors were ASC, AT&T Bell Laboratories, GE Corporate R&D, IGC, and the University of Houston.

Figure 1.1 shows the resistance vs current of a YBCO melt-processed rod that contains a single weak-link grain boundary, as illustrated in the inset. The resistance rises rapidly at the onset of dissipation at $I \leq 2$ A and then rises much more slowly to current levels that are more than 100 times I_c . For comparison, the resistance of an equivalent sample of pure silver at 77 K is plotted. Obviously, such a weak-linked material is not useful compared with a good normal metal; however, the resistance level at nearly 300 A remains well below the estimated normal-state resistance (R) of YBCO, which for this sample is in the range of 2 m Ω at 77 K. This observation implies that the superconducting grains on either side of the grain boundary remain at a low dissipation level, with nearly all of the loss at the grain boundary. On the other hand, an assumption that all loss occurs at a "normal" grain boundary would indicate a grain boundary's effective length of about 15 μm .

In contrast, Fig. 1.2(a) illustrates results on a similar rod that has a single well-coupled grain boundary. Even though the sample cross section is smaller by a factor of 7, the critical current is nearly 15 times larger, and the resistance in the dissipative state is smaller by a similar factor. Figure 1.2(b) shows a logarithmic plot of the resistivity vs current density (J),

Fig. 1.1. The resistance of a YBCO melt-textured rod having a single weak-linked grain boundary as a function of pulsed current levels to more than 100 times I_c . The resistance of an equivalent sample of pure silver at 77 K is shown for comparison.

Fig. 1.2. (a) The resistance vs current of a YBCO melt-textured rod having a single well-coupled grain boundary. (b) The resistivity vs current density compared with that of pure silver at 77 K.

and these specific material properties are again compared with those of pure silver. In this case, at J levels up to $40,000 \text{ A/cm}^2$ (4 times the critical value), the YBCO resistivity remains nearly two orders of magnitude below that of silver and about 0.5% that of the weak-linked material. For example, at the 100-A level, the volume joule heating is about 1.7 mW/cm^3 , which corresponds to about 0.6 W/m of length, or only 14-mL/h liquid nitrogen boil-off rate.

Similar results were obtained for spray-pyrolyzed Tl-1223 deposits on polycrystalline YSZ substrates. These 3- μm -thick materials are strongly textured, with the c axis normal and in-plane colony microstructure that yields strongly coupled percolative paths, as described elsewhere in this report. Figures 1.3(a) and 1.3(b) illustrate these results and demonstrate that these materials also might be useful for operation above a critical current density (J_c) at 77 K.

Figures 1.4(a) and 1.4(b) show results for some high-temperature superconducting/silver (HTS/Ag) composite conductors. Figure 1.4(a) contains the data for two Bi-2223/Ag powder-in-tube (PIT) tapes; Fig. 1.4(b) contains data for two Tl-1223 deposits on polycrystalline silver substrates. One BSCCO tape is monocoil and the other is multifilament, as indicated. For the PIT tapes, the HTS/Ag volume fraction is 20–25%, whereas for the 3- μm -thick Tl-1223 deposits, the ratio is just over 1%. One of the Tl-1223 films was given a postanneal in pure oxygen at 550°C , which has been found to increase the J_c . The results of Fig. 1.4(b) indicate that this procedure also reduces the dissipation for $J > J_c$. In this case, it is noteworthy that even though the Tl-1223 comprises ~1% of the conductor, the total resistance remains nearly an order of magnitude below that of the silver substrate, even at a current level of 50 A, which is 10 times the critical current.

Fig. 1.3. (a) Resistance vs current for a TI-1223 3- μ m-thick deposit on polycrystalline YSZ. (b) Resistivity vs current density compared with that of silver.

To obtain a more quantitative assessment of the HTS material properties in the conductors, we have modeled the silver as a parallel conduction path and thereby extracted the HTS current density and resistivity. The silver resistance at 77 K is found from extrapolation of the nearly linear $R(T)$ curve obtained for temperatures above T_c . The overall results are shown in Fig. 1.5, in which the HTS resistivity is represented as a fraction of that for pure silver at 77 K. The current density has been normalized with respect to

Fig. 1.4. The total conductor resistance vs current for (a) two commercial BSCCO PIT tapes and (b) two TI-1223 deposits on polycrystalline silver substrates.

that measured for the HTS of each conductor. Figure 1.5 confirms that YBCO and TI-1223 have intrinsically superior properties for operation at 77 K. This fact and these results should be important considerations in designing conductors for certain applications, such as current leads and transmission cables. Resistivity levels in the HTS materials that are several orders of magnitude below pure silver may provide added stability, or even prospects of low-power-consumption operation, above I_c .

Fig. 1.5. The normalized resistivity and current densities for the HTS components of the conductors. For the resistivity of pure silver at 77 K, $2.8 \times 10^{-7} \Omega\text{-cm}$ was used. The determined HTS current densities are monofilament BSCCO, 17,000 A/cm²; multifilament BSCCO, 3500 A/cm²; unannealed TI-1223 deposit, 14,500 A/cm²; annealed TI-1223 deposit, 30,000 A/cm²; and melt-processed YBCO rod, 10,000 A/cm².

Flux Pinning Enhancements in Bi-2212/Ag Tapes by Energetic Light-Ion Irradiations

The objective of this research was to find a potentially practical and scaleable process by which to increase and optimize flux pinning in Bi-2212/Ag composite tape conductors. The current approach was motivated by previous studies of greatly enhanced flux pinning by nearly ideal columnar defects produced by irradiations with energetic heavy ions such as tin, gold, silver, or lead. In that case, however, the columnar damage production occurs over a limited range of only 20 to 30 μm and is impractical for bulk conductors. In addition, the columnar defects produced by heavy ions are nearly parallel, so that the flux pinning is greatest when the vortices are aligned parallel to the defects. However, previous work showed that this angular selectivity is a weak effect in the

nearly two-dimensional BSCCO superconductors and that the flux pinning is significantly enhanced for all orientations of the field. Recently it was suggested theoretically that randomly oriented (splayed) columnar defects may be more effective pinning sites than parallel columns.

In this study it was demonstrated that splayed columnar defects can be produced in Bi-2212/Ag tapes by irradiation with energetic light particles (0.8-GeV protons) and that these defects provide large increases in the current-carrying capability and large enhancements in the field and temperature range of applicability. The columnar damage tracks are created randomly by the fragments of bismuth nuclei that are fissioned by absorption of an energetic proton. The fission fragments are sufficiently heavy (e.g., krypton or xenon) and energetic enough to create extended damage tracks in the BSCCO material. The principal advantage, however, is the very large projected range of protons in the conductor of nearly a half meter. Thus, bulk conductors and possibly prefabricated forms might be irradiated for improved flux pinning.

The investigation was a feasibility study and was facilitated by a multi-institutional and multidisciplinary effort. The Bi-2212/Ag conductors were fabricated at the State University of New York (SUNY) at Buffalo and comprised 3- to 4- μm -thick, *c*-axis-oriented deposits on polycrystalline silver foils. Irradiations were conducted at the Los Alamos National Laboratory Los Alamos Meson Physics Facility (LAMPF) at the Weapons Neutron Research (WNR) facility. Effects of the irradiations on the critical current density (J_c), irreversibility lines, and flux creep were determined by superconducting quantum interference device (SQUID) magnetometry studies conducted at International Business Machines (IBM) and

ORNL. Microstructural characterizations of the defects were made by transmission electron microscopy (TEM) at Argonne National Laboratory.

Three different proton fluences were chosen to produce calculated defect densities of 3.3, 5.8, and 10.5×10^{13} fission fragments/cm³. The TEM studies confirmed that the defects were columnar in nature, nearly random in orientation, and about 7 nm in diameter and 6–7 μ m long, which is larger than the BSCCO deposit thickness. Measurements of the magnetic hysteresis before and after irradiation were made as a function of temperature for applied magnetic fields up to 5.5 T. At the irradiation doses used, the degradation of T_c was negligible.

Figure 1.6 illustrates the enhancement of J_c at low temperature that occurs for increasing proton fluence. In an applied field of 1 T parallel to the c axis (the applications-limiting orientation), J_c is observed to increase monotonically with irradiation dose, to a total enhancement by a factor of 6, and has not yet reached a saturation value at the highest fluence used.

Fig. 1.6. The critical current density as a function of proton fluence, determined from the magnetic hysteresis at 5 K in an applied field of 1 T.

The relative improvements in J_c are most important and dramatic at higher temperatures. Fig. 1.7 shows J_c as a function of temperature for several magnetic fields applied parallel to the c axis at the highest proton dose, which produces 6.5×10^{15} fission tracks/cm². In fields greater than 2 T, there was essentially no available J_c above 20 K in the unirradiated state. After irradiation, practical levels of $\sim 10^4$ A/cm² were available at 20 K, even for this unfavorable orientation. At 1 T, the temperature range of usefulness has been extended by nearly 20 K. In applications where the field component along the c axis can be minimized, the range of usefulness can be extended to higher temperatures. In addition, it is likely that the range of high-temperature operation can be expanded even further because Fig. 1.6 indicates that higher fluences will result in further enhancements in J_c at low temperature.

The enhancements in the irreversibility regime after irradiation to the maximum dose are demonstrated in Fig. 1.8; results of the current light-ion irradiations are

Fig. 1.7. The temperature dependence of the critical current density before irradiation (open symbols) and after the maximum irradiation dose (closed symbols). Data are presented for three magnetic field intensities applied parallel to the c axis.

Fig. 1.8. Irreversibility lines of the Bi-2212/Ag tapes before and after irradiation with 0.8 GeV to the maximum dose used. The proton irradiation results (open symbols) are compared with near optimum properties of Bi-2212, TI-1223, and YBCO after irradiation with energetic heavy ions to produce parallel columnar defects. Here B_ϕ refers to the columnar defect density, expressed as a matching vortex flux density.

compared with the improvements found in earlier work on Bi-2212, TI-1223, and YBCO after irradiations with heavy ions to near-optimum defects densities. In Fig. 1.8, the areal density of columnar defects is expressed as an equivalent vortex flux density, B_ϕ . (For the case of splayed columnar defects, the physical significance of B_ϕ may be thought of in terms of matching the total length of vortices and defects per unit volume.) Because $B_\phi \approx 1.4$ T for the splayed defects from the maximum proton dose, these comparisons also suggest that further improvements may be realized in Bi-2212 at larger fluences of highly penetrating light ions. Of course, Fig. 1.8 underscores the now well-established, superior properties of the less anisotropic TI-1223 and YBCO materials.

The effectiveness of splayed columnar defects in enhancing flux pinning in Bi-2212 has been established by this study. A direct comparison of their efficacy in comparison with the parallel defects

produced by heavy-ion irradiations must await further experiments in which the proton fluences are sufficient to produce comparable columnar-defect densities (i.e., $B_\phi \approx 3\text{--}5$ T). The most important advantage of the current technique is the large proton penetration range, which raises the possibility of postprocessing for tailored flux pinning in a "batch process" (e.g., irradiating an entire prefabricated structure). Remaining important issues for future work concern establishing the feasibility of the technique for other HTS materials, determining the optimum dose, determining the minimum proton energy needed for practical enhancements, and ascertaining the scaleup possibilities (e.g., determining whether the beam can be made large and intense enough or rastered for irradiation of large structures).

Local Texture and Grain Boundary Misorientations in Bi-2223 PIT Conductor and TI-1223 Deposits

Introduction

The orientations of hundreds of contiguous grains in high- J_c $\text{TiBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ deposits and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ PIT tapes have been determined from electron backscatter diffraction patterns (EBSP). The misorientation angles and axes of rotation (angle/axis pairs) for grain boundaries connecting these grains were calculated. For both materials the population of low-angle boundaries was found to be much larger than expected from calculations based on their macroscopic texture. The $\text{TiBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ deposits exhibit pronounced local texture that has been defined by EBSP and X-ray diffraction (XRD). Locally, grains show good in-plane (a -axis) alignment even though macroscopically a axes are random, indicating the presence of colonies of grains with similar a -axis orientations. In

(Bi,Pb)₂Sr₂Ca₂Cu₃O_y tapes, no local texture was observed. In both materials the existence of connected networks of small-angle grain boundaries can be inferred. Coincident site lattice (CSL) grain boundaries are also present in higher numbers than expected. Grain boundary energy thus appears to play a significant role in enhancing the population of potentially strongly linked boundaries. We propose that long-range strongly linked conduction occurs through a percolative network of small-angle (and perhaps CSL) grain boundaries.

Computer Simulation of the Misorientation Distribution as a Function of Macroscopic Texture

Goyal et al.¹ have shown that the difficult geometrical problem of determining the distribution of misorientation angles for a polycrystalline material of any crystal symmetry can be solved by a conceptually simple numerical simulation. The method involves generating, from the Euler angle description of the orientation of a crystal, a set of randomly oriented grains and then determining the angle-axis pairs that describe the misorientations between all of the pairs of grains that can be formed from the set. A set of 200 randomly oriented grains was used, resulting in nearly 20,000 grain boundaries. The misorientation between two grains can be described by an axis and the angle through which one of the grains must be rotated about this axis to align the grains. For a given crystal structure there is a set of equivalent angle-axis pairs that describe a given grain boundary misorientation. By convention, the pair with the smallest positive misorientation angle is chosen.

Figure 1.9 shows the distribution of misorientation angles obtained from the simulation of a randomly oriented

polycrystalline cubic material. The shape of this histogram is in good agreement with the theoretical calculation of Mackenzie.² The fraction of grain boundaries with misorientation angles less than a given angle can be obtained by summing and normalizing the results in Fig. 1.9 and is shown in Fig. 1.10 (solid curve). Similar curves are shown for tetragonal and orthorhombic materials. It is apparent that for all three the population of boundaries with misorientation angles less than 10° is small. Goyal et al.¹ have shown that specific macroscopic textures can be imposed on the set of grains from which grain boundaries are formed by restricting the range of values from which certain of the Euler angles describing grain orientations are randomly chosen. The effect of *c*-axis texture on the distribution of misorientation angles is shown in Fig. 1.11. The fraction of misorientation angles less than an angle Θ is plotted for cases in which the *c* axes of grains are restricted to angular ranges of 10°, 20°, etc., and the *a* axes are random and not restricted. The number of small-angle

Fig. 1.9. Distribution of misorientation angles for the 20,000 "grain boundaries" that could be formed among 200 randomly oriented grains. The shape of the histogram agrees well with the calculated curve of Mackenzie.²

Fig. 1.10. Fraction of misorientation angles less than a given angle, obtained from 20,000 simulated grain boundaries for cubic, tetragonal, and orthorhombic symmetries.

Fig. 1.11. The effect of macroscopic *c*-axis texture on the misorientation angle distribution from simulations for tetragonal symmetry. Because the 200-grain set from which grain boundaries were formed was randomly selected, deviations of the *c* axes from perpendicular to the sample plane were restricted as indicated.

boundaries increases as the range of variation of the *c*-axis orientation is decreased. For perfect *c*-axis alignment, 22.2% of boundaries would have misorientation angles less than 10°. Bi-2223 PIT conductors typically have *c*-axis rocking curves with full-width-at-

half-maximum (FWHM) of ~15–20°, suggesting that the 10° or 20° curves in Fig. 1.11 may apply to them, whereas the Tl-1223 spray-pyrolyzed deposits have FWHM ~1–2°. These simulations yield misorientation angle distributions based solely upon geometry. Factors such as the variation of grain boundary energy with misorientation and grain boundary plane, grain morphology as determined by surface and interfacial energies, and processing factors may strongly affect the distribution of misorientation angles in a real material. As will be shown in the following paragraphs, this is indeed the case for the Tl-1223 deposits and Bi-2223 conductors we have examined.

Experimental Determination of Grain Boundary Misorientation Distributions

Because the distribution of grain boundary misorientations is not related uniquely to macroscopic texture (e.g., it can be affected by grain boundary energies), it must be determined from measurements of the orientations of contiguous grains. The most rapid and efficient method for obtaining orientations of individual grains is electron backscatter diffraction. The orientations of hundreds of contiguous grains were determined in Tl-1223 deposits and in Bi-2223 PIT conductors in facilities at the GE Corporate Research and Development Center and at TEXSEM Laboratories in Salt Lake City, Utah.

Bi(Pb)-2223 PIT Conductor

Multifilamentary Bi(Pb)-2223 conductors prepared by the oxide PIT method and having $J_c \approx 20,000 \text{ A/cm}^2$ in self-field at 77 K were examined. Silver was removed from one side by chemical etching to expose filament surfaces.

Figure 1.12 shows a scanning electron microscopy (SEM) image of a filament surface. Most grain boundaries are clearly visible, permitting determination by EBSP of the orientations of adjacent grains. Diffraction patterns were obtained for all of the grains that could be distinguished in several small areas containing from 15 to ~100 contiguous grains.³ The dominant pole in the diffraction pattern exhibited fourfold symmetry and was indexed as the (001) pole of the approximately tetragonal Bi-2223 subcell. From the absolute orientation of grains, grain boundary misorientations were calculated in the form of axis/angle pairs. Figure 1.13 shows the proportion of small-angle and CSL boundaries found in an area containing 227 identifiable boundaries. More than 30% of the boundaries have misorientation angles less than 10° . The FWHM for the *c*-axis rocking curve from XRD for this sample is $\sim 20^\circ$, typical of Bi-2223 PIT conductors. From Fig. 1.11 we see that in a textured material in which the *c*-axis directions of grains are similarly restricted and grain

Fig. 1.12. SEM image of the Bi-2223 surface of a filament revealed by etching away the silver from a multifilamentary PIT specimen. Grain boundaries are clearly visible, permitting determinations by EBSP of the orientations of contiguous grains.

orientations are not locally correlated, fewer than 5% of grain boundaries would have misorientation angles less than 10° . The high concentration of small-angle boundaries presumably results from the fact that small-angle boundaries have lower energies. The properties and therefore the importance of CSL boundaries have not been determined, although there are indications that some CSL boundaries may be better than other large-angle boundaries.⁴ The data in Fig. 1.13 suggest that their numbers are only slightly enhanced in PIT Bi-2223; however, the data that follow for Tl-1223 deposits provide a different picture. That $\sim 30\%$ of grain boundaries have small misorientation angles suggests that percolative paths for strongly linked flow exist. Examination of maps of misorientation angles over small areas indicates that two-dimensional percolative paths among grains at the silver-superconductor interface revealed by etching away the silver can indeed be found.³ Moderate *c*-axis texture leaves many misaligned grains, which ensure that current flow is three-dimensional^{5,6} and increase the number of percolative connections.

With moderate *c*-axis alignment, most grain boundaries do not involve pure rotations about a principal axis and have

Fig. 1.13. Statistics for small-angle and CSL boundaries for a Bi(Pb)-2223 conductor.

mixed character (i.e., have both tilt and twist components). The properties of such mixed grain boundaries have not been measured. Although the microstructural origins of weak-link behavior at grain boundaries are not fully known, there are two reasons to expect that small-angle and CSL boundaries may be good. First, impurity and cation constituent segregation to grain boundaries is driven by grain boundary energy. Therefore, low-energy boundaries should be cleaner and more stoichiometric, factors that have been shown to have a secondary effect on weak-link behavior in $\text{YBa}_2\text{Cu}_3\text{O}_7$.⁷ Of greater general importance are the changes in grain boundary structure with misorientation angle. Strain at small-angle boundaries (typically less than 15°) and CSL boundaries is accommodated by a series of dislocations, the spacing between which is inversely related to the misorientation angle. The resulting strain field at the grain boundary has periodically spaced regions of low strain, through which it has been speculated that strongly linked current may flow. As the misorientation angle or deviation from ideal CSL increases, the dislocation core spacing decreases and the areas of low strain decrease. For misorientation angles greater than about 15° , dislocation cores overlap.

TlBa₂Ca₂Cu₃O_{8+x} Deposits

High J_c $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ deposits on yttria-stabilized ZrO_2 substrates have been examined by XRD, TEM, and electron backscatter diffraction.⁸⁻¹⁰ The superconducting phase was formed by vapor-phase thallination of a spray-pyrolyzed thallium-free precursor deposit by procedures that have been described previously.^{11,12} Typically, the FWHM of a c -axis rocking curve is $1-2^\circ$, indicating very good c -axis texture. Thickness is ~ 3 μm , and grains tend to be 0.2 to 1 μm

thick (in the c direction) and 3 to 10 μm in the plane. J_c measured resistively with voltage contact spacing in the range of 1 to 4 mm (therefore spanning hundreds of grains) is typically $0.5-1 \times 10^5$ A/cm^2 in self-field at 77 K and has good field dependence. At 40 K in fields up to 9 T, J_c remains well above 10^4 A/cm^2 .¹¹ X-ray phi scans were used to study the local and macroscopic in-plane texture. A large X-ray beam (4×8 mm), which illuminated most of the specimen surface, indicated random a -axis orientations (i.e., no macroscopic in-plane texture). However, restricted beams of 0.5×1 mm and 100×100 μm showed a very high degree of in-plane texture. These results were interpreted as indicating the presence of colonies of grains with similar a -axis orientations.

The colony microstructure was confirmed by EBSP determinations of the orientations of individual grains. Figure 1.14 is an SEM image of the surface of a Tl-1223 deposit showing growth ledges, pores, and second-phase particles. Both polished and unpolished surfaces were analyzed successfully by

Fig. 1.14. SEM image of the free surface of a polycrystalline $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ deposit. Grain boundaries cannot be discerned.

EBSP. In neither case could grain boundaries be revealed in SEM; the following procedure was required for mapping a -axis orientations. The diffraction pattern was observed while the electron beam was moved in a line over the sample surface. When a shift in the pattern was observed, the new pattern was recorded and analyzed to obtain the local crystalline orientation. Because the c axes were very well aligned, the orientation of a grain can be represented by a single arrow in the a direction. In Fig. 1.15, the a -axis directions are plotted for a 40- by 120- μm area. The beam was moved along parallel lines separated by 12 μm to obtain data over the rectangular grid. An arrow is plotted only where a shift in diffraction pattern was seen (i.e., after crossing a grain boundary). The spacing between arrows is

Fig. 1.15. Arrow map of the projections of a axes onto the sample plane over a 40- by 120- μm area on a Ti-1223 deposit. The arrows have similar directions, indicating that the area is within a colony. The e-beam was scanned along a horizontal line. When the pattern changed, indicating that a grain boundary was traversed, the new grain orientation was calculated and the a -axis projection plotted. The angle-axis pairs were also calculated. For 80% of the boundaries, $\Theta < 10^\circ$.

roughly indicative of grain size, although surface irregularities prevented obtaining patterns in some areas and therefore some shifts in orientation were missed. Clearly this area is within a single colony. The total spread in a -axis orientation is ~ 15 – 20° . Figure 1.16 shows a similar map over a somewhat larger area of the same sample. In this case an irregularly shaped colony intersection can be discerned clearly. The average a -axis orientations of the two colonies differ by ~ 35 – 40° . Figure 1.17 shows an EBSP map of another colony intersection. In this case there appears to be a gradual change of orientation across the intersection; hence, the colony boundary is not easily discerned. Larger, more complex regions contain a mixture of the three cases illustrated in Figs. 1.15 through 1.17. Colony dimensions in the plane appear to be in the range of 0.1 to 1 mm. Colonies have irregular shapes and therefore large areas of intersection. We note that these

Fig. 1.16. An a -axis arrow map for an area that contains a sharp colony intersection, indicated by the hand-drawn curve. For 75% of boundaries, $\Theta < 10^\circ$, and 54% of boundaries with $\Theta < 15^\circ$ are within the Brandon criterion for an ideal CSL.

Fig. 1.17. An a -axis arrow map for an area in which orientation appears to change gradually without a well-defined colony boundary. Fifty-two percent of boundaries have $\Theta < 10^\circ$, and 14% of large-angle boundaries are within the Brandon criterion for an ideal CSL.

colonies are different from those in BSCCO, which consist of stacks of c -axis-aligned grains that are connected by twist boundaries. In these Tl-1223 deposits, colony intersections are made up of a large number of c -axis tilt-grain boundaries. Most grain boundaries within a colony have small misorientation angles and thus should not be weak links. We have proposed that long-range current transfer occurs through a percolative network of small-angle grain boundaries at colony intersections.⁸⁻¹⁰ The number of such small-angle grain boundaries should increase with the spread in orientation of grains within a colony and with any tendency for adjacent colonies to have similar orientations as might result from a local bias of colony orientation. The FWHM of peaks in XRD azimuthal scans tends to be ~ 10 – 20° , indicative of a similar spread in a -axis orientation. Because Tl-1223 is tetragonal,

the maximum misorientation angle between c -axis-aligned grains is 45° . Thus, if colonies are randomly oriented and if each colony intersects several other colonies, it is probable that a significant fraction of intersection area will have overlapping grain orientation distributions. The critical current of a randomly generated lattice of colonies having a spread in a -axis orientation derived from XRD measurements was simulated using the limiting path method. The model predicts significantly higher in-field J_c for a colony microstructure than for a c -axis-textured deposit with random a -axis orientations.

The nature of grain boundaries at colony intersections appears to largely determine long-range J_c . It is thus important whether grain boundary misorientations at colony intersections are statistically determined by the grain orientation distributions in the adjacent colonies as assumed in the previous discussion or whether the distribution is biased by grain boundary energy or currently undefined aspects of the growth process. In Figs. 1.15 through 1.17, statistics are given for the fraction of small-angle and CSL boundaries obtained by calculating angle-axis pairs for adjacent points along a horizontal line. As expected, in all areas most grain boundaries have small misorientation angles. In Fig. 1.16, which includes a well-defined colony intersection, a high fraction of large-angle boundaries are within the Brandon criterion for an ideal CSL. Because most of these large-angle boundaries are at the colony intersection, this result suggests that grain boundary energy may significantly affect grain boundary misorientations at colony intersections. Among the several specimens and areas examined, the misorientation angle distributions vary considerably, but in all of these areas the population of CSL boundaries appears to be elevated.

Conclusions

The results presented demonstrate that for both the Bi-2223 conductor and Tl-1223 deposits, small-angle grain boundaries are present in much higher numbers than expected statistically from macroscopic textures. This result, in conjunction with the growing body of evidence that large-angle boundaries (possibly excluding CSL boundaries) in most, if not all, oxide superconductors are weak links, strongly suggests that long-range conduction occurs by percolation through a connected network of small-angle (and perhaps CSL) boundaries. Critical current density is determined by local grain boundary misorientations, not macroscopic texture. Texture determines the probability that adjacent grains will have similar orientations. Grain boundary energy provides a driving force that skews the misorientation distribution toward small-angle and probably CSL boundaries. The percolative paths in the two materials are very different. In the Tl-1223 deposits a very high density of small-angle grain boundaries is associated with the colony microstructure, and long-range conduction depends on percolation through a much smaller population of small-angle (and possibly CSL) boundaries at colony intersections. In a Bi-2223 conductor, a randomly distributed but smaller population of small-angle boundaries is sufficient to ensure percolation of current. It is well known that J_c in Bi-2223 conductors does not correlate perfectly with the degree of c -axis alignment and second-phase content as determined from XRD and microscopic examination of polished cross sections. We suggest that the population of small-angle boundaries is the "hidden variable" with which J_c correlates.

Percolation through a network of low-energy boundaries is offered as a general model for long-range conduction in

polycrystalline superconductors. This model lacks the specific drawbacks of previous models: Conduction in the c direction is not required, and grain boundary behavior is assumed to be the same in all high- T_c materials. In addition to the materials discussed in this report, the model also appears to explain strongly linked current flow in multifilamentary YBa₂Cu₄O₈ conductors prepared by the oxidation-of-metallic-precursor method.¹³ In that material, XRD indicates modest biaxial texture, whereas selected area diffraction in TEM indicates a sharper local texture in the regions examined. This material appears to have yet another arrangement of grains leading to a connected network of small-angle boundaries, the complete definition of which requires further study.

The proposed model for long-range conduction is based on the assumption that for clean grain boundaries $J_c(gb)$ is determined by the misorientation angle. It is recognized, however, that because structure and superconducting properties are anisotropic, the axis of rotation and grain boundary plane may affect $J_c(gb)$. These results indicate the importance of further studies of the effects of grain boundary geometry on $J_c(gb)$.

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Model of the Effect of Colonies of Aligned Grains on Critical Current in High-Temperature Superconductors

High-temperature superconductors generally exhibit excellent intrinsic transport properties, supporting high critical currents (J_c 's) even in magnetic fields. Thus far, however, these properties have been realized only in highly aligned materials such as epitaxial thin films. It remains a challenge to produce aligned materials that will carry current over the

distances required for practical applications (typically 1 m to 1 km).

High J_c 's, both in and out of a magnetic field, have been reported in Tl-1223 films deposited on YSZ substrates.^{1,2} The high values of J_c —more than 10^5 A/cm² in a zero magnetic field at a temperature of 77 K, and 10^4 A/cm² in a 2 T field at 60 K—are of particular interest because the films are made using techniques that are amenable to production of useful quantities of superconducting wire: The substrates are polycrystalline and the films are spray deposited. The high J_c 's are not, however, obtained consistently; J_c 's vary by as much as a factor of 35 between different 1- by 0.2-mm segments of a 4- by 0.2-mm film. Although the films have an overall c -axis alignment normal to the surface, segments of high J_c have been shown to coincide with colonies of grains, up to 1 mm in extent, with aligned a axes; over larger distances, the a axes are aligned randomly in the plane of the film.^{3,4}

The colony microstructure observed in Tl-1223 films clearly leads to high intracolony J_c . It has been suggested that this microstructure can produce high intercolony J_c as well.^{3,4} Because each colony contains grains with a distribution of orientations, even relatively high-angle colony boundaries will contain a fraction of low-angle grain boundaries. These low-angle boundaries may provide a percolative high-current path.

The conditions under which a colony microstructure can enhance J_c significantly are discussed in this section. X-ray microdiffraction is used to map the distribution of grain orientation over a 4- by 5-mm area, providing a statistical measure of colony size and of the mosaic of orientations within each colony. Simulations, based on this orientational map and on measurements of J_c as a function of misorientation at grain

boundaries,⁵ show that grain alignment can account for a great deal of the variation observed in J_c for short segments. Simulations of the critical current of a randomly generated lattice of colonies show that in zero magnetic field this colony structure can increase J_c by a factor of 2.7 over a film with no in-plane alignment. Simulations of J_c in a magnetic field indicate a 15-fold increase for an optimal colony microstructure.

Measurements were made of a Tl-1223 film, 3 μm thick, deposited on polycrystalline YSZ. The deposition process is described in refs. 1 and 2. A monochromatic synchrotron X-ray beam 0.1 mm in diameter was used to map grain orientation as described in ref. 3. Briefly, the sample was mounted in a symmetric geometry (incident and diffracted beams at equal angles to the film normal) at a scattering angle and inclination set for diffraction from $\{1\ 1\ 18\}$ planes of c -aligned grains. A rotation of the sample about the film normal brings each grain into alignment for diffraction at an angle corresponding to its in-plane a -axis orientation. The distribution of grain orientations was measured at each point on a 5- by 4-mm square grid with 0.2-mm spacing. The crosses in Fig. 1.18 indicate the most common orientation at each measured point. The colony structure is reflected in the similar orientation of neighboring points.

The colony microstructure is described quantitatively by an orientational correlation function (Fig. 1.19):

$$C(r, \phi) = \frac{\langle [I(r_o, \phi_o) - \bar{I}] \cdot [I(r_o + r, \phi_o + \phi) - \bar{I}] \rangle_{r, \phi}}{\bar{I}^2}, \quad (1)$$

where $I(r_o, \phi_o)$ is the diffracted intensity from position r_o and orientation ϕ_o , $\bar{I}$ is the average measured intensity, and the brackets $\langle \rangle_{r, \phi}$ indicate an average over all pair of measurements separated by

Fig. 1.18. Map of grain orientations. Each cross indicates the orientation of the a axes for the most common orientation in a region 0.1 mm in diameter.

Fig. 1.19. Orientational correlation function illustrating the decay of correlations with distance.

displacement r and misorientation ϕ . To better understand what the correlation function measures, a distribution of orientations $I(r_o, \phi_o)$, which is Gaussian for each position r_o , must be considered. The zero-displacement correlation function $C(0, \phi)$ will be Gaussian as well, but with a width $2^{1/2}$ as great. Thus, we use $2^{-1/2}$ times FWHM of $C(0, \phi)$ as a measure of the

FWHM of the colony mosaic. For circular colonies of diameter D ,

$$C(0.5D,0) = C(0,0)/2.$$

We use this equation to determine a statistical colony size D . In this way we find that the film consists of colonies with typical size $D = 0.4$ mm and mosaic 16° FWHM.

To test whether this colony microstructure causes the observed^{1,2} variations in J_c , J_c is calculated from the observed map of orientational distributions. For all near-neighbor points i and j in the array shown in Fig. 1.18, critical current is computed from

$$J_c = \frac{\langle i_i(\phi_i)j_j(\phi_j)i_c(\phi_i - \phi_j) \rangle}{\bar{i}_i \bar{i}_j}, \quad (2)$$

where the average $\langle \rangle$ is over all pairs of angles ϕ_i and ϕ_j . The grain boundary critical current i_c , based on measurements of Tl-1223 films on SrTiO₃ bicrystals at 77 K in zero magnetic field,⁵ is 1×10^5 A/cm² for grains aligned to within 12° and 3×10^3 A/cm² otherwise. In Table 1.1, J_c measured for 1- and 4-mm-long segments in a superconducting film was compared with J_c 's calculated for all regions of the same dimensions within the area shown in Fig. 1.18. Calculations based on the observed colony microstructure give an excellent prediction of the average values of J_c and account for most of the variation in J_c for these highly homogeneous films.

To see what effect a colony microstructure will have on long wires, J_c was simulated for a 100×100 square array of colonies, each with random orientation. Grain orientation within each colony follows a Gaussian distribution, with the same FWHM for each colony. Intercolony J_c is calculated from Eq. (2); based on ref. 5, grain boundary J_c equal to intragranular J_c for misalignments less than 12° and 0.003 of intragranular J_c for larger misalignments. For large FWHM within a colony, current transport is limited by intracolony J_c . This occurs for poor intracolony alignment because although a small fraction of the grains at colony boundaries are well aligned and can carry large currents across the boundary, there is no continuous high-current path across each colony. Intracolony J_c is simulated by calculating J_c for a 100×100 square array of grains. Figure 1.20 shows the intracolony and intercolony J_c both with and without a magnetic field, as well as total J_c , considering both intercolony and intracolony conduction.

These simulations suggest J_c of short wires is increased more effectively by a colony microstructure than J_c of long wires. When large variability is observed in J_c for short, narrow wires, as in Table 1.1, J_c for long, wide wires will correspond to the lowest value observed for shorter wires. In zero magnetic field, the colony microstructure produces only a modest variation in J_c for long wires, from 3% of

Table 1.1. Mean and standard deviation of J_c for bridges at 77 K and zero magnetic field^a

Dimensions (mm)		Measured J_c (10^4 A/cm ²)		Calculated J_c (10^4 A/cm ²)	
Length	Width	Mean	Standard deviation	Mean	Standard deviation
1	0.2	4.0	1.3	3.7	0.9
4	0.2	2.7	0.7	2.6	0.4
40	40	—	—	0.40	0.01

^aMeasured J_c 's are for the most homogeneous films (schedule #3, static reactor; see ref. 2). Calculated J_c was obtained from the measured map of grain orientations for 1 and 4 mm (Fig. 1.18) and a simulated array of colonies with the same FWHM for 40-mm-long bridges.

Fig. 1.20. Simulated critical currents for 100×100 arrays of colonies as a function of grain alignment within colonies. High critical current is limited by intercolony transport for low FWHM and by intracolony transport for high FWHM.

the intragranular value in the limit of either very well or very poorly aligned colonies to 8% for an optimum colony FWHM of 29° . In a 0.01-T magnetic field, a more dramatic increase is observed, from 0.03 to 5%.

These models assume that grains at colony boundaries follow the overall distribution of grain orientation within the colony. If the distribution of grain orientation can be made to shift continuously from one colony to the next, J_c would be much larger. "Special" large-angle grain boundaries (e.g., near-coincidence site lattice boundaries) with high J_c may be another means of accommodating large colony misfits. Another method for increasing J_c is to produce an overall, rather than local, grain alignment.⁶ This may occur more readily in a system, such as Tl-1223, that has a propensity for local alignment. A further increase may be effected by increasing the connectivity of the colony microstructure.

Although a square array has been simulated in which each colony conducts to 4 neighbors, each colony in a close-packed, 3-D microstructure would have 12 near neighbors, yielding a much higher J_c .

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THALLIUM CONDUCTOR DEVELOPMENT

Processing of Thallium-Based Conductors

This project is performed in close collaboration with several industrial partners. The work on thallium thick films is performed in collaboration with GE; the work on aerosol powder development and PIT fabrication is performed in

collaboration with IGC. Experiments on PIT conductors involving the use of magnetic compaction are performed in collaboration with IAP Research, Inc.

In the thick-film project with GE, the key objectives are to optimize the properties of their spray-pyrolyzed films and to minimize processing time so as to make a continuous process feasible. Hence, a number of "quenched" films were made by GE and examined at ORNL and GE using a variety of techniques, including electron-microprobe, energy-dispersive spectroscopy (EDS), TEM, and SEM, and XRD. In addition, a modified spray-pyrolysis system is being used at ORNL to fabricate precursor thick films and to study the influence of important process variables during deposition. The films are subsequently thallinated using a two-zone thallium-flow reactor similar to the one used by GE. Efforts at ORNL are focused on preparation of high- J_c thick films on metal substrates by a variety of techniques, including (1) spray-pyrolysis, (2) painting an ink of aerosol-derived powder with an organic vehicle, and (3) sol-gel.

In the PIT project with IGC, aerosol powder production and characterization are done at ORNL. These powders are subsequently used for the fabrication of PIT conductors. Mechanical deformation is carried out at both IGC and ORNL. Subsequent heat-treatment studies, microstructural characterization, and superconducting-property characterization are being carried out primarily at ORNL in collaboration with IGC. In the project with IAP Research, PIT samples are sent to IAP for magnetic compaction and are subsequently processed at ORNL.

Technical Progress

The progress in this project since last year's Annual Review can be divided into

four parts. Each of these is briefly described in the following sections.

Aerosol Powder Development

At last year's Annual Review, we presented initial results on fabrication of Tl-1223 aerosol-derived powders. The work has now been extended to form highly anisotropic powder particles with varying phase assemblages for a fixed stoichiometry (Fig. 1.21). Precursor powders with nominal composition $\text{Ag}_{0.3}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ are generated using

Fig. 1.21. Top: As-produced aerosol powders are spherical and range in size from 1 to 2 μm . Bottom: Morphology of powder after thallination to form primarily 2223. High aspect ratio, platelike grains can clearly be seen.

aerosol pyrolysis. These precursor powders are then mixed with appropriate amounts of thallium oxide and heat-treated under a variety of conditions. Depending on the heat-treatment conditions, we can generate powders having primarily aspected TI-2212, TI-1223, or TI-2223. Powders have also been produced by starting with thallium in the nitrate solution, thereby obviating the need for subsequent thallination.

$Tl_{0.8}Ag_{0.3}Ba_2Ca_2Cu_3O_x$ PIT Conductors

At last year's Annual Review, we presented initial results on the fabrication of TI-1223 PIT materials. We have now conducted a complete deformation-processing study using aerosol powders of this composition. More than 200 samples were processed under a variety of heat-treatment conditions. The effect of processing variables such as heat-treatment temperature and time, uniaxial pressure, and the number of pressings/sinterings was investigated. Critical current density was measured for all samples in magnetic fields up to 1 T at 77 K. Microstructural observation using optical microscopy and SEM as well as XRD phase and texture analysis was performed on some samples.

The formation of 1223 can be correlated with the formation of a liquid phase. There exists an optimum temperature and time wherein the best properties are obtained. The highest zero-field J_c obtained was ~ 9000 A/cm², as indicated in Fig. 1.22. However, it is important to note that unlike Bi-2212 and Bi-2223 PIT tapes, the J_c in applied magnetic fields does not scale with zero-field J_c , as indicated in Fig. 1.23. Hence, a higher zero-field J_c does not necessarily imply reduced weak-link behavior. Unlike BSCCO, J_c is not significantly affected by the number of pressings/heat treatment

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HITACHI Data: R. N. Bhattacharya et al., *Physica C* 211 (1993) 475.

Fig. 1.22. Status of transport J_c in PIT TI-1223 conductors. Shown are best results obtained at ORNL, Hitachi, and SUNY compared with typical results obtained in GE thick films. J_c values are normalized to the zero-field J_c . The zero-field J_c values are indicated on the right. (References. SUNY data: Z. F. Ren and J. H. Wang, *Physica C* 216 (1993) 199. Hitachi data: R. N. Bhattacharya et al., *Physica C* 211 (1993) 475.

cycles, so little texture can be imparted to the microstructure (see Fig. 1.24). In addition to uniaxial compaction, dynamic magnetic compaction was explored. However, it was found that, similar to uniaxial compaction, it had little effect on texture and J_c . The status of transport J_c in PIT TI-1223 is indicated in Fig. 1.22. Best samples are prepared at ORNL and compared with the best results from Hitachi, SUNY, and typical results from GE thick films for $H//c$. From the graph it can be seen clearly that the GE films are far superior to any PIT samples. Although the materials fabricated at ORNL have lower zero-field J_c 's, their in-field behavior is superior to those from SUNY. The Hitachi results are still the best achieved worldwide for PIT samples.

To produce texture, we also explored processing in magnetic fields. Equipment capable of processing samples in an 8-T field at temperatures up to 1000°C was

Fig. 1.23. Top: $I_c(H)$ behavior of two PIT samples; Bottom: $I_c(H)$ normalized with $I_c(OT)$ plotted vs applied field for the same samples shown at the top. The lower I_c sample appears to be less sensitive to applied fields. [Unlike BSCCO, $J_c(H)$ does not scale with $J_c(OT)$.]

constructed. Initial experiments indicate little or no effect of the applied magnetic field, suggesting that, unlike 123, the paramagnetic moment in Tl-1223 at high temperatures may be quite small.

Examination of Precursor Films and "Quenched" Tl-1223 Thick Films

Microstructural studies were performed on spray-deposited precursor films fabricated by varying the method of deposition (i.e., single-coat vs multicoat)

Fig. 1.24. Typical microstructure of a PIT sample showing a random arrangement of the platelike grains.

and heat-treatment conditions (i.e., slow decomposition vs rapid decomposition). Results indicate that the multicoat rapid decomposition films were the most homogeneous in terms of composition as well as morphology. Critical current density measurements on thallinated films made using the various precursor-deposition schedules indicate that the multicoat rapid-decomposition process results in the highest average J_c .

The microstructural evolution of Tl-1223 thick films during the two-zone thallination process was studied by quenching a number of films at various times into the process. Figure 1.25(a) shows a typical processing schedule used to make the films and the location of "quenched" samples examined relative to the entire processing schedule. The inset shows a schematic of the two-zone thallination furnace used to make the samples. The microstructural examination was performed in collaboration with GE

Fig. 1.25(a). Typical thermal profile of the sample temperature and the source temperature during the two-zone thallination procedure used to thallinate the films. The inset shows a schematic of the thallination furnace. (b) Arrows indicate the location of samples examined with XRD and SEM (see text). Inset shows the thallium content corresponding to the times indicated below the arrows.

using techniques of SEM, EDS, electron microprobe, EBSP, and XRD. During the initial stages of thallination the microstructures are changing rapidly. Subsequent to the heat treatment after precursor deposition, a significant amount of silver is precipitated out from the film in the form of nodules. However, as thallium is incorporated into the film, silver particles become faceted and wet the surface of the oxide complex. When the thallium oxide source temperature reaches the second holding temperature ($\sim 730^{\circ}\text{C}$), the microstructure at the film surface becomes equiaxed and quite homogeneous. Most grains are found to contain significant quantities of all elements.

We will now refer to samples as indicated by arrows in Fig. 1.25(b). The numbers correspond to a new reference time scale. "Zero minute" refers to the time when the source temperature stabilizes at 730°C ; "5," for example, refers to a 5-min holding time. Oriented TI-1223 was detected by X-ray Θ - 2Θ scans in the 5-min sample; however, SEM indicated that the film surface was unreacted and had the morphology of the precursor film. On looking through porosities at the film-substrate interface, TI-1223 grains could be seen clearly at the interface (Fig. 1.26). X-ray phi scans indicate that the as-formed TI-1223 is locally textured (Fig. 1.27), indicating that colonies form on crystallization.

XRD and SEM studies of films quenched from holding times of 0, 5, 10, 15, 20, 25, and 34 min at 860°C (with the source temperature at $\sim 730^{\circ}\text{C}$) indicate that the film crystallizes first at the interface (Fig. 1.26) at the side closer to the thallium source. The growth front then moves up through the thickness and along the length of the sample. Figure 1.28 shows a growth front observed in the sample quenched after a 10-min hold at 860°C . It can be seen clearly that the growth front has

Fig. 1.26. SEM micrograph showing the nucleation of TI-1223 at the film-substrate interface.

Fig. 1.27. X-ray phi scans showing the formation of colonies in the as-crystallized material. Two scans separated by 0.125 mm are shown. The structure in the phi-scan changes at each point, indicating that the as-crystallized material has colonies that are small in spatial dimensions.

moved farther along the length below the surface than it has on the surface.

Figure 1.29 shows grey-scale images of the (0010) areal peak intensity for several quenched samples. The data were acquired by moving the sample on a square grid and measuring the (0010) peak intensity at each point on the grid. The intensity of the (0010) peak relates to the amount of material transformed into Bi-1223. The figure clearly demonstrates the motion of a growth front from the right to the left in the sample as a function of processing time at 860°C. Ten minutes at 860°C is sufficient to have the growth completed. This finding agrees with the thallium pickup data [see inset in Fig. 1.25(b)] and the J_c data on the films.

X-ray phi scans indicate that the colonies do not grow significantly on holding at 860°C, although the colonies form on crystallization. However, the

Fig. 1.28. SEM micrograph showing a growth front in a sample quenched after holding 10 min at 860°C. The film can be seen at the top of the micrograph and the precursor at the bottom half. Also apparent on looking through the porosities on the surface is that the film has advanced farther along the length at the bottom than it has at the surface. (The growth front is transverse to the length of the sample.)

FWHM of the colonies (i.e., the spread on the a -axis orientation of the colonies) tends to decrease with holding time. On slow cooling from the high temperature, significant growth in colony size occurs. These findings permit the total processing time at high temperature to be reduced significantly. The effect of silver addition was studied in a set of samples in which the silver concentration was varied from 0.5 to 20 wt %. C -axis-aligned 1223 films with a characteristic colony structure were formed at all silver levels except 0.5 wt %. Microstructural examination of the 0.5 wt % film indicates no evidence of the 1223 phase. These results together with the

observation that most of the silver in 5-wt % samples is precipitated out of the film very early into the thallination schedule indicates that there is only a limited solubility of silver in the oxide complex. The solubility is higher than 0.5 wt % and less than 2 wt %. The key effect of the dissolved silver appears to be lowering of the liquidus temperature. Because previous observations on other quenched films have shown that the formation of 1223 involves a liquid phase, the inability of the 0.5 wt % silver film to attain the liquidus temperature may explain why no 1223 formed. Increasing the silver content beyond 2 wt % results in denser films with greatly reduced porosities. At

Fig. 1.29. Grey-scale images showing the intensity of the (0010) peak. The motion of a crystallization front from the left to the right can clearly be seen on going from the 5-min sample to the 15-min sample.

very high silver contents (17 wt %), compositional segregation is found to occur. These observations suggest an optimum silver content, which from the present investigation appears to be about 11 wt %.

One of the parameters in a continuous-process vapor-phase thallination process is the time required at high temperature for reaction to occur. In addition, there are

issues concerning heating as well as cooling rates from the high temperature in the presence of thallium oxide vapor. Under high thallium oxide partial pressures, *c*-axis parallel grains and spherulites are formed on fast heating and cooling to and from the high temperature. These *c*-axis parallel grains not only limit J_c but also act as crack nucleation centers on thermal cycling of the films. X-ray phi scans on some of the fast-heated samples show no colony structure because of the high density of *c*-axis parallel grains. The formation of these *c*-axis parallel grains and spherulites can be avoided by maintaining a lower thallium oxide partial pressure.

Fabrication of Tl-1223 Thick Films on Flexible Substrates

A new approach using an ultrasonic nozzle mounted on a stepper motor has been set up to spray-pyrolyze precursor films on various substrates. The rate of introduction of the nitrate solution to the nozzle is precisely controlled, so the rate of atomization can be controlled and varied. The sample sits on a heated isothermal stage. The entire system is fully computer interfaced, enabling complicated deposition procedures such as the multicoat, rapid decomposition sequence discussed before to be executed without the presence of an operator. A thallination flow reactor, similar to the one used by GE, has been assembled. In addition, a facility has been set up for sol-gel synthesis of Tl-1223 films. Films are also fabricated by a paint-on process using aerosol powders. In addition, several electrodeposited, precursor films from the National Renewable Energy Laboratory (NREL) are being thallinated and characterized at ORNL in terms of their microstructure and critical current density.

Films have been fabricated on a variety of substrates, including silver, strengthened silver, flexible YSZ, and poly-YSZ. Films made by spray-pyrolysis and sol-gel routes show excellent *c*-axis texture. The colony structure is found to be present in films with good current densities. The highest transport critical current density on a 5-mm bridge for a film on a silver substrate was found to be $\sim 4 \times 10^4$ A/cm² in self-field and 3×10^3 A/cm² in 1 T at 77 K.

The status of transport J_c in Tl-1223 thick films is shown in Fig. 1.30. Data from the best ORNL-GE spray-pyrolyzed sample on silver, ORNL-NREL electrodeposited sample on silver, and ORNL sol-gel sample are indicated. Also shown are best results from Hitachi for films made on silver and typical results from GE for thick films on YSZ. The Hitachi and the ORNL-NREL samples were ~ 1 μ m thick; the rest were ~ 3 μ m thick. It is important to note that the voltage criterion used for all ORNL samples was 0.1 μ V/cm. The criterion for Hitachi results was 0.2 μ V/cm. Using a less stringent criterion for films on silver (e.g., 1 μ V/cm) is meaningless because of the high conductivity of the silver substrate. The results presented in this report are among the highest for films on silver using this voltage criterion.

Future Plans

Work on aerosol powder development will be extended to the (Sr,Ba) system, and the PIT technique will be extended to the (Sr,Ba) system. Several ideas relating to development of strong uniaxial texture or weak biaxial texture in PIT samples will be explored. Work on optimizing precursor deposition and thallination on a variety of substrates using spray-pyrolysis, sol-gel, and aerosol powders will be continued. Microstructural work on quenched samples will be continued to further understand and

Fig. 1.30. Status of transport J_c in thick films. Best results obtained at ORNL on spray-pyrolyzed films on silver (labeled ORNL-GE), electrodeposited films on silver (labeled ORNL-NREL), and sol-gel films on silver (labeled ORNL) are plotted. Also plotted for comparison are the best results from Hitachi on silver and typical results for GE thick films on poly-YSZ. It is important to note that the voltage criterion for all ORNL samples was 0.1 μ V/cm and 0.2 μ V/cm for the Hitachi results. The ORNL-GE films on silver and GE films on YSZ are 3 μ m thick; the rest are all 1 μ m thick.

fine-tune the process. Substrate development is also an important part of this project, and development of nonsilver, flexible substrates as well as strengthened silver substrates will be continued.

BSCCO CONDUCTOR DEVELOPMENT

Thermomechanical Processing of BSCCO Conductors

Introduction

Work on development of Bi-based PIT conductors was carried out largely in collaboration with ASC through the BSCCO Wire Development Group. Activities related to the Wire Development Group included (1) deformation-processing studies aimed at optimizing the dimensional stability of the core and silver-

superconductor interface in PIT fabrication, (2) determination of the mechanical properties of $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Ca}_{2.0}\text{Cu}_{3.1}\text{O}_y$ (Bi-2223) and $\text{Bi}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ (Bi-2212) phases in PIT conductors from nanoindenter measurements, and (3) development of aerosol-process parameters and thermomechanical processes that are appropriate for conductors containing aerosol powders. Other activities in BSCCO wire development included (1) an initial effort with Plastronic, Inc., to develop process parameters for conductors fabricated by a tubular-wire-forming method containing aerosol powders and (2) a project to determine the effects of silver and magnesium oxide fiber additions on the strain tolerance of J_c for PIT conductors.

Determination of Mechanical Properties of Bi-2212 and Bi-2223 Phases in a PIT Conductor

The elastic modulus and hardness of c -axis-aligned, high- J_c , silver-sheathed Bi-2223 and Bi-2212 polycrystalline PIT tapes provided by ASC were measured using a highly spatially resolved mechanical-properties microprobe. Ultralow-load indentation measurements with the load applied along the c axis resulted in a modulus of 54.4 ± 1.8 GPa and 49.8 ± 11.6 GPa for Bi-2223 and Bi-2212, respectively. For loads applied perpendicular to the c axis, modulus values of 90 ± 9.5 GPa and 94 ± 3.5 GPa were obtained for Bi-2223 and Bi-2212, respectively. The measurements indicate a high elastic anisotropy of ~ 1.7 for Bi-2223 and ~ 1.9 for Bi-2212. The hardness was found to be isotropic in both cases; values of 1.7 ± 0.6 GPa and 2.4 ± 1 GPa were obtained for Bi-2223 and Bi-2212, respectively.

Compared with $\text{YBa}_2\text{Cu}_3\text{O}_x$ (Y-123), Bi-2223 and Bi-2212 are much softer and

much less stiff; however, they exhibit a greater elastic anisotropy. The anisotropy is highest for Bi-2212 and lowest for Y-123, consistent with the anisotropy reflected in their crystal structures. The indentation behavior of both bismuth phases was found to be unique in that an unusually large load displacement hysteresis was observed (Fig. 1.31). Such hysteresis in load-displacement cycles during indentation has only been observed for a few materials (such as silicon and germanium) in which a reversible, pressure-induced phase transition has been found to occur beneath the indenter. Experiments were performed on individual grains, varying the peak load during indentation, the percentage of unloading, the number of loading cycles, and the loading rates. More than 300 indentation experiments have been performed and the loading-displacement data analyzed. Additional experiments with muscovite (a common variety of mica), which has a layered structure and fracture behavior similar to that of the BSCCO phases, showed that it too exhibits a large hysteresis on loading and unloading, similar to that of BSCCO. SEM observations of many indentations suggest that the hysteresis occurs by a new

Fig. 1.31. Typical load-displacement curve for Bi-2223 with the load applied along the (100) axis, showing a large, reversible hysteresis.

mechanism in which the material cleaves extensively in both orientations under small loads. Once cleaved, individual plates can undergo significant elastic bending, resulting in hysteretic behavior.

Aerosol Process Development

Development of aerosol powder processing has continued as part of the ASC initiative to develop fine powders and processes for using them in fine-filament multifilament conductors. The effects of oxygen partial pressure in the carrier gas on changes in cation (primarily lead) concentrations were investigated. Lead loss was found to decrease at high and low $P(O_2)$ and was small in 100% oxygen. Evidence for small but significant copper loss was found. The effects of $P(O_2)$ on the phase assemblage of as-prepared Bi-2223 powders were also determined. Aerosol powders with specific compositions and phase assemblages were prepared as requested by ASC for use by ASC staff in PIT processing.

PIT conductors containing aerosol powders in two different phase assemblages were used in a series of experiments to find heat-treatment temperatures and times appropriate for aerosol powders. This is the initial step in a planned effort to define process parameters for aerosol PIT conductors. The oxide cores were dense; secondary-phase particles were small (generally less than 3 to 4 μm), and the Bi-2223 formation occurred rapidly. However, even after long heat-treatment times, some 2212 phase remained. Optimal treatments gave $J_c = 16,000 \text{ A/cm}^2$ at 77 K. chemical analyses by inductively coupled plasma (ICP) technique suggest that some lead and copper loss may have occurred during heat treatment of short samples, the copper presumably diffusing into the silver. Although J_c 's were lower than those that

others have obtained using aerosol powder, the microstructures were quite favorable.

Deformation Processing Studies of BSCCO Wire

The commercial utilization of high- T_c oxide superconductors requires knowledge of the deformation processing of oxide into long-length monofilament and multifilament wires and tapes. Many publications in the literature have described the processing of conductors and their resultant electrical properties. Two recent publications have provided some details of oxide flow in silver tubing.^{1,2} We have investigated the details of variables during the rolling of round wires into flat tapes or ribbons. Ribbon thickness vs width is used as a method of measuring the effect of the rolling variables. For this project, all of the round starting wires were provided in conjunction with ASC.

Experimental Details

Typically, 4-in.-long sections of 0.072-in.-diam wire were used for the rolling studies. Most of the wires were monofilament, but in some cases the multifilament wires of 19, 85, and 361 elements were also investigated. The rolling variables studies included roll diameter, reduction per pass, roll speed, and lubrication. Various rolling diameters were used. The reduction per pass varied from 3 to 50%. The roll velocity varied from 15 to 350 ft/min. A soap solution was tried as one of the lubricants.

In all cases, measurements of thickness and width followed the rolling process. In most cases, the final ribbon thickness was 9 mil. The quality of the ribbon was determined by metallography and, in some cases, by microhardness measurements.

Results

The thickness-vs-width plots for a monofilament wire (OX 0476) processed on four different roll diameters are shown in Fig. 1.32. The percentage of reduction per pass was 24%; the roll speed was 90 ft/min. Figure 1.32 shows that for the same reduction from 0.072-in. diam to 0.009-in.-thick ribbon, the final width increases significantly with increasing roll diameter. The optical micrographs of the transverse section of the 9-mil-thick ribbon for the four roll diameters are compared in Fig. 1.33. Figure 1.33 shows that the consequence of increasing the ribbon width is an increase in the number of cracks in the oxide. Thus, conditions that result in the spread in width (or lateral spread) during rolling of wire into ribbon need to be identified and controlled. The lateral spread during the rolling of a metallic slab into a sheet depends on roll diameter, roll condition, flow properties of the material, and the amount of reduction.³ The lateral spread, ΔW , is given by the following expression:

$$\Delta W = A \times \text{Reduction} \times \text{Contact length} \quad (1)$$

$$\text{Reduction} = \frac{H_o - H_f}{H_o} \quad (2)$$

where H_o = initial thickness and H_f = final thickness.

$$\text{Contact length} = [R(H_o - H_f)]^{1/2} \quad (3)$$

where R = roll radius and $H_o - H_f$ = reduction in thickness per pass. Combining equations (1), (2), and (3) gives the following:

$$\Delta W = \frac{A (H_o - H_f)^{3/2} R^{1/2}}{H_o} \quad (4)$$

The constant A in Eq. (4) incorporates the flow properties of the oxide. $\Delta W = W_f - W_o$, where W_f = final width and W_o = initial width. For wire with a round starting cross section, $W_o = H_o$. Thus, for the same starting oxide, wire diameter, and total reduction in thickness, the plot of ΔW vs R should give a slope of 1/2. Such a plot is shown in Fig. 1.34, and the slope is very close to 1/2, implying that the super-conductor oxide in silver followed the same flow model during rolling as metallic materials.

Effect of Reduction per Pass. In a rolling study on a monofilament wire using a 4-in.-diam mill, the reduction per pass varied from 3 to 24%. The rolls were dry, and the rolling speed was set at 15 ft/min. Results of this study are represented as thickness-vs-width plots in Fig. 1.35. Figure 1.35 shows that a considerable spread in final ribbon width is observed as the reduction per pass is increased. To show the overall effect, the final ribbon width is plotted as a function of reduction

Fig. 1.32. Thickness-vs-width plots demonstrating the effects of roll diameter on lateral spread during the rolling of a monofilament BSCCO wire (OX 0476) into 9-mil-thick ribbon.

Fig. 1.33. Photomicrographs showing transverse sections of monofilament BSCCO wire (OX 0476) rolled from 0.070-in. diam to 9-mil-thick ribbon on four different roll diameters.

Fig. 1.34. Plot of lateral spread as a function of roll diameter for processing 0.070-in.-diam monofilament BSCCO wire (OX 0476) to 9-mil-thick ribbon.

width is plotted as a function of reduction per pass in Fig. 1.36.

Effect of Roll Speed. The effect of roll speed was investigated for a broad range (15 to 350 ft/min) for a percentage of reduction per pass of 3%. The final ribbon-width data for various reductions per pass and rolling speeds are summarized in Fig. 1.37, which shows that, for a 3% reduction per pass, the rolling speed has no effect on the final ribbon width. However, at higher percentages of reduction per pass, the ribbon width can increase with increased rolling speed.

Microhardness Data. The microhardness data for the oxide and silver for a monofilament (OX 0476) wire and the rolled ribbon are plotted in Fig. 1.38. Figure 1.38 shows that oxide hardness is reduced as the wire diameter is reduced by drawing from 0.177 to 0.070 in.; however, the subsequent rolling to flatten the ribbon increases the oxide hardness again. In most cases, the oxide hardness increases to the

Fig. 1.35. Thickness-vs-width plots demonstrating the effect of the percentage of reduction per pass on lateral spread during the rolling of monofilament BSCCO wire from 0.072-in. diam.

Fig. 1.36. Final width vs reduction per pass for data shown in Fig. 1.34 during the rolling of monofilament wires into ribbons.

initial level of 0.177-in.-diam wire, but when the rolling results in a large spread in width, as is the case for the largest diameter rolling mill, the hardness of the oxide increases significantly. The silver hardness increases while the wire is rolled

Fig. 1.37. Effect of rolling speed on lateral spread for two different percentages of reduction per pass for rolling 0.072-in.-diam monofilament wire into 9-mil-thick ribbon.

into ribbon, but it is not affected by increasing the roll diameter.

The detailed microhardness transverse for ribbons rolled on the small and large mills, compared in Fig. 1.39, show that the oxide-core hardness can be varied significantly by increasing roll diameter. Additional hardness data (as a function of the percentage of reduction per pass and after the first wire anneal) are in the process of being correlated.

"Sausaging" and Oxide Cracking.

The sausaging and the oxide cracking can be explained based on the hypothesis reported earlier and on previous research. For smaller percentages of reduction per pass (such as 3%), the compressive stress on the oxide is expected to be low, based on the very small lateral spread. Two benefits are achieved because of low compressive stresses: (1) the oxide does not reach a very high hardness value, which keeps it below its cracking limit as determined by the cold-pressed oxide fracture stress, and (2) for the oxide and silver to deform as a composite, the oxide of relatively lower hardness has to slide at lower forces to pass the softer silver, and thus it is not sufficiently abrasive to cause a rough silver-oxide interface (which is a

Fig. 1.38. Effect of processing variables on microhardness of the silver and oxide in monofilament in BSCCO conductors in wire and ribbon forms. Steps 1 and 2 represent the wires of 0.177- and 0.072-in. diam. Conditions A, B, C, and D represent four different roll diameters.

manifestation of sausaging). Thus, the lighter reduction passes with minimal lateral spread produce less sausaging and a crack-free oxide core.

For larger percentages of reduction per pass, the compressive stresses on the oxide and the silver-oxide interface are expected to be high, as evidenced by the larger lateral spread. The high compressive stresses can cause three effects: (1) the oxide will be packed to high hardness; (2) the oxide hardness can increase to its cracking limit, as determined by the cold-pressed oxide fracture stresses; and (3) for oxide and silver to deform as a composite, the oxide of higher hardness has to slide with greater force past the soft silver and thus become sufficiently abrasive to cause a very rough silver-oxide interface, which results in sausaging. With the limited work hardening of silver, as evidenced by essentially no change in its hardness with increased lateral spread (Fig. 1.39), the

Fig. 1.39. Effect of roll diameter on microhardness transverse across silver and oxide of 9-mil-thick monofilament ribbons of BSCCO (OX 0476). Conditions A and D represent two different roll diameters.

relative increase of oxide hardness gets even more damaging from the silver-oxide interface abrasion (roughening or sausaging).

A sausaging phenomenon occurs in both the longitudinal and transverse directions of the ribbon. The large lateral spread has been shown to cause excessive sausaging in the transverse direction (see Fig. 1.32). Although no transverse sausaging is observed for a small spread, it is still observed in the longitudinal direction (Fig. 1.40). The deformation with minimal lateral spread still has a compressive stress component, but material flow is primarily in the longitudinal direction. Here again, the powder densification to a hardness greater than that of silver and the relative flow of hard oxide against softer silver cause sausaging.

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Fig. 1.40. Longitudinal sections of 9-mil-thick ribbons of monofilament (OX 0476) rolled using two different-diameter mills. Note sausing and oxide cracking.

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Fabrication of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ Tapes by a Tubular Wire Process

Introduction

The PIT technique is the most popular method used to fabricate tapes of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Bi-2223) superconductors. The technology of Bi-2223 fabrication by this technique is at

a stage where tapes several hundred meters in length can be fabricated routinely with uniform current densities on the order of 10^4 A/cm^2 at 77 K.^{1,2} However, the PIT approach suffers from a few drawbacks that could affect large-scale fabrication of superconducting tapes. Some of the drawbacks include the use of more than 70 vol % of silver and numerous drawing operations, both of which affect material and manufacturing costs. In this context, an alternate approach to fabricating Bi-2223 tapes, the tubular wire process (TWP), was evaluated. TWP has been

used successfully in the welding industry and offers the advantages of near net shape manufacturing and a lower ratio of silver sheath to superconducting powder.

Sample Fabrication

A schematic of the TWP used in the fabrication of Bi-2223 tapes is shown in Fig. 1.41. As shown in the figure, the superconductor precursor powder is deposited on a long silver foil formed in the shape of a trough. The precursor powder was prepared by aerosol spray pyrolysis and was of composition $\text{Bi}_{1.8}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_x$. The powder particles are in the form of hollow spheres that are $< 1 \mu\text{m}$ in diameter. After the powder is deposited, the silver foil is folded into a tubular shape and the seam is carefully welded. The tubular wire is drawn to the required diameter and rolled in the form of a tape having a thickness of 0.25 mm. The number of drawing

Fig. 1.41. Schematic of the tubular wire process.

operations is minimal compared with that required in the PIT technique. For comparison purposes, a tape was fabricated by the PIT technique using the same precursor powder and identical drawing and rolling conditions. Both sets of tapes were subjected to a heat treatment to convert the phase assemblage of the powder to Bi-2212, CaO, and CuO. The tapes were then heat-treated in an atmosphere of 7.5% O₂ in the temperature range of 816 to 825°C in 3°C increments for 50 h. After resistivity and current density measurements, the tapes were uniaxially pressed at a load of 1 to 3 GPa and heat-treated at the same temperature as in the first step for 50 h. The thermomechanical treatment process was repeated again under the same conditions.

The critical current densities (J_c) of the TWP and PIT tapes were measured after every 50 h of heat treatment using the conventional four-probe technique. The critical current measurements were performed at 77 K, and the J_c was defined using a voltage criterion of 1 μ V/cm. The magnetic field dependence of J_c was also examined up to a field of 1 T, with the

field applied perpendicular to the tape ($B \parallel c$ axis).

Results and Discussion

The results from the critical current measurements on TWP tapes at various heat-treatment times at 819, 822, and 825°C are shown in Fig. 1.42. As shown in the figure, not much of a difference is seen in the critical current of these tapes at 819°C and 822°C; however, at 825°C, a significant enhancement is observed, with the critical currents reaching up to 15 A after 150 h of heat treatment. It was determined that the cross-sectional area of the oxide in the TWP tapes is about 0.2 mm², which is about twice as much as that of the PIT tapes used in this study. Also, the tapes that were heat-treated at 825°C exhibited zero resistance at a temperature ($T_{c,zero}$) greater than 100 K after 50 h of heat treatment, whereas those heat-treated at 819°C and 822°C showed a $T_{c,zero}$ below 100 K. The development of critical current with heat-treatment time of a PIT tape heat-treated at 825°C is also included in Fig. 1.42. It can be seen from

Fig. 1.42. Development of critical current in tapes fabricated by TWP at various heat-treatment temperatures. Data from a PIT tape fabricated under identical conditions are also shown.

the figure that the development of the critical current of the TWP and PIT tapes at 825°C is similar, with both tapes exhibiting a sharp rise in J_c at 100 h followed by a reduction in the rate of increase of the critical current beyond this time period. The critical currents of both tapes peak at about 15 A, but the core J_c value of the TWP tape is 7500 A/cm², compared with 15,000 A/cm² of the PIT tape. The overall conductor J_c 's of the TWP and PIT tape were roughly the same. It is known that the core J_c of PIT tapes improves with reduction in core thickness. It is possible that a higher core J_c can be achieved in TWP tapes if the core thickness is reduced to an optimal value.

The magnetic field dependence of J_c of a TWP tape ($B \parallel c$ axis) at various heat-treatment times is shown in Fig. 1.43, with the J_c normalized to the respective zero-field values. This figure shows that with extended thermomechanical treatment, the magnetic field dependence of J_c improves, and additionally the zero-field J_c is enhanced. This result indicates that, in addition to the increase in the formation of

the Bi-2223 phase with extended thermomechanical treatments, the links between grains in the TWP tape are also improved and TWP tape behavior is similar to that of the PIT tape.

Figure 1.44 displays the field dependence of J_c of TWP and PIT tapes after 150 h of heat treatment at 825°C. It can be observed from the figure that the magnetic field dependence of J_c is similar in both tapes. This result, along with that shown in Fig. 1.42, suggests that the microstructure development is similar in the TWP and PIT tapes. Therefore, any process developed to improve the current density in the PIT process should be readily applicable to TWP.

The thermomechanical treatment paths used in the processing of the TWP tapes were varied while a constant heat-treatment temperature and deformation load were maintained. Some of the initial results from this study are summarized in Fig. 1.45. It can be seen from the figure that even though the temperature and load are maintained the same, the J_c strongly depends on the thermomechanical treatment

Fig. 1.43. Comparison of the magnetic field dependence of J_c of a TWP tape at various stages of the thermomechanical treatment process. The tape was heat-treated at 825°C.

Fig. 1.44. Comparison of the magnetic field dependence of J_c of tapes fabricated under identical conditions by the PIT process and TWP. The J_c values are normalized to the respective zero-field values.

Fig. 1.45. The development of critical current in TWP tapes processed at 825°C using various thermomechanical treatment paths.

path used. Further optimization of the thermomechanical treatment process and improvement in TWP should yield higher current densities in TWP tapes.

Conclusions

TWP has been evaluated as an alternative to the PIT technique for fabrication of Bi-2223 tapes. Critical currents as high as 15 A have been achieved in these tapes at 77 K. The critical current development with thermomechanical treatment and the magnetic field dependence of the J_c of the TWP tapes are found to be similar to those of the PIT tapes fabricated using the same powder and under the same conditions. The encouraging results obtained in this study suggest the need for further development of TWP for fabrication Bi-2223 tapes.

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Improved Strain Tolerance in Aligned-MgO-Whisker-Reinforced $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ Tapes

Introduction

The capability to sustain a high current density when subjected to a considerable bending strain is essential for successful fabrication and operation of coils of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (Bi-2223) superconductors. Multifilamentary BSCCO tapes have been shown to exhibit enhanced strain tolerance,¹ and it is desirable to find ways to achieve similar properties in monofilamentary tapes because of their higher volume ratio of superconductor to silver. To achieve better strain tolerance characteristics in monofilamentary tapes, it is necessary to prevent crack propagation. It has been observed that the BSCCO grains are most susceptible to fracture along their basal plane grain boundaries; however, if the grains are well aligned along the length of the tape, these cracks should not significantly deteriorate the current-carrying capability. On the other hand, transverse propagation of a crack, perpendicular to the direction of grain orientation, through a colony boundary will

severely degrade the current density. Although the silver sheath provides flexibility to the tape, it does not provide crack-resistant properties. Therefore, it is essential to reinforce the tape so as to provide more resistance to transverse crack propagation along the colony boundaries.

Silver particles of a few microns in diameter and silver flakes of a few microns in length have been used as reinforcements in an effort to improve strain tolerance;^{2,3} however, these reinforcements are not expected to significantly improve the crack-resistance characteristics of most of the colony boundaries because the morphology of the Bi-2223 grains is in the form of thin flat plates. On the other hand, transverse crack propagation, which is the most deleterious to current-carrying capability, can be subdued if the reinforcements are in the form of continuous fibers⁴ or aligned ceramic whiskers. Because these reinforcements are narrow and long, they can provide more resistance to transverse crack propagation. In this section, a method is described to reinforce BSCCO tapes in an effective manner such that the resistance to transverse crack propagation is improved.

Sample Preparation

In this work, aligned MgO whiskers were used as reinforcements. One of the advantages of using MgO is the compatibility of its coefficient of thermal expansion ($13.5 \times 10^{-6} \text{ C}^{-1}$) with that of BSCCO 2223 ($\sim 16 \times 10^{-6} \text{ C}^{-1}$). In addition, because MgO is in whisker form, its tensile strength could be expected to be as high as 10 GPa (about 1/20 of the Young's modulus). Therefore, in addition to the improvement in strain tolerance, the fracture strength of the tape can also be expected to improve through by reinforcement with such strong whiskers. The MgO whiskers used in this study were

fabricated by a molten-salt synthesis method.⁵ In this method, the whiskers are grown from molten MgCl_2 using KCl as a flux. Improvements in the whisker growth technique and optimization of the processing parameters resulted in a successful yield of more than 85% of long (up to 3-mm) whiskers of a small diameter (1 to 10 μm). Such a high yield of whiskers of this morphology has not been reported before and is promising for its mass production of tapes of several hundred meters in length. A micrograph displaying the morphology of the whiskers is shown in Fig. 1.46. The whiskers were separated by sedimentation and mechanical methods and were then individually coated with a 0.2- μm -thick, uniform layer of silver.

Bi-2223 tapes with 15 vol % MgO whiskers were fabricated by the PIT technique using a commercial (SSC, Inc.) precursor powder of overall composition $\text{Bi}_{1.8}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_x$. X-ray powder diffraction revealed that the phase assemblage of the powder comprised Bi-2212, Ca_2PbO_4 , CaO, and CuO. The MgO whiskers were mixed homogeneously with the powder and packed in silver tubes. The whiskers were aligned parallel to the length of the tube by means of mechanical vibration during and after powder packing.

Fig. 1.46. Micrograph of as-grown MgO whiskers used for reinforcing Bi-2223 tapes. The whiskers are typically 1 to 10 μm in diameter and up to 3 mm in length.

Some tubes were cold isostatically pressed at 350 MPa after packing to maintain the orientation of the whiskers during the ensuing mechanical processing. The tubes were then drawn through a series of dies and rolled to tapes of thickness of 0.25 mm. No breaks or cracks were observed in any of the tapes. For purpose of comparison, unreinforced tapes with only the superconductor powder were also fabricated using the same set of drawing and rolling conditions.

The silver-superconductor interface of the tapes with MgO whiskers appeared to be as good as that of the unreinforced tapes. Local variations in the thickness of the oxide core were observed in the reinforced tapes and were attributed to powder-packing density variations caused by the presence of the whiskers. All tapes were first heat-treated in a vacuum at 700°C for 12 h to reduce the carbon content in the precursor powder. The tapes were then heat-treated in an atmosphere of 7.5% oxygen in the temperature range of 816 to 825°C for 50 h. After resistivity and current density measurements, the tapes were uniaxially pressed at a load of 1 to 3 GPa and heat-treated at the same temperature as in the first step for 50 h. The thermomechanical treatment process was repeated under the same conditions.

The superconducting transition temperature (T_c) and the critical current density (J_c) of the reinforced and unreinforced tapes were measured after every 50 h of heat treatment using the conventional four-probe technique. The critical current measurements were performed at 77 K, and the J_c was defined using a voltage criterion of 1 μ V/cm. The magnetic field dependence of J_c was also examined up to a field of 1 T, with the field applied perpendicular to the tape ($B \parallel c$ axis). The strain tolerance of the tapes was investigated after the final heat treatment by subjecting the tapes to bend

strains of up to 1% at room temperature, followed by J_c measurements at 77 K in zero field. In the first set of experiments, the tapes were bent around mandrels of different diameters and straightened prior to J_c measurements. In the second set of experiments, the J_c measurements were performed with the tapes in a bent state. The maximum bending strain at the tensile face of the tape was calculated using the thickness of the tape and the diameter of the mandrels.

Results and Discussion

In the reinforced tapes, it was observed that the MgO whiskers provided a template for a continuous aligned growth of the 2223 phase in the core of the tape even in the early stages of processing. This phenomenon of aligned formation of 2223 phase adjacent to the MgO whisker can be used to enhance the formation and texturing of the 2223 phase in the core. The MgO whiskers have also been shown to impart local grain texture in Bi-2212 bulk polycrystalline samples.⁶ The microstructure of a tape containing 15% MgO after 150 h of heat treatment is shown in Fig. 1.47. It can be seen from the figure that the 2223 phase is aligned along the length of the tape parallel to the orientation of the MgO whisker. Energy dispersive spectroscopic (EDS) analysis of the whisker-superconductor interface revealed no presence of reaction products. Reaction layers of 1 to 5 μ m in thickness have been reported around MgO whiskers used with Bi-2212 bulk polycrystalline samples.⁵ The lower heat-treatment temperature used and the smaller amount of liquid phase formed in the processing of Bi-2223 compared with Bi-2212 could be responsible for the absence of reaction products at the interface in our tapes. No cracks were noticed in the superconducting matrix close to the whiskers.

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Fig. 1.47. Micrograph of the longitudinal section of a Bi-2223 tape reinforced with 15 vol % MgO whiskers and heat-treated at 825°C for 150 h.

The transition temperatures ($T_{c,zero}$) of the reinforced and unreinforced tapes at various stages of heat treatment at 825°C are shown in Fig. 1.48. As seen in the figure, the $T_{c,zero}$ of the reinforced and unreinforced tapes are 69 K and 88 K, respectively, after 50 h of heat treatment and increase to 106 K and 107 K after 200 h. It can be observed from the figure that the transition temperatures of both tapes increase throughout the heat-treatment period, which could indicate a continuous modification of the stoichiometry of the 2223 phase, such as the lead and the oxygen content, toward an optimum value. At all stages, it was observed that the $T_{c,zero}$ of the whisker-reinforced tapes was lower than that of the unreinforced tapes. XRD revealed that the 2223 phase forms at the same rate in both tapes, so the reason for the difference in $T_{c,zero}$ is not currently known.

The critical current densities of reinforced tapes at various stages of heat treatment at 819°C, 822°C, and 825°C and those of an unreinforced tape heat-treated at 825°C are shown in Fig. 1.49. It can be seen from the figure that these tapes exhibit J_c on the order of 10^4 A/cm² at zero field and 77 K even with a reinforcement volume fraction of 15%. The figure shows

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Fig. 1.48. Development of the superconductive transition temperature of Bi-2223 tapes with and without MgO whiskers at various stages of thermomechanical treatment.

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Fig. 1.49. Development of the critical current density of Bi-2223 tapes with (filled symbols) and without (open symbol) MgO whiskers at various stage of thermo-mechanical treatment.

that the highest J_c of 2×10^4 A/cm² was achieved in the tape heat-treated at 825°C, which was the same temperature at which the highest current densities were achieved

in the unreinforced tapes. The optimum heat-treatment temperature for Bi-2223 tapes has been found to be in the vicinity at which a small amount of liquid forms,⁷ and it was expected that the presence of 15 vol % MgO would result in formation of a liquid phase at a lower temperature. Therefore, it is surprising that a high heat-treatment temperature was required to optimize the J_c in the reinforced tapes. The best J_c value of 2×10^4 A/cm² achieved in the reinforced tapes compares with the best value of 28,500 A/cm² attained in an unreinforced tape processed under identical conditions. The lower current densities in the reinforced tapes could be partly ascribed to the low and inhomogeneous packing density that resulted in variations in thickness along the length of the tape. It should be possible to achieve higher current densities by improving the packing procedure to reduce the thickness variations.

The magnetic field dependencies of current densities of reinforced and unreinforced tapes after the final heat treatment at 825°C are shown in Fig. 1.50.

Fig. 1.50. Comparison of the magnetic field dependence of J_c of Bi-2223 tapes with and without MgO whiskers after heat treatment at 825°C for 200 h.

It is seen from the figure that the field dependences of both tapes are identical, indicating that no weak links are created by the presence of MgO whiskers. This result implies that the lower J_c values observed in the reinforced tapes should most likely be caused by a reduced effective cross-sectional area rather than any modification in the intergranular properties.

The results of the strain tolerance studies performed on reinforced and unreinforced tapes are shown in Fig. 1.51. It can be seen from the figure that, in the "bend-and-straighten" tests, the onset of degradation in J_c of the whisker-reinforced tapes is extended to a higher strain level than in the unreinforced tape and also that the rate of further reduction in J_c with increasing strain is lowered. A more impressive tolerance to strain in the reinforced tapes is observed in the "bend-only" tests. As shown in the figure, the reinforced tapes are found to sustain 90% of their initial J_c up to a strain of 0.6%.

Microstructural analyses of the tested tapes after etching away the silver sheath

Fig. 1.51. Comparison of the influence of bend strain on the J_c of Bi-2223 tapes, with and without MgO whiskers after heat treatment at 825°C for 200 h (B&S = bend and straighten).

revealed evidence of the MgO whiskers having provided resistance to transverse crack propagation by means of crack bridging and crack deflection. By crack bridging, the whiskers provide friction to clamp the crack faces behind the crack tip, resulting in deceleration of crack growth. By deflection of a crack along the length of the reinforcement, the distance required for the crack to propagate transversely through the tape is considerably increased. As a result of multiple crack deflections and crack branching, the driving force for the crack becomes less than the resistive force, resulting in crack arrest.

Conclusions

Improved tolerance to bend strain has been demonstrated in aligned MgO-whisker-reinforced Bi-2223 tapes. A superconducting transition temperature of 106 K and a critical current density of 2×10^4 A/cm² have been achieved at 77 K in Bi-2223 tapes reinforced with 15 vol % MgO whiskers. The magnetic field dependence of current density of the reinforced tapes is found to be identical to that of the unreinforced tapes. These properties and the absence of reaction products and cracks at the MgO-superconductor interface are favorable for the potential use of MgO whiskers to reinforce Bi-2223 tapes.

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Technical Progress in Applications Development

DEMONSTRATION OF A MAGNETIC REFRIGERATOR FOR HIGH-TEMPERATURE SUPERCONDUCTING DEVICE APPLICATIONS

Background

Magnetic refrigeration is a type of solid-state cooling process that offers the opportunity for improved efficiency and reliability in cryogenic cooling applications if performance estimates can be achieved in practice. A key requirement for any practical magnetic refrigeration system is the realization of relatively high magnetic fields with relatively low losses, essentially the exclusive realm of superconducting magnets. The discovery of HTS materials has prompted renewed interest in this application of superconductivity. Although material development efforts have raised superconducting critical temperatures substantially, it appears that, for the foreseeable future, practical applications will require cooling at temperatures below the boiling point of nitrogen. Because magnetic refrigerators need superconductors and superconductors need refrigeration, magnetic cooling systems represent a rare combination—both an application of and an enabling technology for superconductors. By the same token, the continued development of HTS materials promises reduced (but still substantial) refrigeration requirements for devices with many applications and improved refrigerators for meeting those requirements.

Objectives

Consistent with the apparent opportunities outlined here, the objectives of this project are to (1) generally advance magnetic refrigeration technology in the

range of interest for HTS applications (20 to 80 K) and (2) specifically develop a prototype magnetic refrigerator that could provide 50-W cooling at 40 K (Fig. 2.1).

Approach

Task 1 emphasized design of the configuration required to implement the magnetic refrigeration cycle, including the specification of magnet and heat-rejection interface requirements. Options were devised to meet the stated interface requirements. Issues addressed in Task 1 included magnetocaloric refrigerant composition and configuration, magnetic field control, energy flows, and candidate gas-cycle refrigerator implementation. Task 2 comprised fabrication efforts based

Fig. 2.1. Prototype magnetic refrigerator for HTS applications (50-W cooling at 40 K).

2-2 Technical Progress in Applications Development

on the designs developed in Task 1. Task 3 included testing of the components created in Task 2 at the subsystem level, integration of the subsystems to form the magnetic refrigerator system (Fig. 2.2), shakedown testing and problem resolution, and performance mapping.

Results

After facility modifications to the Active Magnetic Regenerator Universal Test Apparatus, test ranges were expanded to approximate more closely those expected for the refrigerator. Results verified the high efficiency potential of the primary material operating in an active magnetic regenerative cycle. Procurement, preparation, and characterization of the solid refrigerant were accomplished. Fabrication and acceptance testing of the superconducting magnet subsystem were completed. The bed/displacer/drive subsystem was assembled and subjected to preliminary testing. The heat exchanger and shield subsystems were installed and

checked. Electrical subsystems, including power supplies and instruments, were calibrated and installed. The data-acquisition subsystem assembly and programming were completed. The vacuum containment was assembled, and vacuum leak checks were conducted. Cooldown procedures were verified. Pressure leak checks were conducted and potential problem areas identified. Shakedown testing was initiated, with net cooling first achieved on July 13, 1994 (Fig. 2.3).

Fig. 2.3. Magnet charge and cooldown (0-5 T).

Fig. 2.2. Map for continuous-electron-spin magnetic cryocooler. [★ = current apparatus (50 W at 40 K).]

ALTERNATING CURRENT APPLICATIONS FOR HIGH-TEMPERATURE SUPERCONDUCTING COILS

Introduction

The objective of this project is to develop, in collaboration with industry, the technology needed to produce HTS coils for electric power applications in the ac mode.

A cooperative agreement between ORNL and ASC is used to enable the collaborative development and testing of high-current HTS wires and coils. The samples were tested in a variable-temperature cryostat in background magnetic fields of up to 7 T and a field

ramp rate of up to 2.5 T/s in a cyclic mode. Alternating current losses on the sample from the cyclic fields were measured by a calorimetric technique.

During this report period, substantial progress was achieved in two areas of work. A heavily instrumented 1-T magnet was designed and built by ASC and was successfully tested at ORNL for its electrical performance and stability margins. A design study was performed on an ac inductor, and ac loss measurements were performed on prototype HTS coils wound with twisted filaments.

Stability Measurements on a 1-T HTS Magnet

A 1-T HTS magnet was designed and built by ASC and was successfully tested in the variable-temperature cryostat at ORNL from 4.2 K to 77 K and with background fields up to 2.5 T. The magnet met all specifications and produced a 1-T self-field at 20 K. (Preliminary tests at ASC generated 1.1 T in liquid helium.) Useful data have been collected on the magnet as a function of background field and operating temperature.

Stability and normal zone propagation experiments were performed on the 1-T magnet, a single length of HTS conductor, and a double pancake. The thermal stability margin of an HTS conductor was found to be more than 150 J/cm³, which is two to three orders of magnitude higher than a low-temperature superconductor. No sustained normal zone propagation was observed with the heating-induced normal zone.

Direct Current Test of the 1-T Magnet

An HTS magnet was designed and built by ASC to generate a 1-T center field at 4.2 K. The magnet is to fit inside the 10-cm bore of the variable-temperature

cryostat at ORNL and be instrumented for stability and strain measurements. A react-and-wind approach was adopted to allow the installation of the instrumentation and for ease of applying insulation. The high-temperature superconductor used for magnet winding was manufactured with the metallic precursor (MP) process. The conductor made with this process has shown better strain tolerance compared with that manufactured through the oxide PIT process.

The magnet consists of nine double pancakes wound from 575 m of Bi-2223 tape. The ID is 2.54 cm, OD is 8.70 cm, and the length is 10.75 cm. A resistive heater was placed at the crossover between the two pies of the middle double pancake. Several voltage taps were added on successive turns near the heater to monitor quench propagation. Two thermometers were also installed near the heater. Voltage taps from each double pancake as well as strain gauges on the OD of the middle pancakes were also provided. Figure 2.4 shows a picture of the finished magnet. Terminations of the voltage taps and other instrumentation are located on the top plate.

Preliminary tests at ASC resulted in critical currents of 13.1 A at 77 K in liquid nitrogen and 73.2 A at 4.2 K in liquid helium. A 1- μ V/cm electric field criterion across the entire conductor length (including all the joints) was used. With a field factor of 0.0153 T/A, the magnet generated 1.12 T at 4.2 K and 0.20 T at 77 K. Tests at ORNL were performed in the variable-temperature cryostat with gaseous helium cooling. In addition to the field produced by the magnet itself, background fields of up to 2.5 T were also applied.

Figure 2.5 shows the measured critical current, I_c , of the magnet as a function of temperature at different applied background fields. At 20 K, the I_c was 66 A, which

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Fig. 2.4. 1-T HTS magnet made by ASC. The screw heads on the magnet top plate are the terminations of the voltage taps and other instrumentation.

generated a 1.0-T center field. At this current, the current density of the conductor is 3900 A/cm^2 and the current density over the winding space is 2600 A/cm^2 . With a background field of 1 T, I_c lowered to 62 A, which generated an additional 0.95-T field. No appreciable coil strain was observed during the entire magnet test. Thus, the magnet met the goal of generating a 1-T field and verified the robust MP conductor in a react-and-wind coil construction.

Fig. 2.5. Critical currents of the magnet as a function of temperature at different applied background fields. A $1\text{-}\mu\text{V/cm}$ criterion over the whole magnet (including internal joints) was used to determine I_c .

Stability and Normal-Zone Propagation Experiments

Stability and normal-zone experiments were first performed on a single length of HTS tape conductor, then on a double pancake, and finally the 1-T magnet. The same type of conductor was used in all these tests. The separate double pancake was constructed and instrumented similarly to the middle double pancake of the 1-T magnet. In all three tests, a resistive heater attached to the conductor was used to drive a section of the conductor normal, and the voltage and temperature of the conductor were monitored to observe the recovery or propagation of the normal zone.

Measurements were made from 4.2 K to 77 K and in a background field of up to 2 T. The conductor was first charged with a current close to or higher than the critical currents (defined by the $1\text{-}\mu\text{V/cm}$ criterion). For the single-length conductor, up to 2 J of heating energy was then applied in 350 ms to create a local normal zone. For the double pancake and the 1-T magnet, up to 12 J of heating energy was applied in 300 ms. No sustained normal-zone

propagation was observed in any of the tests.

Figure 2.6 shows an example of the heater current and the heated-zone voltage in a test sequence. The test shot was made on the 1-T magnet at 4.2 K in a 1-T background field. The magnet was charged to 60 A. A 4-A heater current was pulsed for 150 ms. The heated-zone voltage went up and saturated the amplifier at 3.3 mV. (The voltage across the pancake indicated that it went to 25 mV.) After the heat was removed, the heated-zone voltage disappeared in about 1 s. Figure 2.7 shows that in that same shot the temperature of the conductor near the heater went up to 36 K. The conductor was then cooled back down to 4.2 K in a few seconds after the heat was removed.

Because no quenching was experienced by the heating, a lower limit for the thermal stability margin of an HTS conductor was found to be 150 J/cm^3 , which is two to three orders of magnitude higher than a low-temperature superconductor. The reason for this high stability margin is thought to be twofold: (1) the HTS has a high T_c and thus a high temperature margin, and (2) it takes higher energy to heat it above the current sharing temperature. The HTS has a low n -value (3–8) in the V - I curve. The transition to resistive state is gradual, and the HTS core still shares a good fraction of the current after it goes "normal"; thus the joule heating is low, and the conductor can recover to the superconducting state more easily.

Inductor Study and ac Loss Measurements

A design study was performed for an HTS inductor for commercial applications such as in a current-fed inverter. In the study it was assumed that the critical current of the HTS conductor was a

Fig. 2.6. The heater pulse and the heated-zone voltage. The heated-zone voltage went up and saturated the amplifier at 3.3 mV and subsequently recovered in less than 1 s after the heat was removed.

Fig. 2.7. Temperature of the conductor near the heater for the same shot as in Fig. 2.6. The thermometer indicated that the conductor was driven to more than 36 K and subsequently cooled back down to 4.2 K after the heat was removed.

function of field and temperature, and design criteria for a coil shape and operating temperature were sought that would minimize cost. Design information and optimization methodology were established by this study. These results will be incorporated in the inductor to be built later. Alternating-current calculation of the

2-6 Technical Progress in Applications Development

inductors revealed the definitive need to increase the matrix resistivity and to twist the filaments of an HTS conductor to reduce the ac losses to a tolerable level.

Alternating-current losses were measured in a series of HTS pancake coils fabricated from twisted multifilamentary Bi-2223/Ag tapes. The pancake coils were produced by ASC from tapes having twist pitches of 0, 3.6, and 5.6 twists per inch. These twisted-filament conductors are believed to be the first successful attempt at twisting a multifilament HTS cable while maintaining superconducting properties. A calorimetric technique was used to measure the ac loss. Figure 2.8 shows a schematic of the measurement setup. System calibration is established by using the simulation heater imbedded in the pancakes. Figure 2.9 shows an example of the temperature-vs-time curves of the calibration runs. The curve of an ac-loss run lay between the 104- and 209-mW curves. Thus, an ac loss of 160 mW was determined in that run.

In this report period, the ac losses were induced by applying an oscillating (sinusoidal and triangular) field of up to 2 T/s. If the loss is dominated by the hysteresis loss, the loss rate would be proportional to dB/dt . If the loss is dominated by the eddy/coupling loss, the loss rate would be proportional to $(dB/dt)^2$. Dividing the loss rate by dB/dt and plotting against dB/dt would result in a horizontal or slanted line. The results are shown in Figs. 2.10 and 2.11 for the 3.6-twist-per-inch and 5.6-twist-per-inch samples, respectively. The data indicated decreasing ac losses with the filament twist pitch. However, it also indicated that the filaments were forced into their dissipative flux creep/flow regimes at ramp rates of 0.15 to 0.35 T/s, substantially lower than expected. Additional experiments using

Fig. 2.8. A schematic of the calorimetric ac-loss-measurement setup. The simulation heater imbedded in the pancake is used for system calibration.

Fig. 2.9. Calibration curves of a test coil. An ac-loss-run curve is plotted among the calibration curves to determine the loss.

transport current measurements should reveal the reason for this dissipation and should provide information for optimizing the performances of future cables and coils. Furthermore, raising the matrix resistivity by poisoning the silver should significantly cut down on the eddy losses. Efforts are under way to address this issue, too.

Fig. 2.10. (Alternating current loss rate/field rate) vs field rate for the 3.6 twist-per-inch test coil. The changeover at 0.15 T/s (marked with an arrow) is believed to be caused by the superconducting filaments being driven to the flux creep/flow dissipative state.

Fig. 2.11. (Alternating current loss rate/field rate) vs field rate for the 5.6-twist-per-inch test coil. The changeover at 0.34 T/s (marked with an arrow) is believed to be caused by the superconducting filaments being driven to the flux creep/flow dissipative state. Note that the loss rate of this coil is lower than that of the 3.6 twist-per-inch coil.

SUPERCONDUCTIVITY PARTNERSHIP INITIATIVE: AN ALTERNATE STATOR DESIGN FOR THE GENERAL ELECTRIC 100-MVA SUPERCONDUCTING GENERATOR

Introduction

The advent of HTS materials has greatly enhanced prospects for the practical application of superconductivity in electric power system components. In the autumn of 1993, DOE awarded a Superconductivity Partnership Initiative (SPI) grant for design assessment and component development on a 100-MVA-class generator with an HTS field winding. ORNL is teaming with several other organizations on this project, which is being led by GE. The objective is to predict efficiency, size, weight, and costs in comparison with conventional generators.

Activities in FY 1994 centered on collaboration with GE in the specification of a three-phase, room-temperature, 13.8-kV stator winding appropriate for use

with an HTS rotating dc field winding. At the start of the project, highly informative visits were made to GE's factory and corporate R&D laboratory in Schenectady, New York, for orientation, project kickoff, and brainstorming sessions. Tours of GE's generator shop were very useful in helping us to understand GE's current generator-manufacturing practices. Besides these visits, frequent contact has been maintained with GE by telephone and fax.

General Electric's favored stator design concept was an adaptation of their conventional design, which uses straight stator bars mounted in a toothed silicon-steel core, and a double-layer, conical-involute end winding, which resides outside the core and active region. GE recognized that the high magnetic fields from the HTS rotor would lead to saturation of the core teeth, causing much higher tooth losses and stronger forces on the stator-coil conductors than in a conventional generator. Thus, an "air-gap" winding with little or no magnetic material in the core teeth was preferred.

Selection of Helical Configuration

At the DOE Cryogenic Rotating Machines Workshop in March 1994, American, Russian, and Japanese superconducting generators using helical stator windings were described. In this design, the stator coils follow a helical path around the active region (i.e., the region of a rotating dc field in which three-phase ac power is induced in the stator coils), either along its whole length (fully helical) or in the end-turn sections only (partially helical). It was decided that ORNL would conduct an investigation of this alternative. Several advantages and design considerations of the partial-helical stator design are summarized below.

- The helical end turns are inside the steel core close to the rotor and contribute to the power output. The total winding length and resistance can be reduced for a given power rating. This partially offsets the resistive and ac losses of the end turns and improves generator efficiency and compactness.
- Generator capacity can be scaled up simply, by increasing the length of the straight section with a standardized helical end section.
- Because most of the stator winding is active, fewer bars are needed to produce the required voltage. Reducing the number of bars gives a corresponding reduction in the amount of ground insulation and increases the winding area fraction available for copper. Manufacturing costs are also reduced with fewer bars.
- Ease of assembly and repair are important considerations. Because the windings are helical only near the ends, the helical sections have good

accessibility. This feature should facilitate assembly and repair.

Techniques exist for repairing heavy industrial motors, which are commonly treated with epoxy. Therefore, should the helical sections require epoxy treatment, it seems reasonable that repairs can still be conducted.

- Although conventional 100-MVA generators are currently built with air-cooled stator windings, air cannot sufficiently cool the windings for higher ratings. The compact size of a 100-MVA HTS generator limits the area available for heat transfer in the stator windings; for that reason, water cooling is also required for the 100-MVA design. For a water-cooled 100-MVA design to be commercially feasible, it must be demonstrated that advantages (such as increased efficiency or reduction in size and weight) can offset the capital and operating costs associated with water cooling.
- The power produced by the helical section is only about 65% of the power of an equivalent-length straight section. Thus, it is advisable to make the helical section as short as possible by making the helical angle as sharp as possible. However, this decreases the space between coils in the helical section. This space must still be adequate for the mechanical components that support the helical bars.

Summary of Design Study

The results of the design study have been documented in a conceptual design report. Table 2.1 summarizes calculated parameters of the design. As noted, several of the loss figures have been scaled from

Table 2.1. 150-MVA partial-helical stator design

Core	OD, in.	74
	ID, in.	51.1
	Yoke flux density, T	1.58
Armature	Slots/bars per slot	24/4
	Circuits/turns per coil	1/1
	Turns per phase	16
	Winding pitch	5/6
	Mean length of turns, in.	250
	Active length, in. (same bar length)	117.1
	Eff. current density, A/cm ²	95.5
	OD, in.	51.1
	ID, in.	36.9
Subtransient reactance		0.090
Losses, kW	Windage ^a	20
	Fan loss	38
	Core loss ^a	136
	Tooth and helical support pin loss	45
	Armature I ² R	288.9
	Extra copper loss ^a	24
	Stray losses ^b	300
	Cryocooler compressor ^b	15
	Total loss (excluding bearings)	867
Efficiency, %		99.36

^aScaled from GE-calculated value by core length ratio.

^bScaled from GE-calculated value by power output ratio.

values previously calculated by GE.

Figure 2.12 shows an elevation view of the proposed conceptual design, in comparison with the nonhelical design described in GE's SPI proposal. The armature and core outer and inner diameters are chosen to equal those of the GE design. The number of stator slots is reduced to 24, with four bars (two top and two bottom bars) in one slot. The teeth between the slots in the straight section can sustain high torques because they are wide. The core is lengthened from 63 in. to 117 in., and the HTS rotor is correspondingly lengthened. With 96 bars, an output of 150 MVA is possible in the same physical envelope used by GE's 100-MVA design. Fabrication of the stator would be very similar to the process used for conventional generators.

Figure 2.13 shows a cross section of one slot in the straight section. The 24 teeth are each ventilated with five holes. These holes reduce the losses in the teeth, which are proportional to the weight of flux-carrying material. The holes also provide air paths for cooling the tooth directly. Finally, they prevent excessive flux from going through the teeth and minimize flux ripples that may generate surface losses on the electromagnetic (EM) shield of the rotor. The rigidity and mechanical strength of the teeth are not significantly weakened by the holes. Although this arrangement is not loss free, we feel that it is stronger and more practical to assemble than designs that attempt to insert composite or stainless-steel teeth into the silicon-steel core. Heat-transfer calculations indicate that air

Fig. 2.12. Cross section of partially helical stator design.

cooling can easily handle the tooth losses. A composite inner ring is installed at the inner radius of the teeth to support radially inward short-circuit forces and to compress the bars into the slots.

The peak full-load forces on the bars were calculated in detail. The per-unit subtransient reactance was estimated at 0.09 and was used to determine the peak short-circuit per-unit torque of 17.2. The peak short-circuit tangential-bar forces of 1328 lb/in. for a bottom bar and 1562 lb/in. for a top bar were estimated by multiplying the peak full-load forces by this factor. These forces were used to estimate the short-circuit mechanical stresses in the teeth. Figure 2.14 shows a finite-element calculation of the tooth stresses using the ALGOR® code. The stresses are well within the yield strength of transformer steel, although the intensification at the slot corners shows that they need to be rounded. Further work is needed to find the values of the radial short-circuit forces and the zero-sequence current forces. It will be necessary to wedge and shim the bars tightly into the slots (black areas in Fig. 2.13) to prevent damage to the insulation from transient and vibratory forces.

Figure 2.15 shows a cross section of a slot in the helical section. Wedge-shaped composite spacers are inserted between the bar pairs. These spacers would probably have to be machined or molded in sections because they must follow the helical

Fig. 2.13. Stator bars and teeth of straight portion (total of 24 slots).

curvature of the bars. If metallic support pins are used, air cooling passages will have to be provided in the spacers to handle the eddy-current heating in the pins. Grooves can be molded or machined along the outside of the spacers, as shown for the bottom layer of bars. However, this leads to greater compressive forces on the insulation; therefore, it would be better to produce the spacers in two halves so that the cooling channels could be machined on the inside. This technique would also allow room for wedges and shims to be inserted between the spacer halves without fear of damaging the bar insulation.

The forces in the helical section are borne by pins and sleeves that are threaded into composite inserts in the inner surface of the steel yoke. The purpose of the sleeves is to support the bottom bars and to allow them to be properly located and shimmed before installation of the top bars.

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Fig. 2.14. Stresses and deflections in teeth.

The sleeves also help carry the short-circuit forces of the bottom bar layer. Both the pins and the sleeves would be tapered to allow a tight, zero-clearance installation. The pins and sleeves must be made of nonmagnetic materials. Epoxy would be injected into the area between the yoke inserts and their cavities in the yoke. This could be done either before or after the bars are installed, depending on how much positional error of the diamond-shaped holes between bars builds up because of manufacturing variations in the bars. A hole could be provided through each pin for injecting epoxy.

The pin-sleeve assemblies would pass through holes in the wedge-shaped spacers and through the diamond-shaped holes between the helical bars into an inner ring

Fig. 2.15. Cross-sectional view of stator bars and bolts of helical portion (total of 24 slots).

of composite material, where they would be retained with threaded composite caps. This ring helps carry the peripheral forces and also takes any inward radial forces from the bars.

Calculations of the bar spacing in the helical section show that the support pins must be less than 1 in. in diameter at the stator inner radius. Because the pins cover only a small fraction of the helical winding area, the peak short-circuit forces (which occur on only a few bars) cannot be carried by only the pins next to a bar with high forces; stresses greater than 100,000 psi result from this assumption. Thus, it will be necessary to wedge and shim the helical windings very tightly so that they form a solid arch structure that transfers loads relatively evenly in shear to all 288 pins. In this case, the shear stresses are only about 3000 psi.

The support pins produce eddy-current losses of about 100 W per pin. The losses are removed by air flowing through the spacers between the helical bars. The area around the pins is confined, but the pin thermal conductivity is low and the air must be spread out over most of the pin surface to prevent hot spots. Further work is needed in this area. High-strength, insulating glass or graphite composite pins would be greatly preferred because they would produce no eddy-current losses.

Conclusion

It remains to be seen how the cost of a partially helical stator will compare with one having conventional end windings. The mechanical complexity in the end-turn area is undoubtedly greater. The extra output of the helical generator is not free, considering that the core and HTS rotor must be lengthened by nearly a factor of 2 for a 50% output increase. This is because the helical end turns utilize the flux from the HTS rotor only 65% as efficiently as straight bars. Cost reductions from the smaller size and greater efficiency with a partially helical generator have to be balanced against these considerations. The cost advantages of smaller size are difficult to quantify and will depend on a particular customer's plant. General Electric's knowledge of its market will be of most help here. The ultimate cost of a practical

cryogenic HTS rotor is still a major unknown. Hawsey, Sokolowsky, and Haldar¹ have given a target cost for HTS wire in rotating machinery of \$5 to \$10 per kA-m. This cost would be competitive with Nb₃Sn tape, but the current manufacturing cost is orders of magnitude higher. If the rotor cost turns out to be a much higher fraction of the total generator cost than for a conventional generator, then designs that do not fully utilize the rotor flux become less attractive. Rotor cost will thus be a strong factor in the choice of the design of the rest of the generator.

The design calculations will be refined in FY 1995, and it is hoped that the mechanical design will be simplified. Further work is particularly needed to determine the radial short-circuit forces and to improve cooling and mechanical structure in the helical region. New activity will begin on a second task element to define the cryogenic HTS rotor instrumentation system.

Reference

1. R. A. Hawsey et al., *Development of a Practical High-Temperature Superconducting Wire for Electric Power Applications*, presented at the Fourth International Conference and Exhibition of the World Congress on Superconductivity, Orlando, Florida, June 27 to July 1, 1994.

Summary of Technology Partnership Activities

BACKGROUND

ORNL is a key part of DOE's national effort on electric power applications of high-temperature superconductivity. ORNL has formed effective teams that combine the resources of the Laboratory with the entrepreneurial drive of private companies. New technology transfer methods, a feature of the ORNL Superconducting Technology Program for Electric Power Systems since its inception in 1988, have resulted in 31 superconductivity "pilot center" cooperative agreements and 2 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 commercial viability, or both. Licensing of Laboratory spinoff technologies is how spectator firms can participate in this national program. 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 requires combined resources and expertise, with a clear objective of industrial commercialization. For the project to succeed, each partner depends on the success of the other.

Most of the industrial competitiveness 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 high-temperature superconductivity are expected if the project succeeds. For example, several companies continue to search for innovative ways to apply YBCO in the manufacture of long lengths of wire. This wire may still be the only option for practical performance levels in high magnetic fields at temperatures greater than 77 K.

RELATIONSHIP TO THE DOE MISSION

The ORNL program mission is that of its program sponsor, DOE's Office of Energy Management, Advanced Utility Concepts Division: to develop the technology base necessary for industry to proceed to commercialization of electric energy applications of high-temperature superconductivity. High-temperature superconductivity will enable new energy-efficient motors, generators, 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 smaller size and weight of the next generation of electric power equipment.

3-2 Summary of Technology Partnership Activities

FUNDING

DOE funding for the program, subcontracting activities in 1994, and a summary of funds-out cooperative agreements are shown in Tables 3.1 and 3.2 and in Fig. 3.1.

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, including the Electric Power Research Institute (EPRI).

Cooperative agreements ensure that technology development is industry-driven. The Office of Guest and User Interactions 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 1994 more than \$1 million funds-out to industry 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.

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

	New budget authorization/outlay (\$ × 1000)				
	1989/1990	1991	1992	1993	1994
Direct scientific and technical ^a	2072	3146	3213	3511	3334
Management and outreach	<u>230</u>	<u>219</u>	<u>280</u>	<u>294</u>	<u>298</u>
Subtotal	2302	3365	3493	3805	3632
Subcontracts ^b	0	154	439	428	496
Funds-out cooperative agreements	<u>1068</u>	<u>681</u>	<u>1072</u>	<u>867</u>	<u>821</u>
Total program	3370	4200	5004	5100	4949

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

^bDetails are provided in separate tables. Funds-out cooperative agreements provide direct financial support to U.S. industry for cost-shared cooperative research and development.

Table 3.2. Superconductivity Program—summary of cooperative agreements as of September 30, 1994

Participant	Approved term	Type ^a	Total agreement cost share (\$ × 1000)			Technology area
			By DOE to ORNL	By DOE to industry	By industry	
Advanced Fuel Research (completed)	2/1/90–9/30/92	NFE	230	0	442	In situ HTS film deposition monitor
American Magnetics (completed)	8/10/89–8/9/92	NFE	100	0	480	Char. of MOCVD deposited multifilament conductors
American Superconductor	9/1/91–11/15/95	FO	839	500	558	Coil fabrication, tech. development, and testing
American Superconductor	4/1/89–11/15/95	NFE	1615	0	1252	Fabrication of powder-in-tube wire and tape
Astronautics	9/1/91–2/28/95	FO	600	450	820	Magnetic refrigeration
CeraNova Corporation	8/1/93–1/31/95	FO	90	25	75	Melt-processed YBCO wire for leads and coils
Consultec Scientific (completed)	6/1/89–12/31/90	FO	38	45	64	Deposition target device
Corning (completed)	6/1/89–12/31/93	FO	325	275	316	Deposition on flexible ceramic substrates
CPS Superconductor (completed)	4/1/91–3/31/93	NFE	80	0	50	Conductor fab.—continuous filament melt-textured YBCO
Dow Corning (I-IIa) (completed)	7/1/90–9/31/91	FO	110	50	67	Thick film deposition
DuPont (completed)	7/1/89–3/31/91	NFE	225	0	250	Thin film devices and bulk applications
Electric Power Research Institute	7/13/93–7/12/96	C	190.5	0	214.9	Variable speed superconducting motors, power electronics, and SMES
Energy Conversion Devices (completed)	5/1/91–3/31/93	NFE	90	0	90	Deposition of conductors
General Electric (A1) (completed)	12/15/88–2/28/89	FI	5	0	45	Thallium HTSc material processing
General Electric (SPI)	12/1/93–11/30/95	NFE	400	0	1173	Thallium wire development and generator design
General Electric (B1)	10/1/89–12/31/94	FO	670	420	514	Laser deposition of conductors; thallium-deposited conductors
General Electric (C1) (completed)	4/1/90–12/31/90	NFE	135	0	140	Thallium HTSc material processing
HiTc Superconco (completed)	3/1/90–4/30/91	NFE	40	0	50	Magnetic bearings
Innovative Materials Technology (completed)	10/1/89–3/31/90	FI	50	0	50	Composite tape fabrication

Table 3.2 (continued)

Participant	Approved term	Type ^a	Total agreement cost share (\$ × 1000)			Technology area
			By DOE to ORNL	By DOE to industry	By industry	
Intermagetics General Corporation	10/1/91–12/31/96	FO	1452	940	831	Electric power application; BSCCO 2212 tapes
Intermagetics General Corporation	9/1/91–8/31/95	NFE	300	0	300	Thallium powder-in-tube conductor
IBM (completed)	2/1/90–1/31/94	NFE	255	0	673	Optimize flux pinning via ion-induced defects
IBM	2/1/90–5/31/95	FO	201	389	186	Optimize flux pinning via ion-induced defects
Neocera (completed)	2/1/91–1/31/93	FO	80	111.6	95.7	Laser ablation multitarget deposition
Oxford Instruments	1/94–12/95	C	50	0	75	Develop technology for dip-coated BSCCO-2212 wire
Plastronic, Inc.	10/22/93–9/30/95	NFE	165	0	225	Apply wire-forming technology to produce BSCCO wire
Saphikon (completed)	2/1/92–4/30/94	NFE	50	0	492	Deposited conductor fabrication
SUNY-Buffalo (completed)	7/1/89–10/30/92	FO	165	250	255	Laser deposition of conductors
Stevens Institute of Technology (completed)	1/1/90–5/31/92	FO	90	105	100	MOCVD deposition for electronic devices
Superconductivity, Inc. (completed)	10/1/89–3/31/93	NFE	180	0	133	Magnetic energy storage for end-use applications
Textron Specialty Materials (completed)	8/1/89–3/31/91	NFE	60	0	45	Deposition of conductors
University of Wisconsin—Madison	8/1/92–5/31/95	FO	120	80	200	Aerosol powder synthesis
Westinghouse Electric (completed)	4/1/89–12/31/93	FO	1200	750	800	Powder scale-up, BSCCO wire fabrication, and leads
Total			10200.5	4390.6	11061.6	
<i>FY 1993/94 subcontracts</i>						
University of New Mexico	4/1/93–3/31/94			45		Study the generation of Pb-Bi-Sr-Ca-Cu-O (BSCCO) powders by aerosol decomposition
H. Hsu	11/15/93–11/14/94			48		Material synthesis and conductor fabrication
Imtech	9/23/94–9/22/95			65		Superconducting powder synthesis/scale-up

Table 3.2 (continued)

Participant	Approved term	Type ^a	Total agreement cost share (\$ × 1000)			Technology area
			By DOE to ORNL	By DOE to industry	By industry	
University of Tennessee	4/1/93–11/30/93			58		Advanced analytical electron microscopy techniques for HTS conductors
Georgia Institute of Technology	4/15/93–4/14/94			20		Study of combustion pyrolysis method for processing YBCO superconductors
SAIC	4/94–9/94			19		Prepare paper on evaluation of technology in Lab-industry partnership
National Institute of Standards and Technology (via Interagency Agreement)	8/93–7/95			200	200	BSCCO and TBCCO phase diagram support

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

Fig. 3.1. ORNL funding distribution: FY 1994 new budget authorization and outlay.

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. 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 Laboratories 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 and Energetics 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;
- coordination of Superconducting Technology Program workshops (one per year), including all subcontracting required for guest speakers and workshop arrangements; and
- review of industrial collaboration opportunities through multi-laboratory 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. ORNL manages the Energetics subcontract and works with Energetics and with other national laboratories to produce a program annual operating plan.

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

PROGRAM MEASURES

Three new cooperative agreements were executed during FY 1994: Plastronic, Inc., Oxford Superconducting Technology, and the General Electric Company (for SPI). New statements of work were negotiated and agreements were extended with ASC, IGC, GE, IBM, and the University of Wisconsin-Madison.

Eight new invention disclosures were submitted by ORNL or industry principal investigations. These are listed in Table 3.3 together with all others for the program.

Table 3.3. Superconducting Technology Program invention disclosures

ESID No.	Subject	Submitted by
935-X	Method for Fabricating Continuous Ribbons of High-Temperature Superconductors	V. K. Sikka and C. E. Dunn
1018-X	Improved $Y_1Ba_2Cu_3O_7$ Superconductor	A. D. Marwick and L. Civale (IBM), and J. R. Thompson (ORNL)
964-X	Chemically Compatible Substrate/Jacket Alloy for Oxide Superconductors	D. M. Kroeger, F. A. List III, and J. Brynstad
1039-X	Method for Preparation of $(Bi-Pb)_2Sr_2Ca_2Cu_3$ Oxide Powders	D. M. Kroeger, J. Brynstad, and H. S. Hsu
1040-X	Method for Preparing Superconducting Wires from Oxide Powders	D. M. Kroeger and H. S. Hsu
1058-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
1131-X	Method of Forming Superconducting Joints Between Tapes of Oxide Superconductors (87X-SE934V) ^a	R. H. Arendt and K. W. Lay (GE)
1155-X	Method for Fabricating High-Current-Density, Oxide Superconductor Ribbons (HTSPC-001) ^a	V. K. Sikka
1124-X	Improved, Strain-Tolerant High-Temperature Superconductor (87X-SD925C) ^a	G. A. Whitlow and W. R. Lovic (Westinghouse)
1129-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)
1193-X	Process for Fabricating Continuous Lengths of Superconductor (86X-SD925C) ^a	D. M. Kroeger and F. A. List III
1233-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 III (ORNL)
1185-X	Bipolar Pulse Field for Magnetic Refrigeration	M. S. Lubell
1384-X	Process to Enhance Superconducting Phase Formation, Grain Alignment, and Fracture Properties of High-Temperature Superconductors	V. Selvamanickam and D. M. Kroeger
1450-X	Improved-Efficiency High- T_c Superconducting Magnet Lead Materials	R. K. Williams
1467-X	Superconducting Structure and Method for Making Same	R. K. Williams and J. Brynstad
1471-X	HTS Coil Grading to Compensate for Anisotropic Behavior of HTS Conductor (86X-SK700V)	D. Aized and R. Schwall (American Superconductor)

Table 3.3 (continued)

ESID No.	Subject	Submitted by
1511-X	Enhancement of Persistent Currents in High- T_c Superconductors (86X-SF645V)	L. Krusin-Elbaum, A. D. Marwick, and J. F. Ziegler (IBM), J. R. Thompson (ORNL), and P. Lisowski (LANL)
1512-X	Method for Preparation of Textured $YBa_2Cu_3O_x$ Superconductor	V. Selvamanickam, A. Goyal, and D. M. Kroeger
1632-X	Materials and Fabrication Method for Producing High- T_c Superconducting Tapes (ORNL 93-0180)	R. K. Williams (ORNL) and K. R. Marken, Jr. (Oxford)
1636-X	Low-Loss Multifilamentary Superconductor for ac Applications	M. S. Lubell
1638-X	Buffer Template for c -Axis-Oriented Perovskite Films on Crystalline Metals	David P. Norton and J. D. Budai
1640-X	Method of Fabricating High-Temperature Superconductors with Enhanced "Bi-Axial" Texture	A. Goyal, E. D. Specht, D. M. Kroeger

"Numbers in parentheses are cooperative agreement numbers under which the work was conducted.

FY 1994 Presentations and Publications

- D. M. Kroeger, A. Goyal, E. D. Specht, Z. L. Wang;¹ J. E. Tkaczyk, J. A. Sutliff, and J. A. DeLuca,² "The Path for Long-Range Conduction in High J_c $TlBa_2Ca_2Cu_3O_{8+x}$ Spray-Pyrolyzed Deposits," presented at the Fall 1993 TMS Meeting; to be published in symposium proceedings.
- W. B. Carter, G. W. Book, and A. T. Hunt,³ "Combustion Chemical Vapor Deposition of $YBa_2Cu_3O_x$," to be published in the proceedings of the European Conference on Applied Superconductivity '93, held in Göttingen, Germany, Oct. 1993.
- M. Paranthaman, J. Brynestad, D. K. Christen, P. M. Martin, R. K. Williams, and D. M. Kroeger;¹ Y. R. Sun;⁴ and J. G. Ossandon,⁵ "Synthesis and Magnetic Properties of Hg-Ba-Ca-Cu-O Superconductors," abstract submitted to the Materials Research Society 1994 Spring Meeting, April 4-8.
- D. M. Kroeger, A. Goyal, E. D. Specht, and Z. L. Wang;¹ J. A. DeLuca, J. E. Tkaczyk, and J. Sutliff,² "Colony Microstructure and the Path for Strongly Linked Current Flow in $Tl-1223$ Deposits," abstract submitted to the Materials Research Society 1994 Spring Meeting, April 4-8.
- Z. L. Wang;⁴ R. Kontra;⁶ and D. M. Kroeger, A. Goyal, and R. K. Williams,¹ "Interface and Grain Boundary Chemical Structures in YBCO Materials," submitted to *Interface Science Journal*.
- D. M. Kroeger, A. Goyal, E. D. Specht, and Z. L. Wang;¹ J. A. DeLuca, J. E. Tkaczyk, and J. Sutliff,² "Local Texture and Percolative Paths for Long-Range Current Flow in High J_c $TlBa_2Ca_2Cu_3O_{8+x}$ Deposits," abstract submitted to Sixth Annual U.S./Japan Joint HTS Workshop, Houston, Texas, Dec. 6-7, 1993.
- R. W. Dull⁷ and H. R. Kerchner,¹ *A Teacher's Guide to Superconductivity for High School Teachers*, ORNL/M-3063, Oct. 1993.
- A. Goyal, D. M. Kroeger, E. D. Specht, and Z. L. Wang,¹ "Dependence of Critical Current Density on Microstructure in High- T_c Superconductors," abstract submitted to 1994 TMS Spring Meeting, San Francisco, Feb. 27-March 3, 1994.
- C. L. Briant, A. Goyal, J. A. DeLuca, P. Karas, and D. M. Kroeger,¹ "The Microstructural Evolution of Silver-Containing Spray Deposited 1223 $Tl-Ca-Ba-Cu$ Oxide Superconductor," abstract presented to 1994 Materials Research Society Spring Meeting, San Francisco.
- A. Goyal, G. N. Riley, L. Riester, and D. M. Kroeger,¹ "Anisotropic Elastic Modulus and Hardness of Well-Aligned Bi-2223 and Bi-2212 Powder-in-Tube Materials," abstract submitted to 1994 Materials Research Society Spring Meeting, San Francisco.
- J. D. Budai, D. P. Norton, D. K. Christen, R. Feenstra, Q. He, B. C. Chakoumakos, E. C. Jones, and R. T. Young,¹ "In-Plane Alignment of $YBaCuO$ Films on Metal Substrates and Buffer Layers," paper presented to 1993 Fall Materials Research Society Meeting, Boston.
- V. Selvamanickam, A. Goyal, and D. M. Kroeger,¹ "A New Method to Fabricate Textured Bulk $YBa_2Cu_3O_x$ Superconductor," abstract presented to 1994 TMS Annual Meeting, San Francisco, Feb. 27-March 3, 1994.
- G. Cui, J. Zhang, C. P. Beetz, J. Steinbeck, Z. L. Wang, and D. M. Kroeger,¹ "Epitaxial Growth of $YBa_2Cu_3O_{7-x}/BaTiO_3$ Thin Film Heterstructures by Magnetron Sputtering," abstract submitted to Materials Research Society Spring Meeting, San Francisco.

4-2 FY 1994 Presentations and Publications

- M. Paranthaman, Y. R. Sun, and J. R. Thompson,¹ "Synthesis and Magnetic Characterization of Bulk $\text{HgBa}_2\text{CuO}_{4+x}$, $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+x}$, and $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ Superconductors," abstract submitted to 1994 American Physical Society March Meeting, Pittsburgh.
- D. B. Pulling and H. A. Blackstead,⁸ M. Paranthaman and J. Brynestad,¹ "Field and Temperature Dependent Surface Resistance of Superconducting Polycrystalline Hg-Ba-Ca-Cu-O," abstract submitted to 1994 American Physical Society March Meeting, Pittsburgh.
- J. R. Thompson, J. G. Ossandon, D. K. Christen, B. C. Chakoumakos, Y. R. Sun, M. Paranthaman, and J. Brynestad,¹ "Vortex Fluctuations, Magnetic Penetration Depth, and H_{c2} in Hg- and Tl-Based High- T_c Superconductors," *Physical Rev. B*, Vol. 48, No. 18, 1 November 1993.
- J. A. DeLuca, P. L. Karas, C. L. Briant, and J. E. Tkaczyk;² A. Goyal,¹ "Progress in the Development of the Silver-Addition Process for Preparing Textured '1223' Tl-Ca-Ba-Cu-Oxide Thick Films," presented at Fall TMS Meeting, Pittsburgh PA, October 1993.
- H. A. Blackstead and D. B. Pulling;⁸ M. Paranthaman and J. Brynestad,¹ "Field- and Temperature-Dependent Surface Resistance of Superconducting Polycrystalline Multiple-Phase Hg-Ba-Ca-Cu-O: Evidence for 'Dirty-Limit' Behavior," paper submitted to *Phys. Rev. B*.
- C. K. Subramaniam and A. B. Kaiser;⁹ M. Paranthaman,¹ "Thermoelectric Power and Resistivity of Bulk $\text{HgBa}_2\text{CuO}_{4+y}$ Superconductors and the Effects of Annealing," paper submitted to *Physica C*.
- L. Civale, L. Krusin-Elbaum, A. D. Marwick, F. Holtzberg and C. Feild;⁶ J. R. Thompson;¹ R. Wheeler and M. A. Kirk;¹⁰ and Y. R. Sun,⁴ "Arresting Vortex Motion in YBaCuO Crystals with Splay in Columnar Defects," paper submitted to *Nature*.
- J. R. Thompson, D. Paul, Z. L. Wang, D. K. Christen, H. R. Kerchner, B. C. Sales, and B. C. Chakoumakos;¹ Y. R. Sun and Y. J. Chen;⁴ and L. Civale, L. Krusin-Elbaum, A. C. Marwick, and F. Holtzberg,⁶ "Enhanced Vortex Pinning and Current Density in High- T_c Materials via Tailored Defects," book chapter of *Proceedings of the Sixth Annual U.S.-Japan Joint Workshop on Superconductivity*, ed. K. Salama, World Scientific.
- V. Selvamanickam, A. Goyal, and D. M. Kroeger,¹ "A New Process to Texture Bulk $\text{YBa}_2\text{Cu}_3\text{O}_x$ Superconductor," paper submitted to *Applied Physics Letters*.
- G. Stejic, A. Gurevich, E. Kadyrov, R. Joynt, and D. C. Larbalestier;¹¹ D. K. Christen,¹ "The Effect of Geometry on the Critical Currents of Thin Films," paper submitted to *Physical Review B*.
- L. Dresner,¹ "Quench Energies of Uncooled Superconductors," *Cryogenics 1994*, Vol. 34, No. 1, pp. 77-82.
- L. Dresner,¹ "On the Connection Between Normal Zone Voltage and Hot-Spot Temperature in Uncooled Magnets," *Cryogenics 1994*, Vol. 34 No. 2, pp. 111-118.
- D. M. Kroeger, A. Goyal, and E. D. Specht;¹ Z. L. Wang;¹² J. E. Tkaczyk, J. A. Sutliff, and J. A. DeLuca,² "Local Texture and Strongly Linked Conduction in Spray-Pyrolyzed $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$ Deposits," to be published in proceedings of Sixth Annual U.S./Japan Joint HTS Workshop held Dec. 6-7, 1993, in Houston.
- L. J. Masur, E. R. Podtburg, C. A. Craven, and A. Otto;¹³ Z. L. Wang and D. M. Kroeger;¹ and J. Y. Coulter and M. P. Maley,¹⁴ "Bi-axial Texture in $\text{Ca}_{0.1}\text{Y}_{0.9}\text{Ba}_2\text{Cu}_4\text{O}_8$ Composite Wires Made by Metallic Precursors," paper submitted to *Physica C*.

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- J. R. Thompson, D. K. Christen, R. Feenstra, B. C. Sales, and H. R. Kerchner;¹ J. G. Ossandon;⁵ E. C. Jones and Y. R. Sun,⁴ "Supercurrent Density and Vortex Pinning in $Y_1Ba_2Cu_3O_{7-x}$ Materials Versus Oxygen Content," to be published in Proceedings of the Seventh International Workshop on Critical Currents, World Scientific, Singapore.
- Y. R. Sun;⁴ J. R. Thompson, H. R. Kerchner, D. K. Christen, M. Paranthaman, and J. Brynstad,¹ "Strong Surface Pinning Effects in Polycrystalline $HgBa_2CuO_{4+x}$ Superconductor," submitted to *Physical Review B*.
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- S. W. Schwenlerly, J. W. Lue, and M. S. Lubell;¹ M. S. Walker, D. W. Hazelton, P. Haldar, J. A. Rice, J. G. Hoehn, Jr., and L. R. Motowidlo;¹⁶ "Performance of Pancake Coils of Parallel Co-Wound Ag/BSCCO Tape Conductors in Static and Ramped Magnetic Fields," abstract submitted to Applied Superconductivity Conference, Boston, Oct. 16–21, 1994.
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- Z. L. Wang;¹² D. K. Christen, C. E. Klabunde, D. M. Kroeger, D. H. Lowndes, and D. P. Norton,¹ "Flux-Pinning Related Defects in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Thin Films Grown on Mismatched LaAlO_3 (001) Substrates," paper submitted to 52nd Annual Meeting of Microscopy Society of America, July 31–Aug. 5, 1994, New Orleans.
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- S. Zhu, D. H. Lowndes, J. D. Budai, and D. P. Norton,¹ "In-Plane Aligned CeO₂ Films Grown on Amorphous SiO₂ Substrates by Ion-Beam Assisted Pulsed Laser Deposition," paper submitted to *Applied Physics Letters*.
- E. D. Specht, A. Goyal, and D. M. Kroeger;¹ J. A. DeLuca, C. L. Briant, and J. A. Sutliff,² "X-Ray Microdiffraction Analysis of mm-Scale Orientational Correlations in TI-1223 High-Critical-Current, High-Temperature Superconducting Films," *Physica C*, 226, p. 76, 1 June 1994.
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- A. Goyal, E. D. Specht, and D. M. Kroeger;¹ C. L. Briant, J. A. Sutliff, and J. E. Tkaczyk,² "Formation of Colonies of Locally Aligned Grains During Thallination of Spray-Pyrolyzed Ba₂Ca₂Cu₃O_x Thick Films," invited abstract submitted to 1995 TMS Annual Meeting and Exhibition, Las Vegas, Feb 12-16.
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