ORNL/HTSPC--4

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ORNL SUPERCONDUCTING TECHNOLOGY PROGRAM FOR ELECTRIC ENERGY SYSTEMS

ANNUAL REPORT FOR FY 1992

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Manuscript Completed—December 1992
Date Published—February 1993

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

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for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

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ACRONYMS AND INITIALISMS

ACA	Astronautics Corporation of America
ASC	American Superconductor Corporation
DARPA	Defense Advanced Research Projects Agency
DOE	U.S. Department of Energy
EDS	energy-dispersive spectroscopy
EELS	electron energy loss spectroscopy
EPRI	Electric Power Research Institute
HTS	high-temperature superconductor
IGC	Intermagnetics General Corporation
MR	magnetic refrigerator
OBES	Office of Basic Energy Sciences
ORNL	Oak Ridge National Laboratory
R&D	research and development
SEM	scanning electron microscopy
SSD	superconducting magnetic energy storage device
TEM	transmission electron microscopy
UPS	uninterruptible power supply

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ABSTRACT

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 (DOE's) Office of Conservation 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 two major elements of this program are wire development and systems development. 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 1992 Peer Review of Projects, conducted by DOE's Office of Program Analysis, Office of Energy Research. This ORNL program is highly leveraged by the staff and other resources of U.S. industry and universities. 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 to U.S. industry. Working together, the collaborative teams are making tremendous progress in solving the scientific and technical issues necessary for the commercialization of long lengths of practical high-temperature superconductor wire and wire products.

1. TECHNICAL PROGRESS IN HIGH-TEMPERATURE SUPERCONDUCTOR WIRE DEVELOPMENT

1.1 IMPROVED STARTING MATERIALS

1.1.1 High-Temperature Superconductor Powder Synthesis by Aerosol Pyrolysis

1.1.1.1 Project Overview

Specific project objectives

Several characteristics of the oxide superconductors, and the geometric and microstructural requirements for conductors using them, place stringent requirements on powder precursors and the processes by which they are synthesized. They generally contain several cations. They exhibit complex stability behavior, and phase development is often slow. Phase purity, microstructure, and properties may be affected by impurities (in particular carbon), by small variations in composition, and by low concentrations of dopants. Multifilamentary configurations require very small particle size and a degree of compositional homogeneity that is difficult to achieve by most synthesis processes. Processes for powder synthesis that offer accurate control of composition, uniform doping, good control of impurities, small particle size, and high homogeneity are needed. The goals of this project are to investigate aerosol pyrolysis as a commercially scalable process that can offer the advantages listed, to develop process parameters needed for preparation of the important oxide superconductor compounds, and to investigate the processing of aerosol powders in conductor configurations.

Relationship of project to DOE mission

Work on the development of a commercially scalable powder synthesis process for preparing powders with superior characteristics for use in conductor fabrication is carried out in support of the mission of the Superconducting Technology Program to promote commercialization by American industry of oxide superconductors. Preparation of powders for more basic studies of properties and processing is also in support of that mission. As part of our cooperative projects with industry on conductor development, aerosol powders are provided to companies for use in conductor fabrication and processing studies (see Fig. 1).

Relationship to other DOE projects

This project interfaces closely with Office of Basic Energy Sciences–supported (OBES) projects at Oak Ridge National Laboratory (ORNL) on synthesis, processing, and properties of high-temperature superconductors (HTSs). Development of processes for preparing superconductor precursor powders with superior properties is of importance to all U.S. Department of Energy–supported (DOE) work on oxide superconductors. Transfer of aerosol process technology to DOE-supported programs at Brookhaven National Laboratory and the University of Wisconsin has been accomplished through visits of personnel to ORNL. Aerosol pyrolysis systems have been set up at those institutions, PHOTO YP 15927

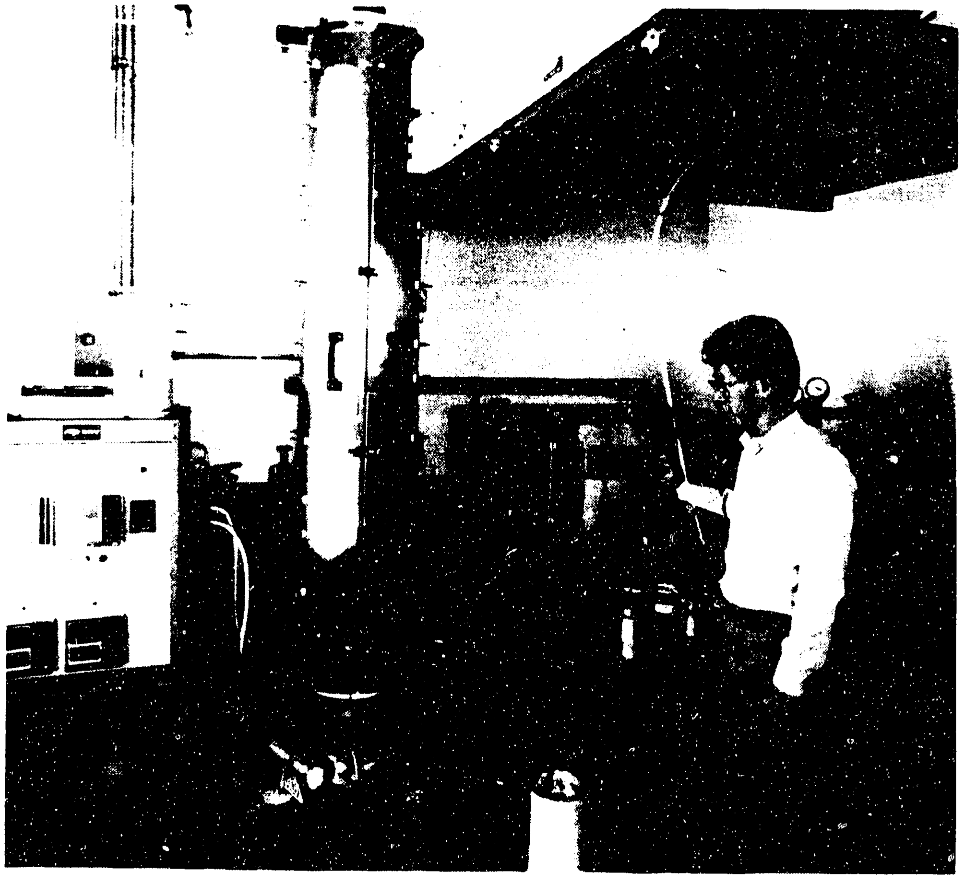

Fig. 1. H. Hsu, consultant to ORNL and to the American Superconductor Corporation, produces aerosol powder for high-temperature superconducting wire development.

and studies involving aerosol powders are in progress. Industry is cooperating through projects partially supported by DOE in development of conductors utilizing aerosol powders.

Project history

DOE funding for this project is shown in the following table:

	DOE funding ($ × 1000)		
	FY 1990	FY 1991	FY 1992
Direct scientific and technical	250	250	250
R&D subcontract—University of New Mexico	45	45	45
Consultant	15	15	30
Total DOE	310	310	325

1.1.1.2 Scientific and Technical Content

Schedule of major research activities

Early activities of the project centered on preparation and processing of low-carbon, highly homogeneous, submicron YBCO powders of both the 123 and 124 compositions. It was shown, partly in cooperation with AT&T Bell Laboratories, that aerosol powders can be used to prepare melt-processed deposits and bulk materials with reduced 211 particle size. Such deposits were used in studies of 123/substrate compatibility and in transmission electron microscopy (TEM) studies of possible flux-pinning defects associated with 211 particles. The effects of aerosol process parameters on the rate of conversion to the 124 phase of aerosol 123 + CuO precursor was studied.

Recent activities have been directed toward preparation and processing of bismuth-based powders for use in conductor fabrication studies. Process parameters have been determined to limit lead loss during aerosol synthesis of Bi(Pb)-2223 precursor powder. The effects of process parameters on phase content and particle morphology for both Bi-2212 and Bi(Pb)-2223 compositions have been examined. Studies are in progress of the effects of processing parameters and powder characteristics on processing and properties of conductors prepared from aerosol powders. Alternative approaches to conductor fabrication, taking advantage of the characteristics of aerosol powders, are being explored. With proper treatment, conversion to the Bi(Pb)-2223 phase can be rapid, and high-J_c conductors can be prepared with heat treatment times substantially shorter than commonly used. Studies of aerosol synthesis and subsequent processing of thallium-based superconducting compounds have also been initiated.

Scientific and technical issues

HTS compounds occur in oxide systems containing several cations and many compounds. They form only in restricted oxygen pressure and temperature intervals, and phase pure materials are often difficult to obtain. Phase assemblages depend on processing routes as well as composition, and heat treatment times are often long, indicating the importance of kinetics in phase and microstructure development. As a consequence, compositional homogeneity, compositional control, and particle size are very important characteristics of precursor powders used both in applications and in basic studies. Powders prepared by aerosol pyrolysis are exceptional in these characteristics.

Current efforts largely relate to technical issues in the use of aerosol powders in silver-sheathed conductors. The issue of lead loss during aerosol synthesis of Bi(Pb)-2223 precursor powder has been addressed, and process parameters have been found that result in negligible loss of all cations, including lead. It is known that the Bi-2223 phase forms only in restricted oxygen pressure and temperature ranges. In the case of aerosol powders, this processing window is affected by aerosol process parameters and subsequent powder characteristics such as phase content. The effects of aerosol process parameters on powder characteristics and the processing window for 2223 phase formation in a silver-sheathed conductor are being studied; the goals are to reduce heat treatment times and to improve microstructures. Aerosol process parameters for synthesis of Tl-1223 and Tl-2223 precursors are also being investigated.

Experimental and theoretical approach

This project involves coordinated activities of personnel and facilities in the Metals and Ceramics, Chemistry, and Solid State Divisions at ORNL and at the Center for Micro-Engineered Ceramics at the University of New Mexico. The participation of T. Kodas at the University of New Mexico, a recognized expert in aerosol synthesis processes, is obtained through a subcontract from the Superconducting Technology Program at ORNL. Aerosol pyrolysis systems are operated at both ORNL and the University of New Mexico. Current emphasis at the University of New Mexico is on very fine powders prepared with gas jet atomization and most recently, addition of various dopants to BSCCO compositions, while at ORNL preparation and processing of larger particles prepared by ultrasonic atomization, a faster process, is studied. While the activities reported in this project are carried out primarily on ORNL's base program (i.e., without industry participation), the potential of aerosol powders for commercial application is being explored through cooperative programs with industry. The extensive facilities at ORNL for microstructural characterization and analysis, including optical metallography, X-ray diffraction, scanning electron microscopy (SEM), TEM, electron microprobe, energy-dispersive spectroscopy (EDS), and differential thermal and thermogravimetric analysis, are used to characterize both powders and materials made from them.

Aerosol pyrolysis was chosen for study and development because it is a commercially scalable process by which exceptionally homogeneous micron or submicron powders can be prepared. These characteristics were expected to be of benefit in silver-sheathed conductors, resulting in easier fabrication, more rapid phase formation, and smaller secondary phase particles. The high degree of compositional homogeneity and absence of large, hard agglomerates are especially important in fabrication and properties of multifilamentary configurations and in improving the uniformity of properties of conductors over long lengths.

Importance of solving the problem being addressed by this research

This project is directed toward improving the properties of HTS wires and solving problems in their fabrication. Such improvements are essential for realizing the potential benefits of HTSs in a wide range of energy-related applications.

1.1.1.3 Project Output

Major research accomplishments

Superconductor precursor powder synthesis by aerosol pyrolysis involves preparation of a nitrate solution of the cations in the desired ratio, atomization of that solution to obtain a fine mist, and entrainment of the mist in a carrier gas that is then passed through a hot zone. In the hot zone, water is removed and nitrate is decomposed, leaving, in general, a mixture of oxides. Particles may be collected in a variety of ways, most simply by a filter in the gas stream. Process variables that significantly affect powder characteristics include droplet/particle residence time in the hot zone, hot-zone temperature, and carrier gas composition. Particle size is determined by the solution concentration and the method of atomization. Solutions other than nitrates may be used, but most other choices contain carbon and are therefore considered poor choices for preparation of oxide superconductors.

Aerosol synthesis is a commercially scalable process by which highly reactive, homogeneous, micron-sized (oxide) powders, usually containing one or two cations, can be produced. Production rates of many kilograms per day are possible. The overall goal of this project is to explore the applicability of this process to preparation of superconductor precursor powders for use in conductor fabrication. Specific problems that have been addressed include loss of volatile components (e.g., lead and thallium) during aerosol synthesis, carbon contamination, and effects of aerosol process parameters on phase content and particle morphology. Studies of the formation of Bi(Pb)-2223 phase from aerosol precursors are in progress. Rapid conversion in a conductor configuration has been demonstrated. Short samples of Bi(Pb)-2223 powder-in-tube conductor with superior properties have been prepared, and a conductor fabrication process involving spray-drying of aerosol powder is being studied. Work on preparation of thallium-based superconductor precursors is at an early stage.

Exceptional compositional control and homogeneity on a scale smaller than the particle size is obtained in aerosol pyrolysis. The cation ratio in a particle is the same as that in its parent droplet, provided vaporization losses during pyrolysis are negligible. This condition is easily met for the Y-Ba-Cu-O system, but compositions containing lead and thallium potentially present problems. However, we have determined that there is a range of aerosol process parameters for which lead loss from Bi(Pb)-2223 compositions is negligible. Our first attempt at aerosol synthesis of a thallium-based compound resulted in measurable loss of thallium (~30%), and measures to reduce thallium loss are under investigation. An alternative approach by which we have synthesized both 1223 and 2223 compounds is to prepare by aerosol synthesis a precursor without thallium to be blended with Tl_2O_3 prior to conductor fabrication. Studies of the use of thallium-based aerosol precursors in a powder-in-tube conductor are at an early stage.

A powder-in-tube conductor fabricated using Bi(Pb)-2223 aerosol precursor has been shown to require shorter heat treatment time than a conductor containing solid state reaction powder. Rapid formation of the 2223 phase at temperatures as low as 800°C has been demonstrated. First-stage heat treatment times of only a few hours were found to be desirable in contrast to the 50 to 100 h often used for solid state reaction powders. Using a two-stage roll and sinter process, short samples of powder-in-tube conductor have been prepared with J_c values as high as 13,000 A/cm^2 in self-field at 77 K. Values up to 16,500 A/cm^2 have been obtained with final deformation by pressing. Metallography indicates that secondary phase particles in the oxide core are small and that a well-aligned layer of 2223 forms near the silver/superconductor interface. However, overall grain alignment was poor, suggesting that substantial improvements in properties may be expected with optimization of the deform/sinter process. The rate of formation of the 2223 phase and apparently the route by which it forms vary with the initial phase content of the powder and the temperature and oxygen partial pressure, $P(O_2)$, at which it is reacted. Impurities such as carbon may also play a role. Phase content of the powder is determined by aerosol process parameters such as pyrolysis temperature, $P(O_2)$ in the carrier gas, and residence time in the hot zone as well as composition. In general, the phase assemblages found in aerosol powders are very different from that of solid state reaction powders used in the powder-in-tube process, and the heat treatment conditions required to form the 2223 phase are also different.

The primary source of carbon contamination is reaction of the powder on the collector with CO_2 in the carrier gas stream. Carbon content of the powder can be reduced by minimizing the time that powder spends in contact with the gas stream and by reducing the concentration of CO_2 and hydrocarbons initially in the carrier gas. Since the particles serve as a getter of CO_2 very efficiently, even very low concentrations of CO_2 at the collector result over time in significant carbon content in the powder. Therefore, chemical approaches to cleaning the gas stream have been only partly successful. Powders presently being produced and studied have ~300 to 400 wppm carbon. Obtaining lower concentrations is clearly possible but may require use of very high purity gases and/or use of a powder collection method that removes particles from contact with the gas stream.

The effect of pyrolysis temperature, from 700 to 900°C, on phase content and particle morphology has been examined. For low-pyrolysis temperatures SEM indicates that the particles tend to be hollow spheres containing many very small grains. At higher temperatures, where liquid formation is likely, the particles are smaller and apparently dense. The phase content as determined by X-ray diffraction also varies. For low- and high-pyrolysis temperatures substantial amounts of 2201 and little 2212 are present. In an intermediate temperature range significant amounts of each are seen. Other phases, such as Ca_2PbO_4 and alkaline earth bismuthates, are also seen and vary in amount over the range investigated. Using selected powders, studies of phase development as a function of heat treatment temperature and oxygen pressure are in progress.

Two patent disclosures have been made to DOE concerning aspects of the use of aerosol powders in conductor fabrication by the powder-in-tube process and by a method involving spray-drying. Decisions have been made to file patent applications in both cases.

YBCO. Initially, our aerosol synthesis work involved Y123 and Y124. Synthesis by aerosol pyrolysis of phase pure Y123 powder had already been demonstrated by one of our principal investigators (T. Kodas) prior to the beginning of this project. For pyrolysis temperatures near the peritectic temperature, single-phase powder consisting primarily of faceted single-crystal submicron particles can be produced. Studies of melt processing, both of deposits on silver-palladium alloy substrates (at ORNL) and of bulk material (by S. Jin et al. at AT&T Bell Labs, using powder from T. Kodas at the University of New Mexico) indicate that use of submicron aerosol powders can result in very small 211 particles embedded in the 123 matrix. Studies at ORNL that are not part of this project indicate there are significant benefits of small 211 particle size with respect to flux pinning and mechanical strength.

Relatively rapid conversion to $YBa_2Cu_4O_8$ of precursor powder prepared by aerosol pyrolysis was demonstrated. From X-ray diffraction the precursor contained Y123 and CuO and converted to Y124 at 800°C in 1 atm of oxygen. The rate of conversion depended strongly on aerosol pyrolysis parameters, suggesting the importance of the distribution and size of CuO grain within a particle. These results provided direction for our work on rapid conversion of aerosol powder precursors in the much more complicated Bi(Pb)-Sr-Ca-Cu-O system.

1.1.1.4 Bibliography of Recent Publications Emanating from This Project

1. D. M. Kroeger, H. S. Hsu, J. Brynestad, V. K. Sikka, T. Ward, and T. Kodas, "Processing and Properties of Powder-In-Tube Conductors Containing Bi (Pb) 2223 Powder Prepared by Aerosol Pyrolysis," presented at the Proceedings of the International Workshop on Superconductivity, Honolulu, Hawaii, June 23–26, 1992.

2. F. A. List, H. Hsu, O. B. Cavin, W. D. Porter, C. R. Hubbard, and D. M. Kroeger, "Phase Development in the $BiSr_2CaCu_2O_y$ System: Effects of Oxygen Pressure," *Phys. C* (1992); submitted for publication.

3. T. L. Ward, S. W. Lyons, T. T. Kodas, J. Brynestad, D. M. Kroeger, and H. Hsu "Characterization of Bi-Pb-Sr-Ca-Cu-O Powders Produced by Aerosol Decomposition and Their Rapid Conversion to the High-T_c Phase," *Phys. C* (1992); submitted for publication.

4. T. L. Ward, T. T. Kodas, A. H. Carim, D. M. Kroeger, and H. Hsu, "Powder Characteristics and Sintering Behavior of Ag-Doped $YBa_2Cu_3O_{7-x}$ Produced by Aerosol Decomposition," *J. Mater. Res.* 7(4), 1–1D (1992).

5. S. Jin, G. W. Kammlott, T. H. Tiefel, T. T. Kodas, T. L. Ward, and D. M. Kroeger, "Microstructure and Properties of the Y-Ba-Cu-O Superconductor with Submicron '211' Dispersions," *Phys. C* 181, 57–62 (1991).

6. S. Chadda, T. L. Ward, A. Carim, T. T. Kodas, K. Ott, and D. Kroeger, "Synthesis of $YBa_2Cu_3O_{7-y}$ and $YBa_2Cu_4O_8$ by Aerosol Decomposition," *J. Aerosol Sci.* 22(5), 601–16 (1991).

7. G. A. Whitlow, J. C. Bowker, W. R. Lovic, F. A. List, and D. M. Kroeger, "High Critical Current Silver—$Bi_2Sr_2CaCu_2O_{8-x}$ Superconducting Multilayer Ribbons Produced by Rolling," presented at the Sixth Annual Conference on Superconductivity and Applications, Buffalo, N.Y., September 15–17, 1992.

1.1.1.5 Patentable or Potentially Patentable Inventions

Martin Marietta Energy Systems has elected to file patent applications on two invention disclosures involving aerosol powders. Their titles are:

1. "Method of Producing Pb-Stabilized Superconductor Precursors and Method of Producing Superconductor Articles Therefrom," and

2. "Process for Fabricating Continuous Lengths of Superconductor."

1.2 IMPROVED CURRENT DENSITY THROUGH MELT-PROCESSING

1.2.1 Grain Boundary Chemistry and Pinning Site Generation in Y and RE-123 and Y-124

1.2.1.1 Project Overview

Specific project objectives

The objectives of this project are to investigate the relationship between weak-link behavior and grain boundary chemistry and to evaluate chemical methods for introducing flux-pinning defects. Studies of phase stability and synthesis methods link these two areas of research (this point is expanded in Subsect. 1.2.1.2).

Relationship of project to DOE mission

The DOE Superconducting Technology Program is developing the technology base necessary to produce long lengths of technologically useful HTS conductors. At present, none of the high-T_c compounds can be processed into conductors capable of carrying useful current densities at 77 K while operating in magnetic fields necessary for most electric power applications. Work on this project is directed toward determining causes for weak-link behavior and improving flux pinning in 123 and 124 structure superconductors.

Relationship to other projects funded by DOE

This project is coordinated with other ORNL DOE-funded efforts related to materials synthesis and microstructural characterization. It is supplemented by related research funded at ORNL through the DOE OBES. A significant amount of interaction has also occurred with two Argonne National Laboratory researchers, U. Balachandran and S. J. Rothman.

Project history

DOE funding for this project is shown in the following table:

	DOE funding ($ × 1000)		
	FY 1990	FY 1991	FY 1992
Direct scientific and technical	380	320	260
Total DOE	380	320	260

1.2.1.2 Scientific and Technical Content

Schedule of major research activities

Major research activities include:

- Synthesis of high-T_c compounds and production of dense polycrystalline samples for both grain boundary and pinning site studies. Phase stability information is developed as needed, and the emphasis is on the 123, 247, and 124 compounds containing yttrium and selected rare earths.
- Grain boundary characterization by both Auger spectroscopy and TEM. The purpose is to study the relationship between grain boundary chemistry and weak-link behavior.
- Investigation of chemical methods for producing flux-pinning centers.

Scientific and technical issues

The ultimate application of HTS materials as high-current conductors in the presence of large magnetic fields requires an understanding of the factors leading to the optimization of current flow in these highly anisotropic materials. These factors include the effectiveness of current transfer between grains or domains of practical bulk HTS materials, the pinning of magnetic vortex lines by material inhomogeneities within the HTS crystalline grains, and the minimization of thermally activated flux motion. The latter effect arises from the relatively high operating temperatures now contemplated, at which thermal energies may be comparable to the depth of the pinning wells. For HTS materials, this challenge is complicated by the very large crystalline anisotropy, which leads to drastically different intrinsic superconducting properties for magnetic fields oriented along different crystal axes, by the variable oxygen composition that can lead to modified (depressed) electronic and superconductive properties, and by the contribution of these and other effects to the problem of current coupling between grains (the "weak-link" problem). Studies of grain boundary chemistry are relevant to the weak-link problem. Evaluating alternative flux-pinning approaches may be applicable to development of bulk conductors.

Experimental and theoretical approach

The grain boundary studies involve using TEM and Auger spectroscopy to characterize the cation content and oxygen levels at grain boundaries in polycrystalline $YBa_2Cu_3O_{7-x}$ and $YBa_2Cu_4O_8$. Phase stability data are developed as required and used in sample synthesis and as an aid to understanding TEM and Auger observations. Three chemical methods for producing the pinning centers have been investigated: (1) forming disordered $YBa_2Cu_4O_8$ by diffusion at ~900°C, (2) forming defected $YBa_2Cu_3O_{7-x}$ by decomposing dense $Y_2Ba_4Ca_7O_{15-x}$ and $YBa_2Cu_4O_8$ samples, and (3) forming precipitates in nonstoichiometric rare-earth 123 materials. The studies involve sample characterization by physical property measurements (i.e., susceptibility, resistivity, and transport J_c), by microscopy [i.e., microprobe analysis, analytical TEM and electron energy loss spectroscopy (EELS), SEM, and Auger spectroscopy], and by X-ray diffraction. Sample synthesis and phase stability studies involve glove box operations and a high-pressure oxygen-annealing apparatus that can be operated at 110 bar O_2 at 1000°C.

Importance of solving the problem being addressed by this research

Improvements in J_c vs H performance, especially at temperatures near 77 K, are essential to use of HTS oxides in energy-saving electrical systems applications. The objectives of this project relate directly to improving J_c through improved flux pinning and improving our understanding of weak-link behavior.

1.2.1.3 Project Output

Major research accomplishments

Studies of the properties of bulk polycrystalline samples were initiated because transport measurements showed very low J_c values. A comparison with measurements on single-crystal films showed that the limitation is associated with grain boundaries, and Auger electron spectroscopy was used to study the chemistry of grain boundaries in sintered stoichiometric Y123 samples. These data showed that the grain boundaries contained excess copper and were deficient in oxygen. Sputtering showed that the nonsuperconducting layer was 15 to 50 Å thick and thus could contribute to the current density problem.

Alternate processing methods were investigated as a possible route to higher current densities. Hot isostatic pressing, which could be used to densify at lower temperatures, was explored. Orthorhombic samples, hot isostatically pressed at 925° C, were found to decompose into a three-phase mixture, and ambient pressure anneals restored the orthorhombic phase. The current densities of these samples were not improved, but TEM showed that the two phases formed during decomposition were identical to those formed during high-pressure oxygen exposures. These phases were 211 and a barium cuprate.

High-pressure synthesis showed that the latter phase was a peroxide. It then became clear that the decomposition of Y123 involved interaction with the gas phase:

$$4(YBa_2Cu_3O_{7-x}) + (1/2 - 3/2d + 2x)O_2 = 2Y_2BaCuO_5 + CuO + 3Ba_2Cu_3O_{6-\delta}\ .$$

The data are shown in Fig. 2, and the enthalpy change is about equal to the value for the oxidation of Cu_2O to CuO. These results demonstrate that the high-T_c orthorhombic phase is metastable. At atmospheric pressure decomposition begins at temperatures below about 800° C. The data shown in Fig. 3 demonstrate that decomposition, which takes place along grain boundaries, can severely degrade the transport properties of Y123. The stability data, Fig. 2, also show that processing routes are very important, and this result has been useful in developing procedures for thin film preparation.

Studies of the chemistry of grain boundaries have been extended by determining the effect of crystallite misorientation on the oxygen content at the boundary. EELS for the oxygen K edge was performed at and near grain boundaries in Y123. A 20-Å-diam electron beam was used, and the results revealed that the polycrystals contain both oxygen deficient (~100 Å wide) and fully oxygenated grain boundaries.

A parallel TEM investigation is being conducted on another high-T_c compound, $YBa_2Cu_4O_8$ - Y124. Auger data have been obtained, and these results indicate that grain boundary and bulk compositions do not differ significantly. EELS and EDS measurements of oxygen and cation compositions at grain boundaries in dense Y124 sintered material are

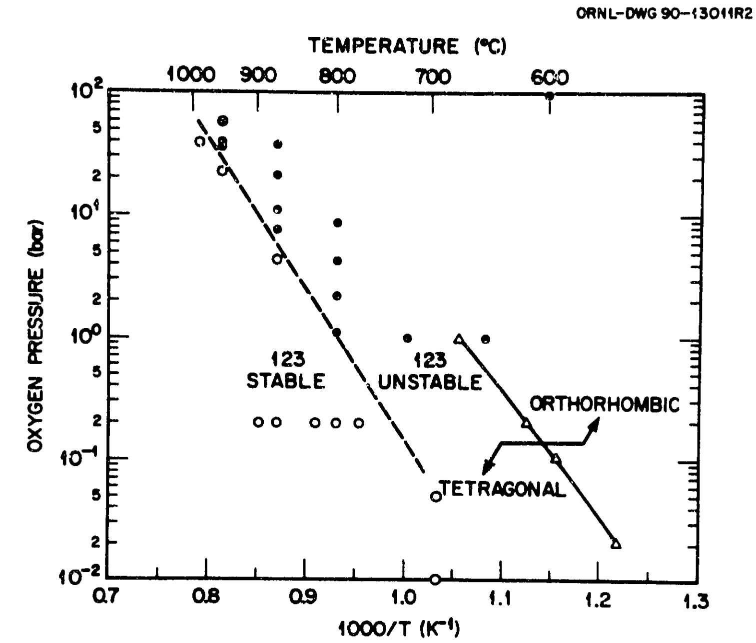

Fig. 2. Effect of oxygen pressure and temperature on the staiblity of $YBa_2Cu_3O_{7-x}$. The 960°C data marked O denotes formation of $YBa_2Cu_4O_8$.

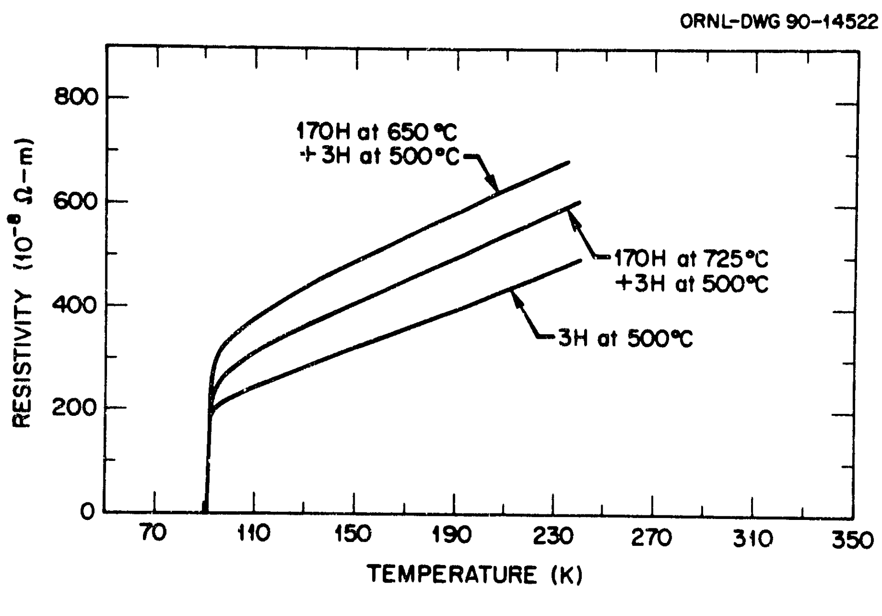

Fig. 3. Resistivity data for $YBa_2Cu_3O_{7-x}$ samples that were sintered at 950°C and then given indicated heat treatments.

in progress. Interest in Y124 arose because it appears to have some advantages over Y123. These include a smaller thermal expansion anisotropy, the oxygen content is relatively fixed, the compound does not undergo a phase change, and it also appears to be more stable than Y123. The disadvantages are that T_c is only 80 K, that synthesis involves high-pressure, high-temperature oxygen, and that the J_c appears to be weak-link limited. Intragranular J_c measurements yielded values comparable to those for Y123.

Dense ceramic samples are required for the studies of Y124, and high-pressure oxygen synthesis is not straightforward. Convective heat transfer is a major problem, and ultrapure gas is required to avoid carbon contamination. The results of a synthesis and phase stability study are shown in Fig. 4. These data indicate that Y124 is stable over a wide pressure range and conflict with reported values. The 1030°C 83-atm observation is within 10 K of liquation, and cold-pressed Y124 pellets sinter reasonably well under these conditions. A photomicrograph is shown in Fig. 5. Phase pure samples of another high-T_c compound, $Y_2Ba_4Cu_7O_{15-x}$ -Y247, have also been prepared.

These dense Y247 and Y124 samples are currently being used in a study of methods for producing fluxoid-pinning centers. Jin et al. have shown that ~65% dense Y124 samples rapidly decompose to Y123-CuO mixtures at 920°C. The decomposition generates defects that were shown to enhance intragrain flux pinning. Similar studies are now in progress using 92% dense Y124 and Y247 samples. Initial results indicate that the dense material decomposes more slowly.

Another approach to producing pinning centers is based on thermally induced decomposition of nonstoichiometric RE123. It has been reported that Ba^{2+} can be

ORNL-DWG 92-12441

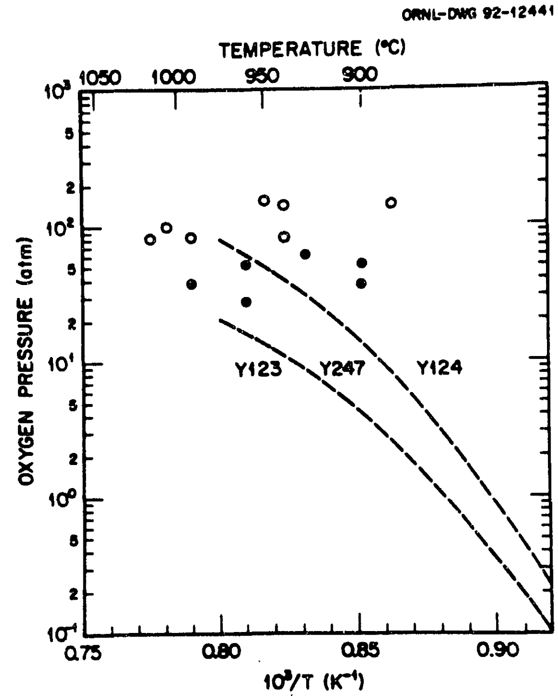

Fig. 4. Effect of oxygen pressure and temperature on the stability of $YBa_2Cu_4O_8$. (O) Phase did not decompose when aged. (●) Phase formed from other Y-Ba-Cu-O phases. The dotted lines on the stability regions reported by Morris et al. and Pooke et al.

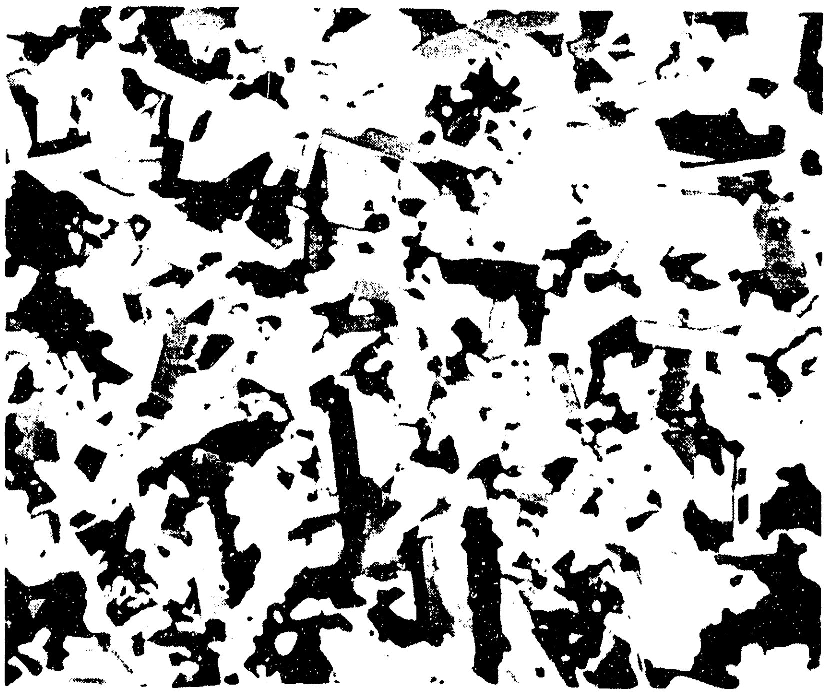

Fig. 5. Microstructure of a 93% dense $YBa_2Cu_4O_8$ sample. Polarized light.

extensively replaced in the 123 structure by La^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+} and Gd^{3+}. These results are based on high-temperature studies, and the goal of our research is to determine whether the equilibrium amount of Ba^{2+} replacement decreases at lower temperatures. Such a decrease would yield precipitate particles that might pin flux. This work has also been extended to Ba^{2+} replacement in Y123. Microprobe analysis and XRD show that Gd^{3+} can replace up to about 5% of the Ba^{2+} in Y123. The T_c of this compound was 92 K.

1.2.1.4 Bibliography of Recent Publications Emanating from this Project

1. D. M. Kroeger, A. Choudhury, J. Brynestad, R. K. Williams, R. A. Padgett, and W. Coghlan, "Grain Boundary Compositions in $YBa_2Cu_3O_{7-x}$ from Auger Electron Spectroscopy of Fracture Surfaces," *J. Appl. Phys.* **64**, 331–35 (1988).

2. R. K. Williams, K. B. Alexander, J. Brynestad, T. J. Henson, D. M. Kroeger, T. B. Lindemer, G. C. Marsh, and J. O. Scarbrough, "Some Observations of the Effects of High Pressures and Temperatures on the Stability of $YBa_2Cu_3O_{7-x}$," *J. Appl. Phys.* **67**, 6934–39 (1990).

3. R. K. Williams, K. B. Alexander, J. Brynestad, T. J. Henson, D. M. Kroeger, T. B. Lindemer, G. C. Marsh, J. O. Scarbrough, and E. D. Specht, "Oxidation Induced Decomposition of $YBa_2Cu_3O_{7-x}$," *J. Appl. Phys.* **70**, 906–13 (1991).

4. Yimei Zhu, Z. L. Wang and M. Suenaga, "Grain Boundary Studies by the Coincidence Site Lattice Model and Electron Energy Loss Spectroscopy of the Oxygen K-Edge in $YBa_2Cu_3O_{7-\delta}$," *Phil. Mag.* (1992); accepted for publication .

5. R. K. Williams, J. Brynestad, T. J. Henson, D. M. Kroeger, G. C. Marsh, R. A. Padgett, and J. O. Scarbrough, "Preparation and Grain Boundary Chemistry of Dense Polycrystalline $YBa_2Cu_4O_{\sim 8}$," *J. Appl. Phys.* **69**, 2426–30 (1991).

6. K. Doverspike, C. R. Hubbard, R. K. Williams, K. B. Alexander, J. Brynestad, and D. M. Kroeger, "Anisotropic Thermal Expansion of the 1:2:4 Yttrium Barium Copper Oxide Superconductor," *Phys. C* **172**, 486–90 (1991).

7. J. R. Thompson, D. K. Christen, H. R. Kerchner, L. A. Boatner, B. C. Sales, B. C. Chakoumakos, H. Hsu, J. Brynestad, D. M. Kroeger, R. K. Williams, Yang Ren Sun, Y. C. Kim, J. G. Ossandon, A. P. Malozemoff, L. Civale, A. D. Marwick, T. K. Worthington, L. Krusin-Elbaum, and F. Holtzberg, "Studies of 'Non-Ideal' Superconductors Using D.C. Magnetic Methods" in *Magnetic Susceptibility of Superconductors and Other Spin Systems*, ed. R. A. Hein, T. L. Francavilla, and D. H. Liebenberg, Plenum, New York (1992).

8. K. B. Alexander, R. K. Williams, D. M. Kroeger, and J. Brynestad, "The Structure and Chemistry of Grain Boundaries in Ceramic Superconductors," pp. 365–72 in *Ceramic Transactions*, Vol. 18, ed. K. M. Nair, U. Balachandran, Y. M. Chiang, and A. S. Bhalla, American Ceramic Society, Westerville, Ohio, 1991.

9. B. N. Lucas, W. C. Oliver, R. K. Williams, J. Brynestad, and M. E. O'Hern, "The Hardness and Young's Modulus of Bulk $YBa_2Cu_3O_{7-x}$ (1:2:3) and $YBa_2Cu_4O_8$ (1:2:4) as Determined by Ultra Low Load Indentation," J. *Mater. Res.* **6**, 2519–22 (1991).

10. K. B. Alexander, R. K. Williams, and S. J. Pennycook, "Stacking Variations in Bulk $Y_2Ba_4Cu_8O_{16}$ Materials," pp. 106–7 in *Proceedings XII International Congress for Electron Microscopy*, 1990.

11. L. Martinez, W. C. Oliver, and R. K. Williams, "Characterization of $YBa_2Cu_3O_{7-x}$ in a Mechanical Properties Microprobe," *Scri. Metall.* **26**, 7–12 (1992).

12. D. M. Kroeger, "Grain Boundaries and J_c in High Tc Oxide Superconductors, *J. of Metals* 41, 14–17 (1989).

13. R. K. Williams, R. S. Graves, D. M. Kroeger, G. C. Marsh, J. O. Scarbrough, and J. Brynestad, "Ambient Temperature Thermal Conductivity of $YBa_2Cu_3O_{7-x}$," J. *Appl. Phys.* **66**, 6181–84 (1989).

14. J. Bentley, A. T. Fisher, C. P. Haltom, J. Brynestad, R. J. Lauf, R. K. Williams, and D. M. Kroeger, "Electron Microscopy of High-Temperature Oxide Superconductors," in *Proceedings 45th Annual Meeting, EMSA*, 1987.

15. S. J. Collcott, G. K. White, S. X. Dou, and R. K. Williams, "Thermal Properties of High T_c Superconductors $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$," *Phys. Rev. B* 36, 5684–85 (1987).

1.2.1.5 References

1. D. E. Morris, A. G. Markelz, B. Fayn, and J. Nickel, *Physica C* 168, 153-60 (1990).

2. D. M. Pooke, R. G. Buckley, M. R. Presland, and J. L. Tallon, *Phys. Rev. B* 41, 6616–20 (1990).

3. S. Jin, T. H. Tiefel, S. Nakahara, J. E. Graebner, H. M. O'Bryan, R. A. Fastnacht, and G. M. Kammlott, *Appl. Phys. Lett.* 56, 1287–89 (1990).

4. Winnie Wong-Ng, B. Paretzkin, and E. R. Fuller, Jr., *J. Solid State Chem.* 85, 117–32 (1990).

1.2.2 Melt-Processing of High-Temperature Superconductors

1.2.2.1 Project Overview

Specific project objectives

The objectives of this project are to fabricate bulk, melt-processed Y-123 by several melt-processing techniques for potential passive (e.g., magnetic bearings and flywheels) and active (e.g., conductors and electromagnets) electric power applications at temperatures and fields higher than which the bismuth-based superconductors can be used (i.e., at 77 K and a few tesla). This involves a systematic study of powder production, bulk processing, microstructural and superconducting property characterization, and the development of scaleable processes for the fabrication of high-J_c Y 123 in suitable configurations. A significant effort is directed towards identifying, understanding, and controlling the key microstructural characteristics of these materials to achieve the desired goals. Specific objectives are summarized as follows:

- synthesis and evaluation of precurser powders with controlled size and homogeniety and with varying phase assemblages for melt processing;
- fabrication of high-J_c superconductors in suitable configurations by isothermal and thermal gradient melt-processing techniques;
- understanding of the solidification mechanism of 123 from the melt;
- finding suitable substrates or sheath materials to melt-process 123 thick films;
- understanding of the microstructure and mode of current transport in domains of melt-processed 123;
- identification of potential flux-pinning sites in 123 by extensive microstructural characterization; and
- determination of microstructure-property correlations in melt-processed 123, which includes both superconducting and mechanical property correlations with the microstructure.

Relationship of project to DOE mission

The activities of this project are directed toward fabricating high-J_c bulk superconductors in configurations useful for practical applications and toward identifying and optimizing the key materials factors that limit their performance. Because fabrication of practical superconductors with high J_c, especially for use at high temperatures (i.e., 77 K), is essential for the use of HTSs in many energy-related applications, this project is in direct support of the Superconducting Technology Program mission to promote rapid commercialization of these materials.

Relationship to other projects funded by DOE

This project is coordinated with other ORNL DOE-funded efforts related to deposited conductor development, microstructural characterization, materials modification through ion beam processing, and superconducting electromagnetic properties studies. The project is supplemented by related research funded both through the Superconducting Technology Program and through the DOE OBES.

Project history

DOE funding for this project is shown in the following table:

	DOE funding ($ × 1000)	
	FY 1991	FY 1992
Direct scientific and technical	300	300
Total DOE	300	300

1.2.2.2 Scientific and Technical Content

Schedule of major research activities

The major research activities of this project include:

- Generation of suitable precurser powders for fabrication of bulk superconductors. Fine (<1 mm), homogeneous, near single crystal 123 and 211 powders were produced by an aerosol flow reactor process. Powders were also produced by quenching preformed 123 from high temperatures to generate particles, with desired phase assemblages, suitable for melt processing.
- Fabrication of high-J_c materials by isothermal and thermal gradient melt-processing techniques.
- Studies to understand the physical processes dominating the formation of high-J_c domains of 123 from the semisolid melt. The studies are aimed at understanding the final microstructure of melt-processed 123 domains and to suggest ways to enhance the growth rates of 123 from the melt.

- Microstructural studies, involving a combination of macroscopic and microscopic techniques, to determine the paths for nonweak-linked current flow in high-J_c melt-processed $YBa_2Cu_3O_{7-x}$. The studies are aimed at determining ideal microstructures for obtaining high critical currents.
- Studies to identify microstructural features that may act as potential flux-pinning sites in melt-processed 123. The studies are aimed at optimizing defect structures in melt-processed 123.
- Evaluation and development of metallic substrates or sheath materials for melt-processing 123 in conductor form. The studies resulted in the identification of a suitable metallic substrate.
- Superconducting (i.e., resistivity, ac susceptibility, magnetization, and J_c) and mechanical property (i.e., hardness, elastic modulus, and fracture toughness) characterization of melt-processed 123.

Scientific and technical issues

Practical applications of HTSs at 77 K and at high fields requires an understanding of the materials issues leading to an optimization of their performance, as well as development of synthesis techniques, to enable their fabrication in suitable configurations. So far, the best J_c performance at 77 K in bulk HTS materials has been obtained in melt-processed 123. It has been our objective to determine the microstructural characteristics that lead to this superior performance. Efforts have also been directed on various synthesis aspects including a systematic study of powder production and bulk processing and on fabrication of melt-processed 123 in conductor configuration.

It is now well established that "domains" of melt-processed $YBa_2Cu_3O_{7-x}$ have the best critical current density performance. Furthermore, both resistive and magnetic measurements indicate weak-link free conduction in the *c*-direction as well as in the *ab* plane. Highly textured BSCCO powder-in-tube conductors can also exhibit weak-link free current flow. In view of the extensive evidence that large-angle grain boundaries generally inhibit current flow, it is important to determine the path for nonweak-linked conduction in these materials. First efforts have been directed toward high-J_c melt-processed $YBa_2Cu_3O_{7-x}$ together with extensive microstructural examination of chemistry and orientation at platelet boundaries. Information relevant to the so-called "brick-wall microstructure" model, which has been proposed to explain high-current densities in textured materials, has been obtained.

It is important to identify and to understand the origins of flux-pinning centers that arise during thermal and mechanical processing. The observation, although somewhat controversial, that J_c increases with the 211/123 interfacial area in melt-processed 123 provides an opportunity to examine microstructures likely to contain high densities of pinning centers. Although it has been suggested that the interface itself pins flux, this idea is not consistent with current understanding of the geometrical requirements for a flux pin. Extensive TEM examinations of the 123 near the surfaces of 211 particles were undertaken in an attempt to define microstructural features likely to pin flux.

One of the key factors that hinders practical applications of melt-processed 123 is the slow processing rate required to form the domain microstructure. Hence, identification of the physical processes that lead to the formation of such domains during solidification from the melt is important. Nucleation and growth of 123 from the melt was studied, and a growth model that explains the formation of 123 domains was proposed.

For active applications of melt-processed 123, its fabrication in suitable conductor configurations is necessary. The ability to carry high currents with little or no dissipation is not the only requirement for a conductor. It must also have sufficient strain tolerance and strength to permit device fabrication and to withstand magnetic forces associated with operation. Because the oxide superconductors are brittle and have little strength, composite conductors containing the superconductor as thin layers or filaments backed or encased by a metal are likely configurations for a practical conductor. The metal also promotes operational stability by providing an alternate path for current in the event local injections of heat result in a decrease in critical current. Most conductor fabrication work in other superconducting oxide systems (i.e., Bi-2212 and Bi-2223) has used silver as the metallic sheath because of its chemical compatibility. Although silver is chemically compatible with 123, it cannot be used as the sheath material to form melt-processed 123 conductors because its melting point is tens of degrees lower than the peritectic melting temperature of 123. Work at ORNL on finding a suitable substrate or sheath material has resulted in the identification of silver–10% palladium alloy as a suitable material.

Isothermal melt-processing of 123 thick films (~20 mm) on silver–10% palladium results in a microstructure comprising several domains of 123. These domains are in general randomly oriented with respect to one another. To fabricate a high-J_c conductor, alignment of these domains is necessary. Although thermal gradient processing of 123 to obtain essentially a single domain has been achieved, the presence of a high-thermal-conductivity metallic layer makes the situation far more complicated. Considerable effort has been directed at ORNL toward the design and testing of several thermal gradient furnaces in order to fabricate high-J_c thick films and powder-in-tube conductors. Efforts have also been focused on the fabrication of dense and continuous thick films and powder-in-tube wire and tape conductors for subsequent melt processing.

As mentioned before, in any practical application bulk HTSs may have to sustain significant stresses. Hence, a detailed characterization of the mechanical properties and their correlation with the microstructure is important. Various kinds of microhardness testers and a special mechanical properties microprobe have been used to obtain information on the hardness, elastic modulus, and fracture toughness of the high-J_c 123 domains.

Besides the above-mentioned issues, considerable emphasis has been placed at ORNL on precursor powder production, the effect of varying phase assemblages, and the presence of additives during melt processing. Fabrication of monolithic high-J_c samples of 123 by isothermal melt processing was carried out using several methods.

Experimental and theoretical approach

This project is coordinated with groups from the Metals and Ceramics Division, Chemistry Division, and the Solid State Division at ORNL as well as by several informal collaborations with industrial and university partnerships. This project investigates various important aspects of melt-processing 123 and addresses critical issues in enhancing their superconducting properties. Besides specimens fabricated in-house, other high-J_c, melt-processed 123 specimens (i.e., from K. Salama at the University of Houston, P. J. McGinn at the University of Notre Dame, T. R. Armstrong at Allied-Signal Aerospace, M. V. Parish at CPS Superconductor Corporation, and R. D. Blaugher, formerly at Intermagnetics General Corporation) were examined. This includes materials melt-processed isothermally, under a stationary thermal gradient, and by zone melt processing. Specimens from Allied-Signal Aerospace were fabricated using the quench-melt-growth technique of M. Murakami at ISTEC, Japan. Sample preparation at ORNL includes aerosol flow reactor processes to generate fine. homogeneous precursor powders, isothermal and thermal gradient melt processing, substrate and alloy development, and deformation processing. Physical characterization is carried out using optical microscopy, X-ray diffraction, SEM, EDS, electron microprobe, Auger spectroscopy, TEM, scanning transmission electron microscopy, EELS, and high-resolution electron microscopy. Superconducting property characterization includes resistivity, critical current density, ac susceptibility, and dc magnetization.

Importance of solving the problem being addressed by this research

Fabrication of superconductors with superior J_c vs H performance in suitable configurations, especially for operation at temperatures near 77 K, is essential to the use of HTS oxides in energy-saving electrical systems applications. The objectives of this project relate directly to fabrication of practical superconductors and toward enhancing J_c through improved flux pinning and control of microstructure to reduce weak-link behavior.

1.2.2.3 Project Output

Major research accomplishments

Work at ORNL has resulted in the setup of an aerosol flow reactor system to make fine, homogeneous powders with controlled stoichiometry and phase assemblages. Large domains of melt-processed 123 have been fabricated by isothermal melt processing, quench-melt-growth processing, and thermal gradient melt processing. Extensive microstructure-property correlations resulted in (1) understanding of the mode of current transport with domains of melt-processed 123, (2) identification of potential flux-pinning sites, (3) understanding of the solidification mechanism of domains of 123 from the melt, (4) identification of a metallic substrate or sheath material for melt processing, and (5) determination of the mechanical behavior of melt-processed 123. These accomplishments are discussed in the following subsections.

Mode of current transport within domains of 123. It is well recognized that critical current density in bulk polycrystalline $YBa_2Cu_3O_{7-x}$ is limited by weak-link behavior at grain boundaries. The specific characteristics of grain boundaries that lead to weak-link behavior have been widely investigated, but a consensus has not been reached. The observation by K. Salama and co-workers at the University of Houston and elsewhere that current flow within "domains" of melt-processed $YBa_2Cu_3O_{7-x}$ is not weakly linked was widely interpreted as indicating that some grain boundaries in highly textured Y123 are not weak links. Domains, which are defined from optical metallography, consist of stacks of parallel plates with a common *c*-axis. It has been assumed that the platelets are separate grains that align during growth and that the platelet boundaries involve rotations about the *c*-axis. Therefore, the conclusion of Salama et al. (from resistive measurements of J_c in single-domain specimens cut with their *c*-axis at various angles to the specimen axis) that current flow in the *c*-direction is not weak-linked appeared to provide an opportunity to study "good" grain boundaries. Such a study was undertaken using specimens prepared at ORNL and specimens provided by Salama that were prepared similarly to those used in the above-described resistive measurements and in ac magnetization studies by Kpfer et al. in which it was also concluded that currents in both the *c* and *ab* directions are not weak-linked. From TEM, SEM, and optical microscopy we found that the stacked parallel plates within a domain are in fact portions of a single crystal. The platelet boundaries are not grain boundaries but gaps containing remnants of the liquid phase present during domain growth. However, the gaps are not continuous. Gap terminations within a domain result in interconnected single crystalline material, and the absence of weak-link behavior for current in the *c*-direction is readily understood. It has been proposed that high-basal-plane J_cs in highly aligned materials such as melt-processed 123 and BSCCO powder-in-tube conductor may be explained in terms of the "brick wall" model in which current avoids weak links by using large area *c*-plane boundaries. This work demonstrates that the microstructure within domains of melt-processed 123 is not that of the brick wall model, and an alternative explanation of critical current behavior has been provided.

Identification of potential pinning centers. Flux pinning in melt-processed Y123 has been observed to increase with the surface area of trapped 211 particles, which provides an opportunity to identify flux-pinning structures. TEM and EDS were used to study the 123 microstructure near the 211/123 interface. A high local density of stacking faults was found in 123 near the 211/123 interfaces. The stacking faults lie parallel to the (001) basal plane and are inhomogeneously distributed around the 211 particles. They tend to be disk shaped and have diameters ranging from a few nanometers to ~30 nm. Calculations made using simple energy considerations suggest that these stacking faults may act as effective flux-pinners for magnetic fields directed both parallel and perpendicular to the basal plane. They may account for the observed increase of J_c with volume fraction of 211 and also explain the angular dependence of transport J_c in melt-processed 123. An unusual tendency for the formation of facets on the incoherent, randomly oriented 211 particles parallel to the {001}-type planes in the 123 matrix was also observed. Microanalysis of the 123 region around the 211 particles, which contain few or no stacking faults, consistently shows an enrichment of yttrium and a corresponding depletion in barium concentration. Such cation nonstoichiometry may result in the formation of numerous point defects that could also result in pinning. The presence of ledges on some facets at the 211/123 interfaces, and the observed compositional nonstoichiometry in the 123 phase in the vicinity of these interfaces, suggests that 211 particles continue to change in size after entrapment in 123. The observed compositional variation is consistent with dissolution of trapped 211. Such diffusion effects and stresses due to the thermal and elastic mismatch between 211 and 123 provide mechanisms for generating the observed defects around the 211 particles in the 123 matrix.

Solidification mechanism of 123 from the melt. Nucleation and growth of 123 from the melt via a peritectic reaction into domains of aligned platelets was studied in detail. Based on the microstructural analysis described above, a given domain can be expected to grow from a single nucleus. It was also found that the platelet boundaries are filled in with secondary phases corresponding to the liquid phases at high temperatures, suggesting that constitutional supercooling effects may be operative. Samples quenched from temperatures considerably below the peritectic temperature during the cooling cycle indicated that a large nucleation barrier existed and that only a few 123 nuclei were present. The above observations, coupled with extensive microstructural examination of quenched solid-liquid interfaces, suggest that the 211 size, distribution, and volume fraction control not only the growth rate of 123 along the fast growth *ab* plane (by supply of yttrium) but also the growth rate along the slow growth *c*-direction, since the nucleation barrier for growth is reduced at 211/123 intersections. A growth model consistent with these observations and that explains the formation of 123 domains was proposed.

Substrate for melt-processing 123. Microstructural studies indicate that silver-palladium alloys, with a low content of palladium (<12%), can be used for melt-processing 123 without any deleterious effects. Single-crystal domains of 123 extending throughout the thickness of a melt-processed thick film (~20 mm) have been obtained. Electron microprobe, TEM, and EDS results show that the interface between the melt-processed film and substrate is sharp. No presence of silver or palladium in the film was detected. Also, grain boundaries intersecting the substrate are clean (i.e., no silver or palladium segregation). This is a significant technological step in fabricating melt-processed 123 in conductor form. However, the processing window in this case is limited by the liquidus temperature of the substrate and the peritectic melting of 123. Current research is aimed at thermal gradient processing of such films to obtain long lengths of near single-crystal thick films.

Mechanical properties of melt-processed 123. The microhardness, Young's modulus, and fracture toughness of aligned 123 obtained by melt processing was found to be highly anisotropic. Microindentation measurements showed that the {100} planes are the preferred fracture planes in this material and that the critical stress intensity factor for propagating a crack on the (001) basal plane is the lowest [i.e., $K_c(001) < K_c(100)$ or $K_c(010)$]. Indentation crack length measurements on the (001) basal plane with the impression diagonals aligned parallel and perpendicular to the [100] and [010] directions indicate that the fracture toughness of these planes is $K^{air}(100/010) = 0.8$ MPam$^{1/2}$. The microhardness in this orientation was found to be 6.7 GPa. Measurements on a plane perpendicular to the basal plane resulted in a lower hardness of ~3.8 GPa. This reduction in hardness is influenced by the extensive preferential cleavage of the (001) basal planes.

The Young's modulus was determined using a highly spatially resolved mechanical properties microprobe. Nanoindentation measurements on the (001) cleavage plane of aligned 123 indicated a Young's modulus of 143 ± 4 GPa. For measurements on a plane perpendicular to the cleavage plane, a value of 182 ± 4 GPa for the modulus was obtained. A lower modulus in the *c*-direction is perhaps a result of the layer-like structure of 123, resulting in weak coupling between the layers. Measurements on the trapped single crystalline 211 particles resulted in a Young's modulus of 213 ± 5 GPa. Considerations of the thermal and elastic mismatch effects between the trapped 211 particles and the 123 matrix, the large thermal anisotropy of aligned 123, and microstructural examination of polished and fracture surfaces of aligned samples indicate that the 211 particles serve to enhance the fracture behavior of 123 by energy dissipation due to interfacial delamination and crack bridging. Incorporation of ductile silver particles between and within 123 domains also enhances the mechanical properties.

Bibliography of Recent Publications Emanating from This Project

1. D. M. Kroeger and A. Goyal, "Critical Currents and Microstructures in Oxide Superconductors," *J. of Metals* (Oct. 1992).

2. A. Goyal, Z. L. Wang, K. B. Alexander, and D. M. Kroeger, "Stacking Faults Associated with 211 Particles and Other Likely Pinning Centers in Melt-Processed $YBa_2Cu_3O_{7-\delta}$," p. 356 in *Proceedings of the International Workshop on Superconductivity, June 23-26, 1992, Honolulu, Hawaii, U.S.A.*

3. K. B. Alexander, A. Goyal, D. M. Kroeger, and S. Selvamanickam, "Microstructure and Growth of Melt-Textured $YBa_2Cu_3O_{7-\delta}$," *Phys. Rev. B*, 45, 5622 (1992).

4. A. Goyal, K. B. Alexander, D. M. Kroeger, P. D. Funkenbusch, and S. J. Burns, "Growth of Highly Aligned Melt-Textured $YBa_2Cu_3O_{7-\delta}$," *Phys. C*, 1992; submitted for publication.

5. Z. L. Wang, A. Goyal, and D. M. Kroeger, "Structural and Chemical Disorder Near the 211/123 Interface and Its Possible Relation to the Flux-Pinning Behavior in Melt-Textured $YBa_2Cu_3O_{7-\delta}$," *Phys. Rev. B*, 1992; submitted for publication.

6. D. M. Kroeger, A. Goyal, Z. L. Wang, and F. A. List, "Substrate Reactions and Flux-Pinning Structures in Melt-Processed $YBa_2Cu_3O_{7-\delta}$ Deposits on Ag-Pd Substrates," in *Proceedings of the 1992 TcSUH Workshop on HTS Materials, February 27-28, Houston, Texas.*

7. Z. L. Wang, A . Goyal, D. M. Kroeger, and T. M. Armstrong, "Defects Near the $Y_2BaCuO_x/YBa_2Cu_3O_{7-d}$ Interface and its Effect on Flux-Pinning in Melt-Processed and Quench-Melt-Growth Processed $YBa_2Cu_3O_{7-\delta}$," presented at the Proceedings of the 1992 Spring MRS Meeting, San Francisco, Calif.; to be published in the proceedings.

8. A. Goyal, P. D. Funkenbusch, D. M. Kroeger, and S. J. Burns, "Fabrication of Highly Aligned $YBa_2Cu_3O_{7-\delta}$-Ag Composites," *Phys. C*, 182, 203 (1991).

9. A. Goyal, P. D. Funkenbusch, D. M. Kroeger, and S. J. Burns, "Hardness and Fracture Toughness of Highly Aligned $YBa_2Cu_3O_{7-\delta}$," *J. of Applied Physics*, 71, 2363 (1992).

10. A. Goyal, P. D. Funkenbusch, D. M. Kroeger, and S. J. Burns, "Mechanical Properties of Highly Aligned $YBa_2Cu_3O_{7-\delta}$: *Effect of Y_2BaCuO_5 Particles*," *Phys. C*, 183, 221 (1991).

11. D. K. Christen, C. E. Klabunde, M. J. Neal, M. V. Parish, D. B. Chandler, B. C. Chakoumakos, A. Goyal, and D. M. Kroeger, "The Production and Properties of Melt-Zone Textured $YBa_2Cu_3O_{7-\delta}$ Filaments," p. 181 in *Proceedings of the International Workshop on Superconductivity, June 23–26, 1992, Honolulu, Hawaii, U. S. A.*

12. Z. L. Wang, A. Goyal, and D. M. Kroeger, "Interface Microstructures in Melt-Textured 123 on Ag-Pd and Flux-Pinning Centers Introduced by 211 Particles," presented at the Proceedings of the 50th Annual Meeting of the Electron Microscopy Society of America, Boston, Mass., August 1992; to be published in the proceedings.

13. M. V. Parish, "Microstructure of Continuously-Processed, Melt-Textured $Y_1Ba_2Cu_3O_{7-\delta}$ Monofilaments," p. 232 in *Proceedings of the International Workshop on Superconductivity, June 23–26, 1992, Honolulu, Hawaii.*

14. S. Jin, G. W. Kammlott, T. H. Tiefel, T. T. Kodas, T. L. Ward, and D. M. Kroeger, "Microstructure and Properties of the Y-Ba-Cu-O Superconductor with Submicron 211 Dispersions," *Phys. C* 181, 57–62 (1991).

15. S. Chadda, T. L. Ward, A. Carim, T. T. Kodas, K. Ott, and D. M. Kroeger, "Synthesis of 123 and 124 by Aerosol Decomposition," *J. of Aerosol Science* 22(5) 601–16 (1991).

16. Yang Ren Sun, J. R. Thompson, D. K. Christen, J. G. Ossandon, Y. J. Chen, and A. Goyal, "Effects of Field Sweep Rate on the Magnetization in High-T_c Superconductor Materials," *Phys. Rev. B* (1992); to be submitted for publication.

17. A. Goyal, Z. L. Wang, F. A. List, and D. M. Kroeger, "Melt Processing of 123 Thick Films on Ag-Pd Substrates," manuscript in preparation at ORNL.

18. A. Goyal and D. M. Kroeger, "Low-Angle Grain Boundaries and Inhomogeneous Oxygenation in Melt-Processed $YBa_2Cu_3O_{7-\delta}$," manuscript in preparation at ORNL.

1.3 THERMO-MECHANICAL ROUTES TO PRACTICAL LONG WIRE LENGTHS

1.3.1 Conductor Development by Thermo-Mechanical Processing

1.3.1.1 Project Overview

Specific project objectives

The objective of this project is to aid American industry in developing processes for fabrication of practical conductors containing HTS oxides. Specific project objectives are:

- Development of fabrication processes for powder-in-tube conductors that result in improved dimensional uniformity of the oxide core and smoothness of the silver/superconductor interface.
- Determination of the feasibility of conductor fabrication methods involving incorporation of powder deposits on silver or silver alloys into single and multilayer conductor configurations.
- Development of thermal-mechanical processing schedules for powder-in-tube and deposited conductors containing highly homogeneous powders prepared by aerosol synthesis. Shortened heat treatment times and improved uniformity of characteristics over long lengths are among the benefits sought.
- Investigation of silver-palladium alloys as a chemically compatible jacket/substrate material for Y123 and BSCCO compounds.
- Study of processing and properties of conductors containing thalllium-based powders prepared by aerosol pyrolysis.

Relationship of project to DOE mission

The mission of the Superconducting Technology Program is to develop the technology base needed in order for American industry to proceed to commercialization of HTSs for electric power applications. The activities of this project are directed toward improving processing and properties of conductors containing HTS oxides and are, in large part, carried out in cooperation with industrial partners. These activities are therefore in direct support of the DOE mission (see Fig. 6).

Relationship to other DOE projects

This project interfaces closely with OBES-supported projects at ORNL on synthesis, processing, and properties of HTSs. Project personnel participate in a working group on BSCCO conductor development organized by American Superconductor Corporation, which also includes participants from DOE-supported programs on conductor development at Los Alamos National Laboratory, Argonne National Laboratory, and the University of Wisconsin.

Project history

DOE funding for this project is shown in the following table:

	DOE funding ($ × 1000)		
	FY 1990	FY 1991	FY 1992
Direct scientific and technical	500	500	510
Funds-out cooperative agreements	200	200	100
Total DOE	700	700	610

Funding for industry cost-share on cooperative agreements follows:

	Non-DOE funding ($ × 1000)		
	FY 1990	FY 1991	FY 1992
American Superconductor Corp.[a]	125	200	200
Westinghouse Electric Corp.[b]	200	150	150
Totals	325	350	350

[a]Approved term: 4/1/89–3/31/93.
[b]Approved term: 4/1/89–12/31/92.

PHOTO YP 15922

Fig. 6. Some of the ORNL staff working in conductor development and physical properties measurements gather near the new susceptometer. Shown (l to r) are A. Goyal, D. M. Kroeger, F. A. List, D. K. Christen, P. Martin, and H. Hsu (consultant).

1.3.1.2 Scientific and Technical Content

Schedule of major research activities

Recent and ongoing activities of this project follow:

- The effects on dimensional uniformity of the oxide core and smoothness of the silver/superconductor interface of some variables in the deformation/fabrication process have been investigated.
- In cooperation with Westinghouse Electric Corporation, two different approaches to conductor fabrication involving incorporation of Bi-2212 and Bi(Pb)-2223 deposits into silver-encased conductor configurations have been developed and are being investigated. High-current specimens, up to 200 A at 4.2 K, have been prepared.
- Thermal and mechanical processing schedules for powder-in-tube and deposited conductors containing aerosol powders are being developed. Results have shown that conversion of these highly homogeneous precursor powders to the Bi(Pb)-2223 phase can be rapid and that conductors with high-J_c can be prepared.
- The chemical compatibility of silver-palladium alloys with Y123 and BSCCO compounds and their decomposition products at high temperatures has been investigated. Results have shown that alloys containing up to 12% palladium do not react deleteriously with Y123 at melt-processing temperatures and are thus interesting substrate/jacket materials. These alloys are also compatible with BSCCO and may offer advantages over pure silver in powder-in-tube fabrication.

- Fabrication and processing studies of powder-in-tube conductors containing thallium-based powder precursors prepared by aerosol pyrolysis have been initiated and are at an early stage.

Scientific and technical issues

This project involves thermal and mechanical processing of composite HTS conductors consisting of one or more oxide cores encased in a metallic sheath, specifically silver or a silver alloy. Processing obstacles to preparation of long lengths of such conductors with uniformly good properties are addressed. Critical current densities in such conductors are determined by many factors including dimensional uniformity, phase content, and texture of the oxide core, quality and smoothness of the silver/superconductor interfaces, weak-link behavior, flux pinning, and the intrinsic properties of the HTS compound. The latter will ultimately determine the maximum temperature range at which a compound may be utilized. Current understanding and experience indicate that the BSCCO compounds, for which fabrication processes are most advanced, will be limited in use to temperatures below the liquid N_2 range. Thus, work on the 123 and some thallium-based compounds is justified, even though the weak-link problem in conductor configurations has not been eliminated and the feasibility of long conductors for use in even moderate magnetic fields has not been proved.

Work on BSCCO conductors has addressed four issues: dimensional uniformity of the oxide core, quality and smoothness of the silver/superconductor interface (where, it is suspected, a large fraction of supercurrent flows), the long heat treatment times usually required for phase and microstructure development, and the high degree of compositional homogeneity required of precursor powder for multifilamentary conductor. Work relevant to the first two issues has involved (1) studies of the effects of powder-in-tube fabrication variables on core uniformity and the silver/superconductor interface and (2) development of alternatives to powder-in-tube fabrication involving powder deposits on silver that minimize the amount of deformation required to obtain final dimensions. All four issues are addressed by our efforts to develop thermal and deformation processes for conductors containing highly homogeneous powders prepared by aerosol pyrolysis.

Work on YBCO conductors has focused on the problem of chemical compatibility between oxide and substrate/jacket material during melt processing. The weak-link problem in YBCO has persisted, and high-current densities have been obtained only by melt processing. The relatively low melting point of silver permits melt-processing of silver-YBCO composites over only a very limited range of temperature at low oxygen pressure. The need for a chemically compatible substrate/jacket material with melting point higher than 1000°C led to a study of reactions between silver-palladium alloys and YBCO.

Compositional inhomogeneities and large agglomerates occurring in thallium-based precursor powder prepared by solid state reaction cause problems in fabrication of the powder-in-tube conductor. Fabrication of a conductor containing a thallium-based precursor prepared by aerosol pyrolysis has been initiated recently.

Experimental and theoretical approach

This project involves coordinated activities of personnel and facilities in the Metals and Ceramics, Chemistry, and Solid State Divisions at ORNL and at American

Superconductor and Westinghouse Electric Corporation. ORNL participates in a working group on BSCCO conductor development organized by American Superconductor that also includes participants from Los Alamos National Laboratory, Argonne National Laboratory, and the University of Wisconsin. A consultant for American Superconductor, H. Hsu, is stationed at ORNL to organized fabrication activities, to perform measurements, and to facilitate transfer of information. Hsu is a coprincipal investigator for this project.

The extensive fabrication and deformation processing facilities of the materials-processing group, Metals and Ceramics Division, are utilized in studies of powder-in-tube processing parameters. Long-length conductor fabrication for most cooperative projects is done by the industrial participant. Superconducting property measurements, including J_c, T_c, and magnetization, are performed in the Metals and Ceramics and Solid State Divisions. Capabilities for microstructural characterization and analysis include optical metallography, X-ray diffraction, SEM, TEM, electron microprobe, and EDS.

A major goal of the project is to contribute to the development of high-J_c conductors with uniform properties over long lengths. The problems of nonuniformity of the oxide core, large secondary particles, and nonuniform distribution of the superconducting phase resulting from inhomogeneity of the precursor powder and roughness of the silver/superconductor interface have been addressed through studies of the effects of fabrication process parameters on conductor characteristics and through studies of thermal and mechanical processes for conductors containing aerosol powders. Also, thermal processing times can be substantially shortened by using aerosol pyrolysis powders.

The need for a metallic substrate/jacket material that is chemically compatible with YBCO during melt processing led to studies of the interaction between YBCO and silver-palladium alloys. No deleterious reaction was found for palladium concentrations up to 12 at. %. Thermal gradient melt-processing studies of YBCO with silver-palladium as substrate/jacket are in progress.

Importance of solving the problem being addressed by this research

This project is directed toward improving the properties of HTS conductors and solving problems in their fabrication. Such improvements are essential for realizing the potential benefits of the HTS in a wide range of energy-related applications.

1.3.1.3 Project Output

Major research accomplishments

Major research accomplishments of this project follow:

- A fabrication method that results in improved uniformity of the core dimension (i.e., less "sausaging") has been devised and is being investigated. An invention disclosure has been submitted to DOE, and Martin Marietta Energy Systems, Inc., has elected to file a patent application. A separate study of fabrication variables not involving this invention has also led to improvements in core uniformity and smoothness of silver/superconductor interface.

- Thermal and mechanical processing schedules for both powder-in-tube and deposited conductor configurations containing powders prepared by aerosol pyrolysis are being investigated. The phase assemblages found in aerosol powders are very different from that of solid state reaction powders used in the powder-in-tube process, and the heat treatment conditions required to form the 2223 phase are also different. Phase content of the powder is determined by aerosol process parameters such as pyrolysis temperature, $P(O_2)$ in the carrier gas, and residence time in the hot zone as well as composition. The rate of formation of the 2223 phase, and apparently the route by which it forms, vary with the initial phase content of the powder and the temperature and oxygen partial pressure, $P(O_2)$, at which it is reacted. Impurities such as carbon may also play a role. Because the nitrate solution used in aerosol pyrolysis can contain very low carbon concentrations, aerosol pyrolysis offers the possibility of preparing very low-carbon powders. It has been determined, however, that carbon contamination in the aerosol synthesis process results from reaction of powders on the collector with CO_2 in the gas stream. Aerosol process procedures have been developed that limit carbon concentrations to a few hundred wppm in powders at the point of tube loading. Further reduction is possible if results warrant additional efforts.
- Powder-in-tube conductors fabricated using Bi(Pb)-2223 aerosol precursor have been shown to require shorter heat treatment times than conductors containing solid state reaction powder. Rapid formation of the 2223 phase at temperatures as low as 800°C has been demonstrated. First-stage heat treatment times of only a few hours were found to be desirable in contrast to the 50 to 100 h often used for solid state reaction powders. Using a two-stage roll and sinter process, short samples of powder-in-tube conductors have been prepared with J_c values as high as 13,000 A/cm^2 in self-field at 77 K. Values up to 16,500 A/cm^2 have been obtained with final deformation by pressing. Metallography indica . that secondary phase particles in the oxide core are small and that a well-aligned layer of 2223 forms near the silver/superconductor interface. However, overall grain alignment was poor, suggesting that substantial improvements in properties may be expected with optimization of the deform/sinter process.
- In cooperation with Westinghouse, fabrication of multilayer silver/BSCCO composites from aerosol powder deposits on silver strips has been investigated. Silver strips coated on both sides with Bi-2212 powder prepared by aerosol pyrolysis were stacked, encased in a silver box, and rolled to obtain multilayer tape. Short samples of this ribbon were given a previously optimized heat treatment schedule. Critical currents as high as 200 A corresponding to $J_c = 4.2 \times 10^4$ A/cm^2 were obtained at 4.2 K. An apparatus for preparation of spray-dried coatings with uniform thickness has been developed, and a single oxide layer conductor made by spray-drying of aerosol Bi(Pb)-2223 powder is being investigated.
- It has been determined from TEM and electron microprobe examinations of melt-processed Y123 deposits on silver-palladium alloy substrates that alloys with palladium concentrations up to 12 at. % are chemically compatible with Y123 at melt-processing temperatures (i.e., up to 1010 to 1020°C). Typical melt-processed microstructures have been produced in both Y123 deposits and powder-in-tube specimens using silver–12% palladium as substrate or jacket. Work on thermal gradient processing of such materials is in progress in cooperation with Westinghouse Electric Corporation, which has a patent concerning use of silver-palladium alloy jacket material.

1.3.1.4 Bibliography of Recent Publications Emanating from this Project

1. F. A. List, H. Hsu, O. B. Cavin, W. D. Porter,. C. R. Hubbard, and D. M. Kroeger, "Phase Development in the $Bi_2Sr2CaCu_2O_y$ System: Effects of Oxygen Pressure," *Phys. C*, in press (1992).

2. G. A. Whitlow, N. C. Iyer, A. T. Male, J. C. Powell, and G. R. Wagner, "Silver Encased High Temperature Superconductor Ribbons Produced by Rolling," presented at the Proceedings of Applied Superconductivity Conference, San Francisco, Calif., 1988.

3. G. A. Whitlow, W. R. Lovic, and J. C. Bowker, "High Current Density Bi-Sr-Ca-Cu-O Superconductor Wires Produced by Hot Isostatic Pressing," *Supercond. Sci. Technol.* 4, 353 (1991).

4. J. C. Bowker and G. A. Whitlow, "Effect of Heat Treatment Conditions on Critical Current of $YBa_2Cu_3O_{7-\delta}$/Ag Powder-in-Tube Wires," *Supercond. Sci. Technol.* (1992); submitted for publication.

5. J. C. Bowker and G. A. Whitlow, "Critical Current Enhancements in Silver-Clad $Bi_2Sr_2CaCu_2O_x$ Wires Using a Statistical Experimental Design for Heat Treatment Optimization," *Jap. J. Appl. Phys.* (1992); submitted for publication.

6. G. A. Whitlow, J. C. Bowker, W. R. Lovic, F. A. List, and D. M. Kroeger, "High Critical Current Silver-$Bi_2Sr_2CaCu_2O_{8-d}$ Superconducting Multilayer Ribbons Produced by Rolling," presented at the NYSIS Conference on Superconductivity and Applications, September 1992; to be published in the AIP proceedings.

7. D. M. Kroeger, A. Goyal, Z. L. Wang, F. A. List, and K. B. Alexander, "Substrate Reactions and Flux-Pinning Structures in Melt-Processed $YBa_2Cu_3O_{7-\delta}$ Deposits on Ag-Pd Substrates," presented at the Proceedings of the TCSUH Workshop on HTS Materials, Feb. 27–28, Houston, Texas, 1992.

8. Z. L. Wang, A. Goyal, and D. M. Kroeger, "Interface Microstructures in Melt-Textured $YBa_2Cu_3O_{7-\delta}$ on Ag-Pd and Flux Pinning Centers Introduced by Y_2BaCuO_5 Particles," presented at the Proceedings of the 50th Annual Meeting of the Electron Microscopy Society of America (EMSA), August 1992.

9. T. L. Ward, S. W. Lyons, T. T. Kodas, J. Brynestad, D. M. Kroeger, and H. Hsu, "Characteristics of Bi-Pb-Sr-Ca-Cu-O Powders Produced by Aerosol Decomposition and Their Rapid Conversion to High T_c Phase," *Phys. C* (1992); submitted for publication.

10. D. M. Kroeger, H. S. Hsu, J. Brynestad, V. K. Sikka, T. Ward, and T. Kodas, "Processing and Properties of Powder-In-Tube Conductors Containing Bi(Pb) 2223 Powder Prepared by Aerosol Pyrolysis," presented at the Proceedings of the International Workshop on Superconductivity, Honolulu, Hawaii, June 23–26, 1992.

1.3.1.5 Patentable or Potentially Patentable Inventions

1. D. M. Kroeger, J. Brynestad, and H. Hsu, "Method of Producing Pb-Stabilized Superconductor Precursors and Method of Producing Superconductor Articles Therefrom," Disclosure DOE ESID 1039, 1040.

2. D. M. Kroeger and F. A. List III, "Process for Fabricating Continuous Lengths of Superconductors," Disclosure DOE ESID 1193-X, S-76,061.

3. G. A. Whitlow and N. C. Iyer, "High Temperature Superconductor Having a High Strength, Thermally Matched, High Temperature Sheath," U.S. patent 5,017,553.

4. G. A. Whitlow and J. C. Powell, "Alloy Method of Making a Composite Having Superconducting Capability," U.S. patent 5,075,286.

5. G. A. Whitlow and N. C. Iyer, "Continuous Process for Aligned High Temperature Superconductor Fabrication," Disclosure Westinghouse RDM 89-006.

6. G. A. Whitlow and W. R. Lovic, "Improved Strain Tolerant High Temperature Superconductor," Disclosure Westinghouse RDM 91-017.

7. G. A. Whitlow and W. R. Lovic, "Method for Production of High Current Density, High Temperature Superconductors Using Hot Isostatic Processing," Disclosure Westinghouse RDM 91-025.

8. G. A. Whitlow, J. C. Bowker, D. M. Kroeger, and F. A. List, "Rolled High Current Density, High Temperature Ribbon Superconductors from Stacked Predeposited Strips," Disclosure Westinghouse RDM 91-065.

9. G. A. Whitlow and J. C. Bowker, "An Improved Heat Treatment for Composite Conductors Using $Bi_2Sr_2CaCu_2O_x$ Superconductor Material," Disclosure Westinghouse RDM 91-081.

10. Vinod K. Sikka and Charles E. Dunn, "Method and Apparatus for Fabricating Continuous Ribbons of High Temperature Superconductors," ESID 935-X.

11. Vinod K. Sikka and Edward C. Hatfield, "Method for Fabricating High-Current-Density, Oxide, Superconductor Ribbons," ESID 1155-X.

1.4 DEPOSITED FILM TECHNOLOGY

1.4.1 Deposited Conductor Development

1.4.1.1 Project Overview

Specific project objectives

The purpose of this project is to develop conductor prototypes of high-temperature superconducting materials by deposition on, or coating of, chemically compatible and technologically feasible substrate materials. This work involves the characterization and optimization of techniques for the formation of superconducting materials and the development of substrates as well as measurements of the superconducting properties of conductor prototypes. Program objectives include:

- Development of ceramic and metal substrate materials that can be fabricated as continuous forms for conductor applications.
- Development of (1) textured metallic substrates by physical deformation and heat treatment and (2) epitaxial metal overlayers deposited on single-crystal ceramic substrates.
- Development of techniques to deposit conductors on substrates. Very fine HTS and precursor powders prepared by aerosol pyrolysis are used for the thick film coating of both YBCO and BSCCO HTSs on metal alloy substrates prior to melt processing for phase development and texture. Physical deposition of thin films by pulsed laser ablation provides controlled baseline information.
- Characterization of superconductive properties by dc electrical transport, and ac and dc magnetometry. These properties include the temperature and magnetic field dependence of critical current densities, flux creep, and flux flow dissipation. Results are correlated with the observed phase development, morphology, and microstructure of the deposited HTS.

Relationship of project to DOE mission

The mission of the DOE Superconducting Technology Program is to develop the technology base needed for U.S. industry to proceed to the commercial development of HTS conductors for electric power applications. With industry collaboration, this project is developing materials and methods for fabricating deposited conductor prototypes for use as leads and long-length wires in high-I_c applications.

Relationship to other projects funded by DOE

This program interfaces closely with other ORNL DOE-funded projects within the Solid State and Metals and Ceramics Divisions related to the growth of high-quality epitaxial HTS films and superlattices, materials modification through energetic particle irradiation, characterization of the anisotropic superconductive properties of HTS materials, and investigations of the chemical and microstructural nature of HTS materials.

Project history

DOE funding for this project is shown in the following table:

	DOE funding ($ × 1000)		
	FY 1990	FY 1991	FY 1992
Direct scientific and technical	400	400	400
Funds-out cooperative agreements	450	400	335
Total DOE	850	800	735

Funding for industry cost-share on cooperative agreements follows:

	Non-DOE funding ($ × 1000)		
	FY 1990	FY 1991	FY 1992
Corning, Inc.[a]	147	75	0
Energy Conversion Devices, Inc.[b]		20	70
General Electric Company[c]	100	100	60
Westinghouse Corporation[d]	200	150	100
SUNY-Buffalo[e]	100	100	130
Totals	547	445	360

[a]Aproved term: 6/1/89 -12/31/92.
[b]Approved term: 5/1/91–9/30/92.
[c]Approved term: 10/1/89–12/31/92.
[d]Approved term: 4/1/89–12/31/92.
[e]Approved term: 7/1/89–10/30/92.

Funding for DOE funds-out cooperative agreements follows:

	Funds to industry ($ × 1000)		
	FY 1990	FY 1991	FY 1992
Corning, Inc.	125	50	25
General Electric Company	100	100	60
Westinghouse Corporation	200	150	100
SUNY-Buffalo	25	100	150
Totals	450	400	335

1.4.1.2 SCIENTIFIC AND TECHNICAL APPROACH

Schedule of major research activities

The major research activities for this project are as follows:

- Superconducting thick film deposits of YBCO are melt-processed on silver-palladium alloy substrates. Compatibility of YBCO with several palladium alloys is evaluated using electron microprobe, TEM, and EDS.
- Superconducting YBCO thin films are grown by laser ablation and post-deposition annealing on metal (silver and platinum) substrates. Epitaxial growth on single crystals, on highly textured substrates, and on oriented metallic buffer layers is proposed as a means to induce in-plane alignment of the film, consequently improving electrical transport by reducing the effect of intergranular weak links. The films are characterized using X-ray diffraction, SEM, conductivity, and critical current measurements.
- Feasibility of a silver-encapsulated multilayer ribbon geometry for BSCCO conductor fabrication is assessed. This involves preparation and processing of multilayer conductors followed by determinations of their microstructure, phase content, and electrical transport properties.
- Patterned polycrystalline ceramic substrates for HTS graphoepitaxy study are fabricated. This effort focuses on artificially achieving in-plane crystallographic alignment of HTSs, using randomly oriented polycrystalline YSZ and oxygen-implanted amorphous substrates. The possibility of using substrate texture to induce growth of oriented-defect arrays useful for flux pinning is also studied. This involves the development of techniques for patterning polycrystalline ceramic materials as well as the deposition of HTS films. SEM, four-circle X-ray diffractometry, and dc transport measurements are used to determine how surface micropatterning affects the growth kinetics and in-plane alignment of deposited HTS films.
- Transport measurements are conducted on spray-pyrolyzed $TlBa_2Ca_2Cu_3O_z$ films. This effort involves field-dependent critical current measurements on $TlBa_2Ca_2Cu_3O_z$ thick films to determine and to understand their transport behavior. Efforts will also be made to develop practical metallic substrates for these thick film deposits.
- The potential for aerosol powder precursors to convert rapidly to continuous bismuth-based HTS phases is evaluated. Evaluation involves several silver-clad conductor geometries (i.e., powder-in-tube, multilayer ribbon, and single-layer ribbon). Emphasis is on the relationships of initial phase content, morphology, and composition of the aerosol precursors to final conductor properties and on control of uniformity of the aerosol deposits during processing.
- Values of some critical parameters relevant to processing of thick film BSCCO 2212 conductors on silver are determined. Emphasis is on the role of oxygen partial pressure and temperature in determining phase content, morphology, and electrical properties. X-ray diffraction, thermal analysis, and electron microscopy are used to relate processing parameters to conductor properties.

Scientific and technical issues

To produce practical conductors of the HTS materials, it is essential to understand what material properties limit the superconducting properties (such as the critical current density) as well as to identify the potential and limitations of specific conductor fabrication techniques. For the development of deposited HTS conductors, issues such as the chemical compatibility of the HTS with the substrate material, in-plane and out-of-plane crystallographic alignment of the deposit, and the intrinsic superconducting nature of the HTS material must be addressed. It is known, for instance, that large-angle grain boundaries are detrimental to the critical current density in Y123. Development of Y123 deposited conductors on technologically feasible substrates apparently will require significant in-plane crystallographic alignment to eliminate large angle grain boundaries and thus obtain high critical current densities. In the BSCCO system, crystallographic alignment is also important and seems to occur at the metal-oxide interface for silver-clad BSCCO conductors. Understanding the relationship between this alignment and critical current density is vital for the development of high-J_c BSCCO conductors.

Another issue to be addressed for the BSCCO 2223 system is related to the long times (~100 h) typically associated with thermal processing of oxide precursors to form substantial fractions of 2223. Presumably, transport processes involving diffusion over relatively long distances are in part responsible for this sluggish conversion. Sluggish conversion places a practical limitation on the rate at which 2223 conductors can be fabricated. This limitation may be overcome by reducing diffusion distances with finely divided and compositionally homogeneous precursor powders. Precursor 2223 powders prepared by aerosol pyrolysis are both finely divided (1 to 2 μm diam) and compositionally homogeneous and thus may be ideally suited for rapid conversion to 2223.

Conductor geometry also plays an important role in the conversion of oxide precursors to 2223. Interactions of the precursor with the conductor cladding, precursor phase content and distribution within the cladding, and effective availability of oxygen beneath the cladding are all factors affecting BSCCO conversion and ultimately conductor properties. Identification of the potential and limitations of a particular conductor geometry, therefore, requires identification of appropriate process conditions (e.g., temperatures, times, oxygen pressures, and deformations) specific to that geometry.

Experimental and theoretical approach

This project is coordinated with groups from the Solid State and Metals and Ceramics Divisions at ORNL as well as several industrial partnerships, which provides a multidisciplinary approach to both conductor fabrication and fundamental material issues involved in producing practical deposited conductors of HTS materials. This project investigates the properties of Y123, bismuth-, and thallium-based HTS deposited conductors. Emphasis is placed both on substrate development and on the deposition of the superconducting material itself. Efforts include investigating the fabrication of in-plane aligned Y123 films on patterned polycrystalline or amorphous substrates by means of graphoepitaxy. BSCCO conductor fabrication from aerosol precursor powders is investigated for several conductor geometries. Critical ranges of processing parameters (e.g., sintering temperature, sintering time, and oxygen partial pressure) are identified for each conductor geometry. Samples are characterized utilizing transport measurements, SEM, TEM, X-ray diffraction, and electron spectroscopy.

Importance of solving the problem being addressed by this research

An understanding of both the fabrication and material properties of HTS deposited conductors on technologically feasible substrates is necessary to develop a conductor with a significant current-carrying capability. By developing conductor prototypes of the various HTS materials, we should be able to identify and to understand the current-limiting mechanisms and to identify fabrication techniques that will lead to improved conductor performance. This should ultimately result in the development of a practical HTS conductor suitable for electric power applications.

1.4.1.3 Project Output

Major research accomplishments

Using pulsed-laser ablation deposition, we have grown textured Y123 films on rigid and flexible polycrystalline YSZ substrates (provided by General Electric Company and Corning, Inc.) with the *c*-axis perpendicular to the substrate. However, the *a*- and *b*-axes are randomly oriented in-plane, resulting in large-angle grain boundaries throughout the films. Large-angle grain boundaries in these Y123 films result in low values for J_c, with J_c ~ 10^3 - 10^4 A/cm^2 at 77 K. In addition, J_c decreases quite rapidly as a magnetic field is applied, making such conductors of little use for applications. One possible solution to this problem (suggested by experiments on Y123 bicrystals) is to produce in-plane alignment of adjacent Y123 grains, which reduces the density of weak links (large-angle grain boundaries) and leads to a subsequent increase in J_c. In pursuing this objective, we investigated the possibility of artificially producing in-plane alignment of the Y123 films through graphoepitaxy by patterning the surface of the polycrystalline substrates. A significant effort was necessary to develop methods to pattern ceramic substrates (provided by General Electric Company) at the submicron level. This work was performed at ORNL using photolithography and plasma etching. Large area (~ 20 × 20 mm^2) polycrystalline YSZ substrates with line patterns less than 1 μm in width were successfully fabricated for the graphoepitaxy experiments. Y123 films were subsequently grown on the patterned substrates by pulsed-laser ablation deposition. To date, we have observed no in-plane crystallographic alignment due to graphoepitaxy. However, morphological orientation of the Y123 film due to the presence of a patterned substrate surface was evident from SEM images. X-ray diffractometry also indicates that, for θ-2θ scans near the surface normal, there is a smaller mosaic spread of the rocking curve parallel to the patterned lines than perpendicular to the patterned lines. It thus appears that the Y123 grain size is too small for significant graphoepitaxial alignment to occur with patterned line widths of ~ 1 μm, although arrays of nearly aligned grain boundaries are produced. Future efforts will focus on using these patterned substrates with thallium-based HTS films (see the following paragraphs), as the average grain size is much larger than that for Y123.

Recent developments for $TlBa_2Ca_2Cu_3O_z$ thick films have demonstrated this material's potential as a practical HTS conductor. Measurements of the transport properties of $TlBa_2Ca_2Cu_3O_z$ films deposited on polycrystalline partially stabilized zirconia were performed at General Electric Corporate Research and Development. Large critical currents with a relatively weak magnetic field dependence were measured with J_c (77 K) > 10^5 A/cm^2 in zero field, and J_c (60 K) > 10^4 A/cm^2 in a 2-T field applied along the *c*-axis. These measurements are consistent with recent theories concerning the nature of vortices in highly anisotropic superconductors and the "brick wall" models of intergranular current transport. Future efforts will focus on the development of practical metallic substrates that are sufficiently oxidation resistant to ensure that a smooth surface is maintained during the processing of the $TlBa_2Ca_2Cu_3O_z$ films.

Superconducting Y123 thin films have been grown on metal foils and on bulk single-crystal metal substrates by in situ pulsed-laser ablation. X-ray diffraction measurements show that films can be textured with the Y123 <001> axis aligned predominantly along the substrate surface normal (*c*-oriented). More importantly, we have discovered that films grown on all of the single-crystal surfaces studied, Ag(100), Ag(110) Ag(111) and Pt(100), display particular *in-plane* epitaxial orientations. The observed orientations can be understood using near-coincidence lattice models that maximize the degree of atomic matching in the interface structure. The discovery of in-plane epitaxy on metallic substrates should lead to useful techniques for enhancing the transport properties of superconducting thin films. At present, the critical current density, J_c, for c-oriented films deposited on polycrystalline substrates is limited by "weak links" at the grain boundaries. The ability to align Y123 films on textured metal substrates is thus expected to decrease grain boundary effects and to improve transport properties. Films grown on Ag(110) surfaces appear particularly promising for applications since, in this case, we observe primarily a unique in-plane Y123 grain orientation, and (110) texturing is commonly observed in rolled fcc-metal foils. Our initial electrical measurements from films grown on rolled metal foils show improvements in J_c although the values for T_c are somewhat depressed (<85 K), perhaps owing to quantum mechanical proximity effects. For example, for films deposited on partially textured silver foil, we have measured a low-temperature J_c (H = 0) > 6 × 10^5 amps/cm^2 and a decreased sensitivity to magnetic fields. These studies are being continued for more complete assessment of the effects of film-substrate interactions such as in-plane epitaxy, strain, and interdiffusion on conductor applications.

Phase development in the $Bi_2Sr_2CaCu_2O_x$ system has been studied using thermal analysis and high-temperature X-ray diffraction for a range of oxygen pressures (0.001 to 100% O_2). Several reaction paths have been identified for melt-processing of BSCCO 2212 on silver. Results suggest that intermediate oxygen partial pressures (7.6 to 21% O_2) lead to direct formation of 2212 from the melt on cooling, whereas higher and lower $P(O_2)$ lead to substantial secondary phase formation (i.e., 2201 and $Bi_5Sr_3CaO_x$ respectively).

Silver-clad $(BiPb)_2Sr_2Ca_2Cu_3O_x$ conductors have been prepared from aerosol powder precursors for several fabrication geometries. Collaborative efforts with American Superconductor Corporation and Westinghouse Electric Corporation for powder-in-tube and multilayer ribbon conductor geometries, respectively, have led to a better understanding of the potential of, and limitations associated with, these geometries. Silver-clad single-layer BSCCO 2223 deposits have been prepared from aerosol powder precursors and heat-treated for various sintering temperatures (T_s), times, and oxygen partial pressures, $P(O_2)$, to assess the potential of such precursors to convert to 2223 rapidly. A range of T_s and $P(O_2)$ has been identified for this particular conductor geometry for which conversion to 2223 occurs for short sinter times (4 h). Examination of these samples by X-ray diffraction reveals the presence of both the BSCCO 2223 and 2212 phases. Microstructural examination of samples exhibiting sharp resistive transitions (T_{onset}~108 K, ΔT~4 K) suggests significant alignment of the plate-like grains of the film within ~1 to 2 mm of the film/silver interface. To investigate the role of this aligned region in electrical current transport and the dependence of the thickness of the aligned region on the total film thickness, deposits have been prepared for a range of thicknesses (2 to 50 mm) and processed similarly. Microstructural and electrical characterization of these samples is forthcoming.

An alloy of silver–10% palladium has been identified as a chemically compatible substrate for melt-processing of Y123. Isothermal melt-processing of Y123 thick films (~20 mm) on this alloy results in a microstructure comprised of several domains of Y123. Generally, these domains are crystallographically randomly oriented with respect to one another. To fabricate a high-J_c conductor, alignment of domains is necessary. Although thermal gradient processing of bulk Y123 to obtain essentially a single domain has been achieved, difficulties arise when attempting to thermal-gradient-process thick film Y123 on high-thermal-conductivity metallic layers. We have directed considerable effort toward the design and testing of several thermal gradient furnaces in order to fabricate high-J_c thick films and powder-in-tube conductors.

1.4.1.4 Bibliography of Recent Publications Emanating from This Project

1. D. P. Norton, D. H. Lowndes, J. W. McCamy, J. D. Budai, D. K. Christen, E. C. Jones, T. D. Ketcham, D. St. Julien, K. W. Lay, and J. E. Tkaczyk, "Y-Ba-Cu-O Thin Films Grown on Rigid and Flexible Polycrystalline Yttria-Stabilized Zirconia by Pulsed Laser Ablation," *J. Appl. Phys.* **68**, 223 (1990).

2. D. P. Norton, D. H. Lowndes, J. D. Budai, D. K. Christen, E. C. Jones, K. W. Lay, and J. E. Tkaczyk, "High Critical Current Densities in $YBa_2Cu_3O_{7-x}$ Films on Polycrystalline Zirconia," *Appl. Phys. Lett.* 57, 1164 (1990).

3. J. E. Tkaczyk, J. A. DeLuca, P. L. Karas, P. J. Bednarczyk, M. F. Garbauskas, R. H. Arendt, K. W. Lay, and J. S. Moodera, "Transport Critical Currents in Spray Pyrolyzed Films of $TlBa_2Ca_2Cu_3O_z$ on Polycrystalline Zirconia Substrates," *Appl. Phys. Lett.* **61**, 610 (1992).

4. J. E. Tkaczyk, R. H. Arendt, M. F. Garbauskas, H. R. Hart, K. W. Lay, and F. E. Luborsky, "Critical-State Scaling and Weak Links in Ag-Sheathed $Bi_2Sr_2Ca_2Cu_3O_z$," *Phys. Rev. B* **45** (1992).

5. F. A. List, H. Hsu, O. B. Cavin, W. D. Porter,. C. R. Hubbard, and D. M. Kroeger, "Phase Development in the $Bi_2Sr_2CaCu_2O_y$ System: Effects of Oxygen Pressure," *Phys. C*, in press (1992).

6. G. A. Whitlow, N. C. Iyer, A. T. Male, J. C. Powell, and G. R. Wagner, "Silver Encased High Temperature Superconductor Ribbons Produced by Rolling," presented at the Proceedings of Applied Superconductivity Conference, San Francisco, Calif., 1988.

7. G. A. Whitlow, W. R. Lovic, and J. C. Bowker, "High Current Density Bi-Sr-Ca-Cu-O Superconductor Wires Produced by Hot Isostatic Pressing," *Supercond. Sci. Technol.* **4**, 353 (1991).

8. G. A. Whitlow and J. C. Bowker, "Conductor Development Studies at Westinghouse," in *Proceedings of the HTS Wire Development Workshop—DOE Office of Utility Technologies, Richmond, Virginia, Feb. 19–20, 1992*, CONF-920286, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory, 1992.

9. J. C. Bowker and G. A. Whitlow, "Effect of Heat Treatment Conditions on Critical Current of $YBa_2Cu_3O_{7-\delta}$/Ag Powder-in-Tube Wires," *Supercond. Sci. Technol.* (1992); submitted for publication.

10. J. C. Bowker and G. A. Whitlow, "Critical Current Enhancements in Silver-Clad $Bi_2Sr_2CaCu_2O_x$ Wires Using a Statistical Experimental Design for Heat Treatment Optimization," *Jap. J. Appl. Phys.* (1992); submitted for publication.

11. G. A. Whitlow, J. C. Bowker, W. R. Lovic, F. A. List, and D. M. Kroeger, "High Critical Current Silver-$Bi_2Sr_2CaCu_2O_{8+\delta}$ Superconducting Multilayer Ribbons Produced by Rolling," presented at the NYSIS Conference on Superconductivity and Applications, September 1992; to be published in the AIP proceedings.

12. D. M. Kroeger, A. Goyal, Z. L. Wang, F. A. List, and K. B. Alexander, "Substrate Reactions and Flux-Pinning Structures in Melt-Processed $YBa_2Cu_3O_{7-\delta}$ Deposits on Ag-Pd Substrates," presented at the Proceedings of the TcSUH Workshop on HTS Materials, Feb. 27–28, Houston, Texas, 1992.

13. Z. L Wang, A. Goyal, and D. M. Kroeger, "Structural and Chemical Disorder Near the Y_2BaCuO_5/$YBa_2Cu_3O_{7-\delta}$ Interface and Its Possible Relation to the Flux-Pinning Behavior in Melt-Processed $YBa_2Cu_3O_{7-\delta}$," *Phys. Rev. B* (1992); submitted for publication.

14. Z. L. Wang, A. Goyal, and D. M. Kroeger, "Interface Microstructures in Melt-Textured $YBa_2Cu_3O_{7-\delta}$ on Ag-Pd and Flux Pinning Centers Introduced by Y_2BaCuO_5 Particles," presented at the Proceedings of the 50th Annual Meeting of the Electron Microscopy Society of America (EMSA), August 1992.

15. T. L. Ward, S. W. Lyons, T. T. Kodas, J. Brynestad, D. M. Kroeger, and H. Hsu, "Characteristics of Bi-Pb-Sr-Ca-Cu-O Powders Produced by Aerosol Decomposition and Their Rapid Conversion to High T_c Phase," *Phys. C* (1992); submitted for publication.

1.4.1.5 Patents and Disclosures Emanating from This Work

1. D. M. Kroeger and F. A. List III, "Process for Fabricating Continuous Lengths of Superconductors," Disclosure DOE ESID 1193-X, S-76,061.

2. G. A. Whitlow and N. C. Iyer, "High Temperature Superconductor Having a High Strength, Thermally Matched, High Temperature Sheath," U.S. patent 5,017,553.

3. G. A. Whitlow and J. C. Powell, "Alloy Method of Making a Composite Having Superconducting Capability," U.S. patent 5,075,286.

4. G. A. Whitlow and N. C. Iyer, "Continuous Process for Aligned High Temperature Superconductor Fabrication," Disclosure Westinghouse RDM 89-006.

5. G. A. Whitlow and W. R. Lovic, "Improved Strain Tolerant High Temperature Superconductor," Disclosure Westinghouse RDM 91-017.

6. G. A. Whitlow and W. R. Lovic, "Method for Production of High Current Density, High Temperature Superconductors Using Hot Isostatic Processing," Disclosure Westinghouse RDM 91-025.

7. G. A. Whitlow, J. C. Bowker, D. M. Kroeger, and F. A. List, "Rolled High Current Density, High Temperature Ribbon Superconductors from Stacked Predeposited Strips," Disclosure Westinghouse RDM 91-065.

8. G. A. Whitlow and J. C. Bowker, "An Improved Heat Treatment for Composite Conductors Using $Bi_2Sr_2CaCu_2O_x$ Superconductor Material," Disclosure Westinghouse RDM 91-081.

1.5 MATERIAL/STRUCTURE CHARACTERIZATION

1.5.1 Critical Currents and Microstructures

1.5.1.1 Project Overview

Special project objectives

The objectives of this project are to identify and to control the microstructural characteristics of high-temperature superconducting materials that lead to optimized loss-free electrical current conduction, especially at high temperatures and in the presence of large magnetic fields. Specific objectives are as follows:

- Microstructural studies were undertaken to determine the paths for nonweak-linked current flow in high-J_c melt-processed $YBa_2Cu_3O_{7-x}$
- TEM studies of the 211/123 interface in melt-processed Y123 were conducted to identify microstructural features likely to pin flux and thus to account for the observed increase in J_c with 211/123 interfacial area.
- The modification and tailoring of defect structures in prototypic HTS materials were conducted using light and heavy energetic particle irradiations and through the control of oxygen composition.

Relationship of project to DOE mission

The activities of this project are directed toward removing the materials factors that limit J_c and toward improving flux pinning, since improvement of J_c, especially at high temperatures, is essential for the use of HTSs in many electric power applications and in practical magnetic fields. This project is in direct support of the Superconducting

Technology Program mission to develop the technology necessary to commercialize HTS wires and wire products (see Fig. 7).

Relationship to other projects funded by DOE

This project is coordinated with other ORNL DOE-funded efforts related to crystal growth and materials synthesis, microstructural characterization, materials modification through ion beam processing, and superconducting electromagnetic properties studies. The project is supplemented by related research funded through the DOE OBES.

Project history

DOE funding for this project is shown in the following table:

	DOE Funding ($ x 1000)		
	FY 1990	FY 1991	FY 1992
Direct scientific and technical	170	200	210
Funds-out to industry[a]	210	240	200
Overhead	80	100	100
Total DOE	460	540	510

[a]See next table for breakdown.

Funding for contract and funds-out Pilot Center cooperative agreements follows:

	Funds-out to industry		
	FY 1990	FY 1991	FY 1992
IBM[a]	100	100	100
Ames Laboratory[b]	10	40	40
General Electric Company[c]	100	100	60
Total	210	240	200
Industry cost-share on cooperative agreements	350	350	350

[a]Approved term: 2/90 - 1/93.
[b]Approved term: 2/90 - 5/92.
[c]Approved term: 10/89 - 12/92.

1.5.1.2 Scientific and Technical Content

Schedule of major research activities

The major research activities of this project include:

- Microstructural studies to determine the paths for nonweak-link current flow in high-J_c melt-processed $YBa_2Cu_3O_{7-x}$

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Fig. 7. A team of researchers measures the properties of heavy ion irradiated HTS samples in the ORNL 7-T SQUID vector magnetometer. The vector magnetometer measures both components of the magnetic field, of interest for anisotropic materials. Seated: Ed Jones, University of Tennessee graduate student. Standing (l to r): Stematis Patapis, University of Athens (Greece) summer faculty guest; Jim Thompson, ORNL; Leonardo Civale, post-doctorate from IBM; and Dave Christen, ORNL.

- TEM studies of the 211/123 interface in melt-processed Y123 to identify microstructural features likely to pin flux and thus to account for the observed increase in J_c with 211/123 interfacial area.
- Studies of vortex pinning, critical currents, and flux motion in heavy ion-irradiated YBCO and BSCCO single crystals. The studies are aimed at optimizing the defect structures in prototypic materials to determine the limits to flux-pinning energies and the minimization of thermally activated flux motion. The results allow a relative comparison of expected benefits of the materials for practical, high-current applications.
- Studies of the effects of oxygen composition on the flux-pinning strength of preexisting defects in YBCO materials. Observed changes in the pinning energies and critical current density are related to direct measurements of fundamental superconducting parameters affecting these properties. Optimization of properties for applications is considered.

Scientific and technical issues

The ultimate application of HTS materials as high-current conductors in the presence of large magnetic fields requires an understanding of the factors leading to the optimization of current flow in these highly anisotropic materials. These factors include the effectiveness of current transfer between grains or domains of practical bulk HTS materials, the pinning of magnetic vortex lines by material inhomogeneities within the HTS crystalline grains, and the minimization of thermally activated flux motion. The latter effect arises from the relatively large operating temperatures now achievable; the related activated depinning of vortex lines, from pinning energy wells that may not be large compared with thermal energies (kT). For HTS materials, this challenge is complicated by the very large crystalline anisotropy that leads to drastically different intrinsic superconducting properties for magnetic fields oriented along different crystal axes, by the variable oxygen composition that can lead to modified (depressed) electronic and superconductive properties, and by the contribution of these and other effects to the problem of current coupling between grains (the "weak-link" problem).

The best critical current density performance at high temperatures in bulk HTS material has been obtained in melt-processed $YBa_2Cu_3O_{7-x}$. Furthermore, both resistive and magnetic measurements indicate weak-link free conduction in the *c*-direction as well as in the *ab* plane. Highly textured BSCCO powder-in-tube conductors can also exhibit weak-link free current flow. In view of the extensive evidence that large-angle grain boundaries generally inhibit current flow, it is important to determine the path for nonweak-linked conduction in these materials. First efforts have been directed toward high-J_c melt-processed $YBa_2Cu_3O_{7-x}$ together with extensive microstructural examination of chemistry and orientation at platelet boundaries. Information relevant to the so-called "brick-wall microstructure" model, which has been proposed to explain high-current densities in textured materials, has been obtained.

It is important to identify and to understand the origins of flux-pinning centers that arise during thermal and mechanical processing. The observation, although somewhat controversial, that J_c increases with the 211/123 interfacial area in melt-processed 123 provides an opportunity to examine microstructures likely to contain high densities of pinning centers. Although it has been suggested that the interface itself pins flux, this idea is not consistent with current understanding of the geometrical requirements for a flux pin. Extensive TEM examinations of the 123 near the surfaces of 211 particles were undertaken in an attempt to define microstructural features likely to pin flux.

Experimental and theoretical approach

Specimens for microstructural studies aimed at determining the path for nonweak-linked current flow in melt-processed $YBa_2Cu_3O_{7-x}$ were obtained through an informal collaboration with K. Salama at the University of Houston. The specimens provided were similar to those used by him and his collaborators in resistive and magnetic measurements showing the absence of weak-link behavior for current flow both perpendicular and parallel to the basal plane. Specimens for examination of the 211/123 interface were of two kinds: melt-processed deposits of submicron aerosol powder on silver-pelladium substrates, prepared at ORNL, and quench-melt-growth material prepared by T. Armstrong at Allied Signal Aerospace by methods similar to those of Murakami et al. in which a dependence of J_c on 211/123 interface area was found. Microstructural examinations of these materials included optical metallography, SEM, electron microprobe, and high-resolution and analytical electron microscopy.

Specimens for electrical transport studies of continuous, zone-melt-processed $Y_1Ba_2Cu_3O_{7-\delta}$ filaments were obtained through a cooperative agreement with M. V. Parish at CPS Superconductor Corporation. In this work the characterized crystalline morphology of the filaments were related to the measured critical current densities as a function of magnetic field and filament orientation in the field at temperatures in the liquid nitrogen range.

The issues of limits to critical currents and the minimization of thermally activated flux motion are addressed by research conducted through separate cooperative agreements with the IBM T. J. Watson Research Center and with General Electric Corporate Research and Development. In the cooperative agreement with IBM, ORNL supports the Postdoctoral Fellow Leonardo Civale, who is resident at IBM with periodic guest assignments for collaborative work at ORNL. Additional in-house research at ORNL is jointly supported by the Superconducting Technology Program (with a matching level of effort at IBM) and by base DOE OBES programs within the Solid State Division. In this project, high-quality single crystals of YBCO and BSCCO materials are grown and characterized at both institutions. Controlled, nearly optimal material defects are introduced systematically by irradiations with energetic light and heavy ions. Through the correlation of electromagnetic properties measurement with microstructural studies, the role of anisotropy, reduced dimensionality, and electronic properties modification on the fundamental limits to loss-free electrical conduction is assessed and described.

Importance of solving the problem being addressed by this research

Improvements in J_c vs H performance, especially at temperatures near 77 K, are essential to use of HTS oxides in energy-saving electrical systems applications. The objectives of this project relate directly to improving J_c through improved flux pinning and control of microstructure to reduce weak-link behavior.

1.5.1.3 Project Output

Major research accomplishments

It is well recognized that critical current density in bulk polycrystalline $YBa_2Cu_3O_{7-x}$ is limited by weak-link behavior at grain boundaries. The specific characteristics of grain boundaries that lead to weak-link behavior have been widely investigated, but a consensus has not been reached. The observation by K. Salama and co-workers at the University of Houston and elsewhere that current flow within "domains" of melt-processed $YBa_2Cu_3O_{7-x}$ is not weakly linked was widely interpreted as indicating that some grain boundaries in highly textured Y123 are not weak links. This interpretation was based on certain assumptions concerning the domain microstructure and growth process. Domains, which are defined from optical metallography, consist of stacks of parallel plates with a common *c*-axis. It has been assumed that the platelets are separate grains that align during growth and that the platelet boundaries involve rotations about the *c*-axis. Therefore, the conclusion of Salama et al. (from resistive measurements of J_c in single-domain specimens cut with their *c*-axis at various angles to the specimen axis) that current flow in the *c*-direction is not weak-linked provides an opportunity to study "good" grain boundaries.

Such a study was undertaken using specimens prepared at ORNL and with specimens provided by Salama that were prepared similarly to those used in the above-described resistive measurements and in ac magnetization studies by Küpfer et al. in which it was also concluded that currents in both the *c* and *ab* directions are not weak-linked. From TEM, SEM, and optical microscopy it was found that the stacked parallel plates within a domain are in fact portions of a single crystal. The platelet boundaries are not grain boundaries but gaps containing remnants of the liquid phase present during domain growth. A growth mechanism has been proposed that is consistent with these observations. The anisotropic nature of growth in 123 results in gap formation and entrapment of liquid phase. However, the gaps are not continuous. Gap terminations within a domain result in interconnected single crystalline material, and the absence of weak-link behavior for current in the *c*-direction is readily understood. It has been proposed that high-basal-plane J_cs in highly aligned materials such as melt-processed 123 and BSCCO powder-in-tube conductor may be explained in terms of the "brick wall" model in which current avoids weak links by utilizing large area *c*-plane boundaries. This work demonstrates that the microstructure within domains of melt-processed 123 is not that of the brick wall model, and an alternative explanation of critical current behavior has been provided.

Flux pinning in melt-processed Y123 has been observed to increase with the surface area of trapped 211 particles, which provides an opportunity to identify flux-pinning structures. TEM and EDS were used to study the 123 microstructure near the 211/123 interface. It was found that a high local density of stacking faults exists in 123 near these interfaces. The stacking faults lie parallel to the (001) basal plane and are inhomogeneously distributed around the 211 particles. They tend to be disk shaped and to have diameters ranging from a few nanometers to ~30 nm. Calculations made using simple energy considerations suggest that these stacking faults may act as effective flux pinners for magnetic fields directed both parallel and perpendicular to the basal plane. They may account for the observed increase of J_c with volume fraction of 211 and also explain the angular dependence of transport J_c in melt-processed 123. An unusual tendency for the formation of facets on the incoherent, randomly oriented 211 particles parallel to the {001}-type planes in the 123 matrix was also observed. Microanalysis of the 123 region around the 211 particles consistently shows an enrichment of yttrium and a corresponding depletion in barium concentration. Such cation nonstoichiometry may result in the formation of numerous point defects, which may also result in pinning. The presence of ledges on some facets at the 211/123 interfaces, and the observed compositional nonstoichiometry in the 123 phase in the vicinity of these interfaces, suggests that 211 particles continue to change in size after entrapment in 123. The observed compositional variation is consistent with dissolution of trapped 211. Such diffusion effects and stresses due to the thermal and elastic mismatch between 211 and 123 provide possible mechanisms for generating the observed defects around the 211 particles in the 123 matrix.

From the work described above, and from the body of empirical observations by others, it is now well established that strongly linked, high-J_c YBCO materials can be produced in the form of bulk masses by a variety of melt-processing techniques. Under a cooperative agreement with CPS Superconductor, a technique was developed and utilized that couples a continuous fiber-spinning process with zone-melt processing, resulting in long lengths of high-quality YBCO filaments that have microstructures similar to those of melt-textured bulk materials. At ORNL filaments provided by CPS Superconductor were examined for microstructural morphology and electrical transport current properties.

Briefly, in the fabrication process at CPS Superconductor, $Y_1Ba_2Cu_3O_{7-\delta}$ and $Y_2Ba_1Cu_1O_5$ powders are milled together, mixed with a thermoplastic binder, and spun into fibers of uniform diameter (125 to 500 mm) and several kilometers in length. Continuous binder burnout and sintering is conducted in a belt furnace to produce high-density, polycrystalline filaments. Subsequent zone-melt texturing occurs in a short hot zone furnace at rates of traverse between 4 and 12 mm/h. The resulting melt-processed filaments are remarkably uniform in cross section and morphology, owing to a combination of small diameter and significant 211 second-phase content. The process is considered "continuous" based on observations of filament morphologies that indicate crystal growth in a steady state, as evidenced by direct metallographic examination over a 40-cm length of fiber.

For the superconducting transport properties measurements at ORNL, short segments of 190-mm-diam filaments were prepared by firing on a 30-mm-thick silver layer to ensure good electrical contact and cryostability against heat generated within the fiber. In addition, the entire assembly was potted in epoxy to provide mechanical stability against the large Lorentz forces produced during the high-field, high-J_c transport measurements. The temperature and magnetic field dependent dc transport critical current density J_c (T, H) were determined in magnetic fields to 8 T in the temperature range of pumped liquid nitrogen (65 to 77 K) and as a function of fiber orientation in the applied field. Figure 8 illustrates the technologically significant levels of critical currents observed; J_c in self-field exceeds 10^5 A/cm^2 at 77 K and requires a total current of about 32 A. The samples exhibited a strong and complicated angular dependence with respect to rotation about the fiber axis in the presence of a transverse applied magnetic field. In the optimum orientation with $B \| ab$, Fig. 8 shows that the current density levels at 8 T in liquid

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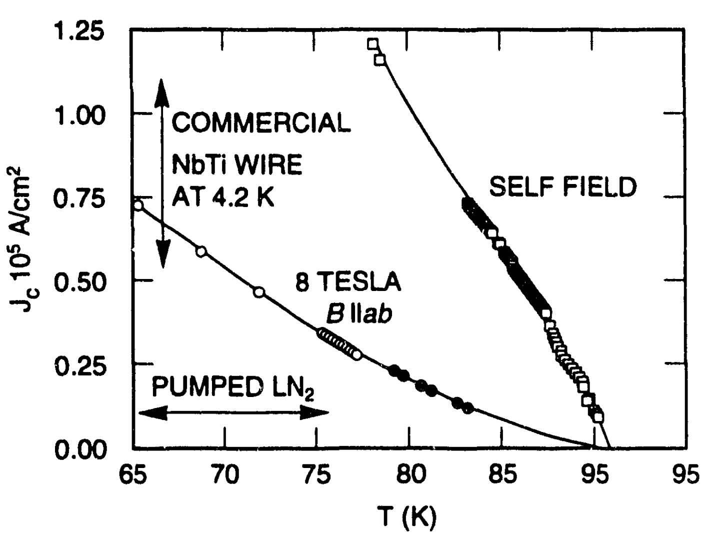

Fig. 8. The temperature dependence of J_c in self field, and in 8 T with $B \| ab$. Open symbols: sample in pumped LN$_2$. Solid symbols: sample in helium gas. Dashed curve in self-field is a guide, while the solid curve at 8 T can be described by a flux creep model. For comparison, a range of J_c values found for commercial niobium-titanium wires operating at 4.2 K in an 8-T field is indicated.

nitrogen approach those of conventional niobium-titanium wire operating at 4.2 K. The microscopy performed on 14 cross-sectional segments cut from one sample revealed virtually single-crystal structure over the entire filament length (~2.5 cm); the YBCO *c*-axis was oriented nearly orthogonal to the fiber axis.

These results confirm that the melt-textured YBCO filaments are composed of strongly linked material with high flux pinning and establish the existence of technologically useful current density levels at high temperatures and magnetic fields in YBCO materials that can be produced continuously over technologically useful lengths. Note that a bundle of such filaments, with an overall diameter as small as ~2 mm, could viably comprise a short, low-field current lead (e.g., for a superconducting magnetic energy storage application) having a 1000-A capacity at 77 K.

As is stated above, the research directed toward materials modification and tailored defect structures is a highly leveraged effort involving Superconducting Technology Program cooperative agreements with IBM and General Electric Company as well as a strong base of support from the DOE OBES programs within the Solid State Division at ORNL. The essential description of these research accomplishments is given in the related Office of Program Analysis Peer Review project summary entitled *Physical Properties of Superconductors* (ERKCS17). For this reason the reader is referred to that document, and those accomplishments will not be duplicated here.

1.5.1.4 Bibliography of Recent Publications Emanating From This Project

1. R. Feenstra, D. K. Christen, C. E. Klabunde, and J. D. Budai, "Role of Oxygen Vacancies in the Flux Pinning Mechanism and Hole Doping Lattice Disorder in High Current Density $YBa_2Cu_3O_{7-x}$ Films," *Phys. Rev. B* **45**, 6569 (1992).

2. J. G. Ossandon, J. R. Thompson, D. K. Christen, B. C. Sales, H. R. Kerchner, J. O. Thomson, Y. R. Sun, K. W. Lay, and J. E. Tkaczyk, "Influence of Oxygen Deficiency on the Superconductive Properties of Grain-Aligned $Y_1Ba_2Cu_3O_{7-\delta}$," *Phys. Rev. B* **45**, 12534 (1992).

3. J. G. Ossandon, J. R. Thompson, D. K. Christen, Yang Ren Sun, and K. W. Lay, "Flux Creep Studies of Vortex Pinning in Aligned $Y_1Ba_2Cu_3O_{7-\delta}$ Superconductor with Oxygen Deficiencies $\delta \leq 0.2$," *Phys. Rev. B* **46** (Aug. 1, 1992).

4. Yang Ren Sun, J. R. Thompson, D. K. Christen, F. Holtzberg, A. D. Marwick, and J. G. Ossandon, "The Temperature and Field Dependent Activation Energy of a Proton-Irradiated YBCO Single Crystal," *Phys. C* **194**, 403 (1992).

5. D. M. Kroeger and A. Goyal, "Critical Currents and Microstructures in Oxide Superconductors," *J. of Metals* (October 1992); accepted for publication.

6. Z. L. Wang, A Goyal, and D. M. Kroeger, "Structural and Chemical Disorder Near the $Y_2BaCuO_5/YBa_2Cu_3O_{7-\delta}$ Interface and Its Possible Relation to the Flux-Pinning Behavior in Melt-Textured $YBa_2Cu_3O_{7-\delta}$," *Phys. Rev. B* (1992); accepted for publication.

7. Z. L. Wang, A. Goyal, D. M. Kroeger, and T. Armstrong, "Defects Near the $Y_2BaCuO_5/YBa_2Cu_3O_{7-\delta}$ Interface and Their Effect on Flux-Pinning in Melt-Processed and Qquench-Melt Growth Processed $YBa_2Cu_3O_{7-\delta}$," presented at the Proceedings of Materials Research Society Symposium Layered Superconductors: Fabrication Properties, and Applications, Spring 1992; to be published in the proceedings.

8. K. B. Alexander, A. Goyal, D. M. Kroeger, V. Selvamanickam, and K. Salama, "Microstructure Within Domains of Melt-Processed $YBa_2Cu_3O_{7-x}$ Superconductors," *Phys. Rev. B* 45(10), 5622–27 (1992).

9. D. M. Kroeger, A. Goyal, Z. L. Wang, F. A. List, and K. B. Alexander, "Substrate Reactions and Flux Pinning Structures in Melt-Processed $YBa_2Cu_3O_7$ Deposits on Ag-Pd Alloy Substrates," presented at the Proceedings of TcSUH HTS Workshop, Houston, Texas, February 27–28, 1992.

10. Z. L. Wang, A. Goyal, and D. M. Kroeger, "Interface Microstructures in Melt-Textured $YBa_2Cu_3O_{7-\delta}$ on Ag-Pd and Flux Pinning Centers Introduced by Y_2BaCuO_5 Particles," presented at the Proceedings of the 50th Annual Meeting of the Electron Microscopy Society of America (EMSA), August 1992.

11. D. K. Christen, C. E. Klabunde, D. B. Chandler, M. J. Neal, M. V. Parish, B. C. Chakoumakos, A. Goyal, and D. M. Kroeger, "The Production and Properties of Melt-Zone Textured $Y_1Ba_2Cu_3O_{7-\delta}$ Filaments," p. 181 in the *International Workshop on Superconductivity, ISTEC/MRS, 1992.*

12. A. Goyal, Z. L. Wang, K. B. Alexander, and D. M. Kroeger, "Stacking Faults Associated with 211 Particles and Other Likely Pinning Centers in Melt-Processed 123," p. 365 in the *International Workshop on Superconductivity, Honolulu, Hawaii, June 22–26, 1992, ISTEC/MRS.*

13. A. Goyal, P. D. Funkenbusch, D. M. Kroeger, and S. J. Burns, "Anisotropic Hardness and Fracture Toughness of Highly Aligned $YBa_2Cu_3O_{7-\delta}$, *J. Appl. Phys.* 71(5), 2363–67 (1992).

14. J. R. Thompson, Yang Ren Sun, H. R. Kerchner, D. K. Christen, B. C. Sales, B. C. Chakoumakos, A. D. Marwick, L. Civale, and J. O. Thomson, "Enhanced Current Density J_c and Extended Irreversibility in $Bi_2Si_2Ca_1Cu_2O_8$ Single Crystals with Heavy Ion Irradiation-Induced Linear Defects," p. 360 in the *International Workshop on Superconductivity, Honolulu, Hawaii, June 22–26, 1992, ISTEC/MRS.*

15. M. V. Parish, "Microstructure of Continuously-Processed, Melt-Textured $Y_1Ba_2Cu_3O_{7-\delta}$ Monofilaments," p. 232 in the *International Workshop on Superconductivity, Honolulu, Hawaii, June 22–26, 1992, ISTEC/MRS.*

16. S. Jin, G. W. Kammlott, T. H. Tiefel, T. T. Kodas, T. L. Ward, and D. M. Kroeger, "Microstructure and Properties of the Y-Ba-Cu-O Superconductor with Submicron '211' Dispersions," *Phys. C* **181**, 57–62 (1991).

17. K. B. Alexander, D. M. Kroeger, J. Bentley, and J. Brynestad, "Grain Boundary Compositions in Stoichiometric and Off-Stoichiometric $Y_1Ba_2Cu_3O_{7-x}$," *Phys. C* **180**, 337–50 (1991).

18. D. K. Christen, C. E. Klabunde, R. Feenstra, D. H. Lowndes, D. P. Norton, J. D. Budai, H. R. Kerchner, J. R. Thompson, S. Zhu, and A. D. Marwick, "Orientation-Dependent Critical Currents in $Y_1Ba_2Cu_3O_{7-x}$ Epitaxial Thin Films: Evidence for Intrinsic Flux Pinning," p. 336 in *Superconductivity and Its Applications (AIP Conference Proceedings 219)*, ed. Yi-Han Kao, Philip Coppens, and Hoi-Sing Kwok, American Institute of Physics, New York, 1991.

19. L. Civale, A. D. Marwick, T. K. Worthington, L. Krusin-Elbaum, F. H. Holtzberg, M. A. Kirk, J. R. Thompson, Y. Sun, and J. R. Clem, "Vortex Confinement by Columnar Defects in $YBa_2Cu_3O_7$ Crystals: Enhanced Pinning at High Fields and Temperatures," *Phys. Rev. Lett.* **67**, 648 (1991).

20. L. Civale, M. W. McElfresh, A. D. Marwick, F. Holtzberg, C. Feild, J. R. Thompson, and D. K. Christen, "Scaling of the Hysteric Magnetic Behavior in $YBa_2Cu_3O_7$ Single Crystals," *Phys. Rev. B* **43**, 13732 (1991).

21. K. B. Alexander, R. K. Williams, D. M. Kroeger, and J. Brynestad, "The Structure and Chemistry of Grain Boundaries in Ceramic Superconductors," *Superconductivity II*, 365–72 (1991).

22. A. Goyal, P. D. Funkenbusch, D. M. Kroeger, and S. J. Burns, "Fabrication of Highly Aligned $YBa_2Cu_3O_{7-\delta}$-Ag Melt-Textured Composites," *Phys. C* **182**, 203–18 (1991).

23. D. K. Christen and R. Feenstra, "Effects of Thermal Processing and Oxygen Composition on Flux Pinning in High-J_c Epitaxial $Y_1Ba_2Cu_3O_{7-x}$ Thin Films," *Phys. C* 185–89, 2225 (1991).

24. D. M. Kroeger, "Grain Boundaries and J_c in High-T_c Oxide Superconductors," *J. of Metals* **41**(1), 14–17 (1989).

25. D. M. Kroeger, A. Choudhury, J. Brynestad, R. K. Williams, R. A. Padgett, and W. A. Coghlan, "Grain-Boundary Compositions in $YBa_2Cu_3O_{7-x}$ from Auger Electron Spectroscopy of Fracture Surfaces," *J. Appl. Phys.* **64**(1), 331–35 (1988).

26. L. Civale, M. W. McElfresh, A. D. Marwick, T. K. Worthington, A. P. Malozemoff, F. Holtzberg, C. Feild, J. R. Thompson, D. K. Christen, and M. A. Kirk, "Critical Currents in Proton-Irradiated $YBa_2Cu_3O_{7-\delta}$ Crystals," in *Proceedings of the Winter Meeting on Low-Temperature Physics*, World Scientific, Singapore, in press, 1992.

27. J. R. Thompson, Yang Ren Sun, D. K. Christen, H. R. Kerchner, A. P. Malozemoff, L. Civale, A. D. Marwick, L. Krusin-Elbaum, M. W. McElfresh, and F. Holtzberg, "Magnetization Studies of Irradiation-Modified Single-Crystal $Y_1Ba_2Cu_3O_7$ Superconductors: Flux Creep and Annealing Effects," p. 573 in *Physics and Materials Science of High-Temperature Superconductors-II*, ed. R. Kossowsky, B. Raveau, and S. Patapis, NATO Advanced Studies Institute Series, Kluwer Academic Publishers, Dortrecht, The Netherlands, in press, 1992.

28. J. R. Thompson, D. K. Christen, H. R. Kerchner, L. A. Boatner, B. C. Sales, B. C. Chakoumakos, H. Hsu, J. Brynestad, D. M. Kroeger, J. W. Williams, Yang Ren Sun, Y. C. Kim, J. G. Ossandon, A. P. Malozemoff, L. Civale, A. D. Marwick, T. K. Worthington, L. Krusin-Elbaum, and F. Holtzberg, "Studies of 'Non-Ideal' Superconductors Using DC Magnetic Methods," in *Magnetic Susceptibility of Superconductors and Other Spin Systems*, ed. T. Francavilla, R. A. Hein, and D. Liebenburg, Plenum Pub., New York, in press, 1991.

29. J. R. Thompson, Yang Ren Sun, L. Civale, A. P. Malozemoff, M. W. McElfresh, A. D. Marwick, and F. Holtzberg, "Effect of Flux Creep on the Temperature Dependence of the Current Density in $Y_1Ba_2Cu_3O_7$ Crystals," *Phys. Rev. B* (1992), in press.

30. J. R. Thompson, Y. R. Sun, H. R. Kerchner, D. K. Christen, B. C. Sales, B. C. Chakoumakos, A. D. Marwick, L. Civale, and J. O. Thomson, "Enhanced Current Density J_c and Extended Irreversibility in Single-Crystal $Bi_2Sr_2Ca_1Cu_2O_8$ via Linear Defects from Heavy Ion Irradiation," *Appl. Phys. Lett.* (1992), in press.

2. TECHNICAL PROGRESS IN SYSTEMS DEVELOPMENT

2.1 APPLICATIONS DEVELOPMENT

2.1.1 Demonstration of a Magnetic Refrigerator for High-Temperature Superconducting Device Applications

2.1.1.1 Project Overview

Specific project objectives

The objectives of the joint project are (1) to develop a prototypic magnetic refrigerator (MR) stage that could provide 50-W cooling at 40 K with heat rejection at 77 K, (2) to demonstrate an integrated system using a gas/magnetic hybrid concept to reject heat at room temperature, and (3) to design an all-magnetic cryocooler, based on the experience gained in this effort, for future development.

Relationship of the project to DOE mission

The mission of the DOE Superconducting Technology Program for Electric Energy Systems is to develop the technology base needed for U.S. industry to proceed to electric power applications of high-temperature superconductivity. The program includes joint development of HTS wire and systems R&D to support mid-term commercialization of the wire. Superconducting magnets, capable of achieving high magnetic fields, have numerous existing and potential applications that include superconducting magnetic energy storage, accelerators, superconducting motors, magnetic fusion, and magnetic refrigeration. HTSs could achieve high magnetic field at elevated cooling temperature, eliminating the need for liquid-helium cryocoolers. While HTSs can be operated around liquid-nitrogen temperature, the present state of wire development suggests that, for practical mid-term applications, temperatures in the 30- to 40-K range will be necessary for high-current density, improved field strength, and magnetic stability. Eventually, a MR that uses HTSs to generate cooling would, therefore, not only be an enabling technology for HTSs but also apply high-temperature superconductivity. Therefore, this project has a relationship to nearly all other projects in the DOE High-Temperature Superconductivity Program in that (1) methods like that being investigated here could provide the cooling capability required to realize practical magnetic field/current density combinations with candidate high-temperature superconducting materials and (2) such materials could ultimately be employed in the magnets of the refrigerator itself.

Relationship to other projects funded by DOE

This project has a direct relation to the Magnetic Hydrogen Liquefier Program at Astronautics Corporation of America (ACA), which is funded in part by DOE's Office of Industrial Technologies under contact DE-AC02-90CE40895. Hydrogen in its liquid or slurry form is a clean and promising fuel of the future. Yet no single and cost-effective means to liquify hydrogen is in use. Objectives for the magnetic hydrogen liquefier program are to design, to construct, and to test a subscale or liquefier prototype

(0.1 ton/day) in the first two phases and, if successful, to extend the developed technology to a full-scale (1 ton/day) commercial liquefier. At present, the project is near the end of the second design and development phase, and a commitment to hardware is expected in FY 1993.

Similarities between the Magnetic Hydrogen Liquefier Program and this project include the use of the active magnetic regenerator concept and some common design features (e.g., active magnetic material configuration). Substantial distinctions between the two include the relative scales of the units, working temperature levels, and optimum methods of implementing the active magnetic regenerator cycle.

2.1.1.2 Project History

Funding for this project is shown in the following table:

	Funding ($ x 1000)			
	FY 1991	FY 1992	FY 1993[a]	FY 1994[a]
DOE				
Direct scientific and technical	50	220	250	80
Funds-out to Astronautics[b]	100	175	225	50
Total DOE	150	395	475	130
Non-DOE				
Astronautics cost share[b]	350	70	450	300
Total project	500	465	925	430

[a]Planned.
[b]Pilot Center cooperative agreement: 9/1/91 - 8/31/94.

2.1.1.3 Scientific and Technical Content

Schedule of major research activities

Using complementary expertise residing in the two organizations, ACA and ORNL, the major research activities outlined below are undertaken jointly by ACA and ORNL under the Superconducting Technology Program. This ACA-ORNL project involves the design, development, fabrication, assembling, integrating, and testing of an MR prototype that is capable of providing 50-W cooling at 40 K aimed for high-temperature superconducting applications. Consistent with ACA objectives as a manufacturer of MRs, most work on design, fabrication, assembling, and integrating is carried out by ACA. Most work on alternative component concept development and testing, magnet design and regenerator fabrication consultation, and unit prototype performance testing will be done by ORNL. Personnel from the two organizations will work together during certain parts of this project, and extensive communication and discussion on R&D will occur through this joint effort.

The major R&D activities of this project include:

- Task 1—MR System Design and Regenerator Analysis (FY 1992). ACA will design 50-W, 40- to 77-K MR stage. Specifications for upper-stage interface requirements and the superconducting solenoid magnet(s) will be determined—in particular, dimensions, field strength, and reaction forces with the regenerator. According to the interface requirement, ORNL will conduct magnet design for the MR system. According to the interface requirements, ORNL will examine available technology and devise an upper-stage to be integrated with the ACA MR stage. ACA will model the MR regenerator for different materials, and ORNL will work with ACA to identify candidates for the device. ACA/ORNL will finalize the complete MR system design and prepare a design review and draft task report.

- Task 2—MR Stage Fabrication (FY 1993). ACA will characterize the selected candidate regenerator magnetic material, fabricate it into regenerator(s), and test it in the MR test apparatus at ACA. ORNL will conduct off-design performance tests of the candidate regenerator designed and provided by ACA. Components for the MR stage will be fabricated by ACA with the help of outside vendors. Major components (such as magnets, power supply, heat exchangers, etc.) built by ACA will be tested by ACA/ORNL (magnets and power supply to be tested by ORNL). ORNL will acquire, modify, and test the selected upper stage; ACA will complete the assembly of the MR lower stage. A project review and draft task report will be prepared.
- Task 3—System Integration, Testing, and Demonstration (FY 1994). ACA/ORNL will conduct the MR stage shakedown test to resolve design problems. ACA will integrate the selected upper stage and the MR lower stage together to form a complete refrigeration unit prototype. ORNL will conduct performance mapping of the prototype unit. Final demonstration testing of the device will be done at ORNL, and system test results will be modeled by ACA. ORNL/ACA will prepare a project final review and project final report.

Scientific and technical issues

Magnetic refrigeration is a type of solid state cooling process that employs materials whose entropy characteristics can be effectively altered by magnetic fields. This technology 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, the essentially exclusive realm of superconducting magnets.

For very large temperature lifts, such as from cryogenic temperatures to room temperature, staged refrigerators are likely to be required. The available options include not only full multistage magnetic units but also hybrid systems combining a low-temperature magnetic stage with either a closed gas cycle or open cryogen high-temperature stage.

Issues that have been addressed in Task 1 include magnetocaloric refrigerant composition and configuration, magnetic field implementation and control, energy flows, and gas cycle refrigerator implementation. Issues currently being addressed include magnetic material particulation techniques and possible bed degradation, reliability in sealing situations involving hoses and bellows, and potential performance improvements from the implementation of layered beds.

Experimental and theoretical approach

For Task 1 (currently scheduled for completion in December 1992), ACA has concentrated on design of the magnetic (lower temperature) stage of the refrigerator, including the specification of magnet and upper-stage interface requirements. ORNL Fusion Energy Division has provided magnet design information to meet lower-stage requirements. ORNL Energy Division has evaluated alternate candidates and devised upper-stage options to meet the stated interface requirements. Based on the designs developed in Task 1, fabrication efforts will comprise Task 2 (currently scheduled for completion in March 1994). The components created in Task 2 will be integrated and tested in Task 3 (currently scheduled for completion in November 1994).

Importance of solving the problem being addressed by this R&D project

From the preceding discussion it is clear that superconductors need refrigeration and that MRs need superconductors. In other words, magnetic refrigeration represents a rare combination—both an application of, and an enabling technology for, superconductors. By the same token, the development of high-temperature superconducting materials promises reduced (but still substantial) refrigeration requirements for devices with many applications and improved refrigerators for meeting those requirements. With HTS wire expected to be limited to temperatures in the 30- to 40-K range for mid-term electric power applications, it is important that efficient, reliable refrigeration be available for such applications.

The ACA/ORNL cryocooler based on magnetic refrigeration with active magnetic regeneration offers the opportunity to demonstrate significant gains in cryocooler systems efficiency combined with high reliability and reduced life-cycle costs. Others have attempted to demonstrate active magnetic regeneration but have either failed or produced only marginal results. This project has already demonstrated large temperature lift capability (up to 50 K) at low cooling capacity (up to 2 W). If successful, subsequent tasks will demonstrate that active magnetic regenerator devices of higher cooling capacity (50 W at 40 K) are practical. Magnetic refrigeration in this capacity/temperature combination range has not been demonstrated to date. The successful completion of this project should provide significant impetus to commercialization of magnetic refrigeration technology. In addition, an efficient, reliable magnetic refrigerator will enable early and mid-term application of HTS wire.

2.1.1.4 Project Output

Major research accomplishments

The project kickoff meeting was held at ORNL on November 8, 1991, to define appropriate project roles for each organization and to develop a tentative project plan. Provisions were made for relevant magnetocaloric material testing using the existing Active Magnetic Regenerator Universal Test Apparatus. Required modifications to the apparatus were developed and implemented to reduce liquid helium consumption, to reduce thermal equilibration times, and to increase service cooler operational stability for the temperature range of interest. Preliminary cycle performance analysis was conducted using both steady state and transient methods. The one-dimensional models written in

Fortran included thermal, fluid flow, and magnetic material effects and employed a standard ordinary differential equation solver.

A conceptual design was developed for the magnetic stage, and the associated review was held at ACA on January 7, 1992. Special attention was given to fluid displacer and refrigerant assembly seal arrangements. Preliminary magnet and upper stage requirements were specified.

Tests with both the primary magnetocaloric material and alternatives were conducted in the Active Magnetic Regenerator Universal Test Apparatus. The primary material showed the capability to span the temperature range of 25 to 80 K with no refrigeration load and 40 to 80 K with a refrigeration load operating in an active magnetic regenerator cycle. Good agreement was found between the experimental results and the performance model. Additional experiments were conducted to characterize the properties of alternative materials and to verify that the addition of cobalt can be used to adjust the magnetic ordering temperatures of rare-earth compounds. A test apparatus was designed and constructed to evaluate the effectiveness of heat exchangers proposed for use in the magnetic stage. Testing indicated adequate performance for these components.

With the magnet size, shape, field, and protection requirements defined, magnet design analysis was performed to characterize winding specifications, flux return options, force predictions, and heat leak/dewar implications for a magnet system using available low-temperature superconductors. Based on the heat rejection requirements of the magnetic (low-temperature) stage, surveys of available and developmental gas cycle refrigerators for applicability to the high-temperature stage of the hybrid machine were conducted. Realistic high-temperature stage options and tradeoffs were summarized, and low-temperature/high-temperature stage interface requirements were established. With the best available information, a preliminary design for magnetic stage was developed, and the associated review was held at ACA on June 30, 1992. Work since then has centered on resolving remaining design issues in preparation for a critical design review tentatively scheduled for November 1992.

The major accomplishments of this project to date are (1) the creation of a conceptual design for a MR to achieve the project goals; (2) the development of analytical models for mechanical, thermal, and magnetic aspects of the system to refine the conceptual design and to provide a framework for option evaluation; (3) the identification of critical design issues that require component-level empirical resolution; (4) the fabrication and modification of component test apparatus to accommodate the most important empirical studies; (5) the execution of relevant experiments to verify hypotheses and performance predictions; (6) the characterization of high- temperature stage options for the hybrid unit; and (7) the creation of a preliminary design that highlights the remaining design issues to be resolved.

2.1.1.5 Bibliography of Recent Publications Emanating from This Project

1. C. B. Zimm and A. J. DeGregoria, "Magnetic Refrigeration: Application and Enabler for HTSC Magnets," presented at the Sixth Annual Conference on Superconductivity and Applications, New York State Institute on Superconductivity, Buffalo, New York, September 15–17, 1992; to be published in the proceedings.

2. S. R. Schuricht, A. J. DeGregoria, and C. B. Zimm, "The Effects of a Layered Bed on Active Magnetic Regenerator Performance," presented at the 7th International Cryocooler Conference, Santa Fe, N.M., November 17–19, 1992.

2.1.2 High-Temperature Superconductor Coil Development for Electric Power Applications

2.1.2.1 Project Overview

Specific project objectives

The basic objective of this project is to develop jointly with U.S. industry the technology needed to commercialize HTS coils for electric power applications (Fig. 9). Experimental measurements of coils and conductors developed by industry are an integral part of the project. Specific objectives are:

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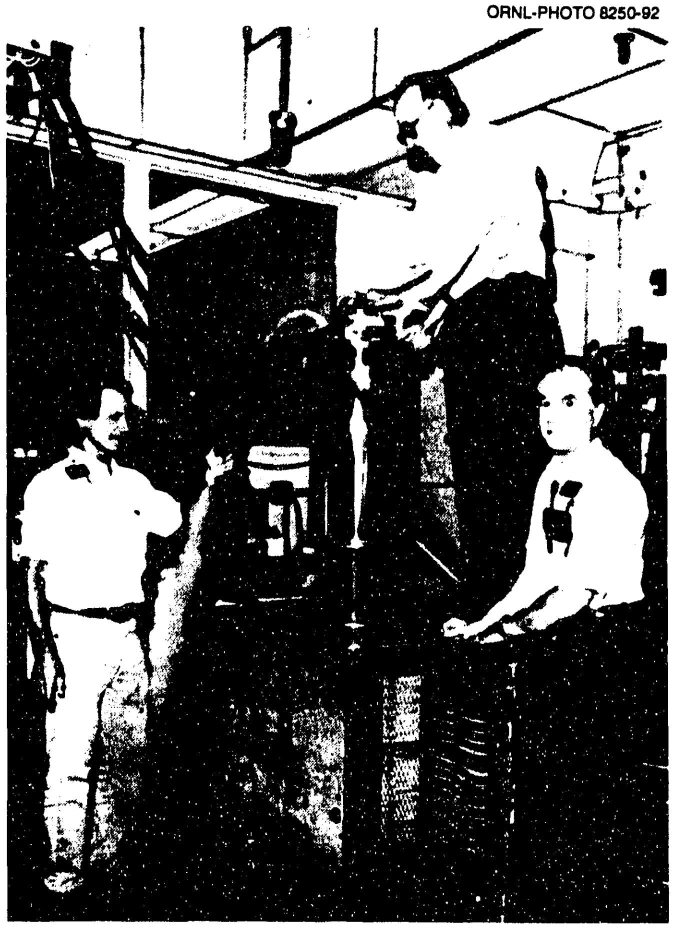

Fig. 9. Mike Walker (top), Intermagnetics General Corporation, adjusts a high-temperature superconducting coil in the ORNL variable temperature cryostat. Looking on are Marty Lubell (r), ORNL's principal investigator, and Bill Schwenterly.

- to measure critical currents of HTS coils provided by commercial partners at temperatures from 4.2 to 100 K and in external magnetic fields ranging up to 8 T;
- to provide information and testing to aid in selection of dielectric materials for HTS coils;
- to aid Reliance Electric Corporation in cryogenic engineering aspects of rotor design and calculation of quench detection and magnet protection parameters;
- to determine whether a sufficient normal-zone voltage will be available to detect an incipient quench before a silver/BSCCO superconductor operated in the 20- to 40-K range overheats;
- to assist Intermagnetics General Corporation in evaluating the viability of a proprietary method for fabricating high-temperature superconducting magnets;
- to develop a motor coil test bed to enable evaluation of superconducting coils in a variable speed, variable horsepower environment;
- to carry out critical current and loss measurements on HTS coils with power frequency ac transport currents and external fields;
- to develop capability to test large coils for Reliance Electric Corporation motor prototypes; and
- to address coil manufacturing issues such as conductor joints, lead attachment, crossovers, and protection of conductor materials during winding and insulating processes.

Relationship of project to DOE mission

This project is conducted in accordance with the mission of the DOE Superconducting Technology Program to develop the technology base needed for American industry to proceed to commercialization of electrical power applications of HTSs. Essentially all such applications involve HTS in wire and coil forms.

Development of high-performance HTS wires and coils for use in electric power systems is directly relevant to DOE's interests in energy conservation and utilization. Such wires and coils can lead to greatly improved efficiency for electric motors, generators, transmission lines, and transformers. Application of HTS materials in magnetic energy storage systems would allow better usage of existing generating and transmission facilities (see Fig. 9).

Relationship to other projects funded by DOE

The DOE Superconducting Technology Program provides funds for collaborative R & D efforts between U.S. industry and several national laboratories. This project is coordinated with efforts of other laboratories that are working with U.S. industry to develop HTS wire, coils, and applications for the wire products.

Project history

Funding for this project is shown in the following table:

	Funding ($ x 1000)	
	FY 1991	FY 1992
DOE		
Direct scientific and technical	250	500
Funds-out to industry	0	325
Total	250	825
Non-DOE (industry cost share)		
American Superconductor Corporation		180
Intermagnetics General Corporation		100
Superconductivity Inc.	50	50
Reliance Electric Inc.	*a*	*a*
Westinghouse Inc.	*a*	*a*
Electric Power Research Institute	50	120
Total	100	450

[a]Informal collaboration.

Funding for contracts and funds-out cooperative agreements with industry follows:

	DOE funding ($ x 1000)	
	FY 1991	FY 1992
American Superconductor Corporation[a]	0	225
Intermagnetics General Corporation[b]	0	100
Total	0	325

[a]Approved term: 9/1/91 - 11/15/92.
[b]Approved term: 10/1/91 - 9/30/94.

2.1.2.2 Scientific and Technical Content

Schedule of major research activities

Major research activities, together with respective institution, follow (see Subsect. 2.1.2.3 for accomplishments):

- American Superconductor Corporation (ASC)—Perform critical current measurements on a 2000-A turn coil provided by ASC June 30, 1992.
- Reliance Electric Corporation—Review design of rotor cryostat for 1-hp iron-core motor (May 31, 1992). Review conceptual design of cryostat for 5000-hp motor (November 1992). Propose ac loss measurements (November 1992). Develop quench scenario (November 1992).
- Westinghouse Electric Company—Perform critical current measurements on a 6.35-cm short sample provided by Westinghouse (June 30, 1992).
- Intermagnetics General Corporation—Perform critical current measurements on coils supplied by IGC in a variable temperature, variable applied magnetic field

environment. Test proprietary coil fabrication technique in an external ramped field to determine if excessive ac losses occur.

- Superconductivity, Inc.—The 5-kJ test magnet being proposed by Superconductivity, Inc., is to have a bore radius of 19.05 cm (7.5 in.) and width and build each of 7.62 cm (3 in). The conductor is to be a multifilamentary silver/BSCCO wire, operated in the temperature range 20 to 40 K. The overall current density, chosen to be 2.5 kA/cm^2, will produce a central field of 0.4 T and a maximum field at the winding of 0.9 T. Owing to (1) the low current densities at which HTSs must be operated at present, (2) the substantial difference between their operating and critical temperatures, and (3) their rather large heat capacities between these temperatures, the growth of normal zones is rather slow. This greatly implicates the detection of incipient normal zones. On the other hand, the low-current density and high-heat capacity cause the hot-spot temperature to rise slowly, so a long time may be available for the detection of normal zones. The purpose of the work is to study the competition between these countervailing influences and to decide if it is possible to detect normal zones before the hot-spot temperature reaches harmful levels.
- Superconducting Motor Coil Test Bed--Complete testing of axial field machine with niobium-titanium magnets and revised control system by October 1992.

Scientific and technical issues

Transport critical current measurements as a function of temperature and external field are being carried out on HTS conductor samples from several manufacturers. These measurements are of key importance in determining the performance ratings, optimum operating temperature, and efficiency of equipment using these conductors. Electrical insulation studies are under way for ASC. Design of the rotating cryostat for the Reliance Electric Company 1-hp motor is under review.

Experimental and theoretical approach

An existing variable-temperature cryostat was modified by the manufacturer, Andonian Cryogenics, to provide a sample space for coils up to 10 cm (4 in.) in diameter and 30 cm (12 in.) in length. Temperatures are measured with silicon diodes and carbon-glass resistance thermometers. Transport critical currents are determined by ramping up the current on the sample and measuring the voltage across it at levels as low as a few microvolts. External magnetic fields are applied by a water-cooled copper magnet driven by motor-generators.

Methods for measuring ac losses are under review. It is expected that an electrical method as opposed to a calorimetric method will be chosen.

Tensile tests on insulation materials are carried out on an Instron tester. A cryogenic appliance is available for tests at liquid nitrogen temperature. A quartz dilatometer is used for thermal expansion measurements down to liquid nitrogen temperature. Insulation resistance is measured by immersing a length of conductor in water. A ground electrode in the water bath completes the circuit to the high-voltage supply. The materials tested so far have been chosen and provided by ASC. ORNL will likely provide additional guidance in this choice in the future.

Importance of solving the problem being addressed by this research

The basic goal of this research is to help the commercial HTS material developers to put their materials to practical use. It is necessary to proceed from short samples produced and tested in the laboratory under ideal conditions to long lengths of conductor that must withstand the stresses of fabrication into coils and then operate under widely varying conditions of temperature, mechanical stress, voltage, and magnetic field. This program will determine the effects of these parameters on HTS conductor performance.

Project Output

Major research accomplishments

Major research accomplishments, together with respective institution, are discussed in the following subsections:

American Superconductor Corporation. Critical current (I_c) measurements in zero external magnetic field were carried out on a 1000-A turn sample coil fabricated by ASC. Another coil rated at 2000-A turns was tested in external fields up to 5.5 T. The conductor for both coils was a thin silver tape containing filaments of lead-doped BSCCO HTS material. V-I curves were obtained at several temperatures ranging from 4.2 to 90 K. I_c was defined as the point where the sample voltage gradient reached 1 μV/cm. Between 20 and 80 K, I_c fell linearly as the temperature rose. This behavior is very similar to what is seen for conventional low-temperature superconductors. The 4.2-K zero-field I_cs for the two samples were 3.6 A (1000-A turn) and 8.9 A (2000-A turn). In an external field of 0.5 T, I_c for the 2000-A turn sample was reduced to about 60% of the zero-field value. Above 2 T, the dependence of I_c on field was weak. The onset of the superconducting transition of this sample was at 110 K, and it was fully superconducting at 101 K. Measurements on both samples agreed well with similar measurements on these samples by ASC, the Naval Research Laboratory, and the Naval Surface Warfare Center. This shows that ASC is producing a very robust and stable high-temperature superconducting material.

In an effort to find better materials for conductor insulation, potting, and coil structures, tensile, thermal expansion, and electrical resistance tests were carried out on several samples supplied by ASC. The first studies investigated the effect of cure time on tensile strength of three epoxies. These epoxies are interesting because their cure times are favorable for a production insulating process. Two samples were tested for each cure time and thickness. Nominal thicknesses of 1.6 and 3.2 mm were used. Observed room-temperature tensile strengths ranged from 300 to over 40,000 psi. The strongest material showed very high strength variation (roughly a factor of 20) between samples but no clear thickness dependence. The two weaker materials had relatively small scatter, but the thick samples showed up to a factor of 2 in lower strength. All the samples showed a generally increasing tensile strength by a factor of 2 to 4 as the cure time increased. The samples had many internal flaws, and many failures occurred in the tester jaws rather than in the gauge length. The thermal expansion of all the unfilled materials between room temperature and liquid nitrogen temperature was four to eight times that of silver.

Westinghouse Electric Company. Zero-field critical current measurements were performed on a high-temperature superconducting sample supplied by the Westinghouse Research and Development Center. The sample was a single core of silver-clad BSCCO material with an overall OD of 0.15 cm and a length of 6.35 cm. The central 5-cm length contained five voltage taps. Three of the four segments defined by the five voltage taps had I_cs in excess of 80 A (the power supply limit) at 4.2 K. The extrapolated 4.2-K critical currents were 87, 91, and 110 A. The critical currents fell linearly with increasing temperature at a rate of about 1.7 A/K. The fourth segment, which was closest to one end, had a 4.2-K critical current of only 43 A. During warmup, the 91-A segment was monitored with a 1-A current and went normal at 75.6 K.

A second test was run on this sample in fields up to 5.5 T. A field of only 0.07 T caused degradation of I_c to roughly 60% of the zero-field value $I_c(o)$. Increasing the field to 1 T caused a further decrease to 50% of $I_c(o)$. Above 1 T, there was little dependence of I_c on field.

Reliance Electric Company. The informal collaboration with Reliance Electric Company was initiated during the second half of FY 1992, and ORNL's role is still being defined. Reliance has a program funded by the Electric Power Research Institute in collaboration with ASC; their ultimate goal is development of a 5000-hp motor. In May 1992 ORNL personnel visited Reliance's factory to familiarize themselves with the program and to examine the rotating cryostat built by Reliance for their 1-hp motor prototype. It was decided that ORNL would initially assist in design improvements and quench detection for the magnets. Another meeting was held in August 1992 at the Applied Superconductivity Conference to discuss provision of demountable flanges in the rotating cryostats to allow easy replacement of the coils.

Superconductivity, Inc. The specific heats of silver and BSCCO and the electrical resistivity of silver were determined, and from them the adiabatic hot-spot function was calculated, as were the normal-zone propagation velocity and the normal-zone voltage. From these quantities it is possible to determine the normal-zone voltage as a function of hot-spot temperature. We conclude that the voltage becomes large enough to detect normal zones reliably before the conductor overheats. In addition, a formula for the estimation of the minimum quench energy is given.

The results obtained apply to silver/BSCCO superconductors operated in the 20- to 40-K range, which was the range of interest to the industrial participant. The question of whether test magnets wound with such conductors could be protected is important because of the present great cost of these conductors. The major conclusion of this work is that normal zone voltages are sufficient to allow detection of incipient quenches before the conductor overheats.

Superconducting Motor/Coil Test Bed. The Superconducting Motor Research Facility at ORNL consists of a test bed on which the rotor is mounted, an axial gap rotor, a cryostat with four superconducting electromagnets, a 3000-A current source, a dynamometer, an encoder, an invertor drive, and instrumentation to measure the system responses. The test component is an axial gap motor that comprises a three-phase rotor driven by an invertor in the constant field of four electromagnets made with low-temperature superconducting wire. Results include:

- Completion of a three-dimensional finite element analyses. Stresses induced in the G-11 Rotor 2 material at operating speed were determined, and modal frequencies and their sources for the rotor were calculated.
- Redesign of the electrical configuration to achieve increased horsepower and efficiency. Design curves for Rotor 2 from Rotor 1's generated voltage were prepared; resistive power consumed by eddy and coil currents was minimized with selection of appropriate wire gage and number of strand; and a flux-focusing system was designed

to increase the field in the vicinity of the rotor coils (unfilled G-11 material was procured, and fabrication of the Rotor 2 armature housing was subcontracted).

- Winding of the new configuration on SCM Rotor 2 together with assembly and characterization of the SCM Rotor 2 in the Superconducting Motor Research Facility.

Intermagnetics General Corporation. The critical current was measured for one coil as a function of temperature (4.2 to 107 K) and background field (0 to 4 T). These results compared favorably with measurements taken at David Taylor Research Center, the Naval Research Laboratory, and General Electric Company at the easily obtainable points of 4.2 and 77 K. A second coil was measured at different temperatures in a background field that was ramp to 2 T at a rate of 4 KG/s. The temperature and voltage both showed no change when the experiments were performed at 60 and 40 K. However, at 20 K a temperature rise of 1/2 K was observed. This showed that there was an effect on their coils, but it was an insignificant one; therefore, the Intermagnetics General Corporation (IGC) proprietary winding method does not lead to undue ac losses.

2.1.2.4 Bibliography of recent publications emanating from this project

1. S. W. Schwenterly, J. W. Lue, M. S. Lubell, J. N. Luton, and C. H. Joshi, "Critical Current Measurements on Ag/Bi-Pb-Sr-Ca-Cu-O Composite Coils as a Function of Temperature and External Magnetic Field," presented at the 1992 Applied Superconductivity Conference, Chicago, Ill., August 1992.

2. M. S. Walker, D. W. Hazelton, P. Halder, J. A. Rice, J. G. Hoehn, Jr., L. R. Motowidlo, E. Gregory, M. S. Lubell, S. W. Schwenterly, and C. T. Wilson, "Development of Coil Technology for Bi-2223 Superconductors," presented at the 1992 Applied Superconductivity Conference, Chicago, Ill., August 1992.

3. L. Dresner, "Stability and Protection of Ag/BSCCO Magnets Operated in the 20-40 K Range," *Cryogenics* (1992); submitted for publication.

3. SUMMARY OF TECHNOLOGY TRANSFER ACTIVITIES

3.1 INTRODUCTION

The High-Temperature Superconductivity Pilot Centers were created in 1989 by DOE to enable cost-shared R&D of HTSs with U.S. industry. Early efforts were devoted to development of the legal mechanisms for cooperative agreements between the national laboratories and industry. Such legal agreements had to offer certainty, speed, and protection of proprietary and limited access data during and after project completion. Early objectives of this project, therefore, included creation of (1) the legal framework, with the DOE Field Office, to enable cooperative agreements and (2) joint laboratory-industry project teams to focus on R&D of high-temperature superconducting thin films and bulk applications.

During the last 2 years, the DOE mission has focused on HTS wire and electric energy applications. Therefore, the ORNL Superconducting Technology Program activities focus on jointly developing with industry the technology base needed to commercialize high-temperature superconducting wire and applications to the electric power industry. These applications are motors, generators, superconducting magnetic energy storage, fault current limiters, and transmission lines.

Objectives of the technology transfer activities within the ORNL program are:

- to conduct technical and economic assessments of energy applications of HTSs;
- to initiate pilot center cooperative agreements with industry;
- to ensure effective use of funds-out to industry;
- to provide scientific and technical coordination of all ORNL superconductivity projects;
- to ensure that programmatic and technical coordination is accomplished with other HTS pilot center laboratories and other federal agencies; and
- to transfer technology to industry through appropriate cooperative agreements, submittal of invention disclosures, and licensing of patented inventions.

Planned future work includes (1) a continuation of applicable cooperative agreements and initiation of new agreements in wire and wire application development, (2) participation in the anticipated DOE Superconductivity Partnership Initiative and industry-led team that will jointly develop an electric power application of HTSs, and (3) implementation of a workshop on superconducting magnetic energy storage for customer power quality applications.

3.1.1 Relationship to the DOE Mission

The ORNL program mission is that of its sponsor, DOE's Advanced Utility Concepts Division: to develop the technology base needed for industry to proceed with commercial development of HTS electric power applications. Superconducting technology can help U.S. industry save energy by replacing electric machines and transmission lines with more efficient HTS systems and may enable new, cost-effective superconducting magnetic energy storage for storing peak-demand electric energy and for stabilizing long transmission lines.

3.1.2 Relationship to Other Projects Funded by DOE

The Superconductor Technology Program builds upon ongoing superconductivity materials research funded by the DOE OBES. The OBES-funded project at ORNL (FWP ERKCS15), "Superconductors with High Critical Temperatures," serves to supplement the basic research program at ORNL on high-temperature superconductivity and to provide basic research support for collaborative industrial research projects sponsored through the Superconductor Technology Program. The specific tasking is related to crystal growth and materials synthesis, microstructural characterization, materials modification through ion beam processing, and superconducting electromagnetic properties characterization.

3.1.3 DOE Funding

DOE funding for the program, together with subcontracts active in 1992 and a summary of funds-out cooperative agreements, is shown in the following tables:

	New budget authorization/outlay ($ × 1000)		
	FY 1989/1990	FY 1991	FY 1992
Direct scientific and technical	2072	3146	3213
Management and outreach	230	219	280
Subtotal ORNL	2302	3365	3493
Subcontracts[a]	0	154	439
Funds-out cooperative agreements	1068	681	1072
Total program	3370	4200	5004

[a]Details provided in separate tables. Funds-out cooperative agreements provide direct financial support to U.S. industry for cost-shared cooperative research and development.

Subcontractor	Term	Technology area
Ames Laboratory	2/90–5/92	Optimize flux pinning
Ferraro, Oliver, and Associates, Inc.	5/92–10/92	Perform superconducting magnetic energy storage technology and market opportunity assessment
Lehigh University	5/92–12/92	Implement deformation and annealing of silver-doped superconducting compound
University of New Mexico	4/92–3/93	Evaluate effects of dopants and compositional variations on powder characterization for superconducting powders produced by aerosol pyrolysis
IMTECH-Hsu	11/91–11/92	Complete material synthesis and conductor fabrication
A. D. Little Inc.	12/92–4/93	Technical and economic assessment of SMES and other storage options (co-funded by Defense Nuclear Agency)

			Total agreement cost share ($ × 1000)			
Participant[a]	Approved term	Type[b]	By DOE to ORNL	By DOE to industry	By industry	Technology area
Advanced Fuel Research	2/1/90–9/30/92	NFE	130	0	342	In situ deposition monitors
American Magnetics (C)[c]	8/10/89–8/9/92	NFE	70	0	400	Char. of MOCVD-deposited multifilament conductors
American Superconductor	9/1/91–11/15/92	FO	200	225	180	Coil fabrication and testing
American Superconductor	4/1/89–3/31/93	NFE	775	0	732.7	Fabrication of wire and tape
Astronautics	9/1/91–8/31/94	FO	600	450	820	Magnetic refrigeration
Consultec Scientific (C)	6/1/89–12/31/90	FO	38	45	64	Deposition target device
Corning	6/1/89–12/31/92	FO	325	275	316	Deposition on flexible ceramic substrates
CPS Superconductor	4/1/91–3/31/93	NFE	80	0	50	Conductor fabrication—continuous filament melt-textured YBCO
Dow Corning (I-IIa) (C)	7/1/90–9/30/91	FO	110	50	67	Thick film deposition
DuPont (C)	7/1/89–3/31/91	NFE	225	0	250	Thin film devices and bulk applications
Energy Conversion Devices	5/1/91–3/31/93	NFE	90	0	90	Deposition of conductors
General Electric (A1) (C)	12/15/88–2/28/89	FI	5	0	45	Thallium HTS material processing
General Electric (B1)	10/1/89–12/31/92	FO	325	250	250	Laser deposition of conductors
General Electric (C1) (C)	4/1/90–12/31/90	NFE	135	0	140	Thallium HTS material processing
HiTc Superconco (C)	3/1/90–4/30/91	NFE	40	0	50	Magnetic bearings
Innovative Materials Technology (C)	10/1/89–3/31/90	FI	50	0	50	Composite tape fabrication
Intermagnetics General Corporation	10/1/91–9/30/94	FO	225	225	225	Coil fabrication and testing
Intermagnetics General Corporation	9/1/91–8/31/93	NFE	100	0	100	Optimize flux pinning
IBM	2/1/90–1/31/93	NFE	255	0	673	Optimize flux pinning

			Total agreement cost share ($ × 1000)			
Participant[a]	Approved term	Type[b]	By DOE to ORNL	By DOE to industry	By industry	Technology area
IBM	2/1/90–1/31/93	FO	65	308	131	Optimize flux pinning
Neocera	2/1/91–1/31/93	FO	80	111.6	95.7	Laser ablation multitarget deposition
SUNY-Buffalo	7/1/89–10/30/92	FO	165	250	255	Laser deposition of conductors
Stevens Institute of Technology	1/1/90–5/31/92	FO	90	105	100	MOCVD deposition for electronic devices
Superconductivity, Inc.	10/1/89–3/31/93	NFE	180	0	133	Magnetic energy storage—small systems
Textron Specialty Materials (C)	8/1/89–3/31/91	NFE	60	0	45	Deposition of conductors
Westinghouse Electric	4/1/89–12/31/92	FO	630	650	650	Powder scale-up and wire fabrication
Total			5048	2944.6	6254.4	

[a]Summary of Pilot Center cooperative agreements as of Sept. 30, 1992.
[b]NFE—no funds exchange; FO—funds out; and FI—funds in.
[c]Completed.

3.2 TECHNOLOGY TRANSFER APPROACH

In FY 1992 an assessment of small superconducting magnetic energy storage for power quality enhancement was initiated. Performance characteristics and application benefits were compared with competitive active power conditioning technologies. Participation in multiorganization committees such as the Superconductivity Coordinating Committee for Electric Power, the Council for Superconductivity and American Competitiveness, the Electric Power Research Institute (EPRI) Power Electronics and Motor Technology Steering Committee, and the SMES Utility Interest Group ensures coordination of the ORNL program with other federal and private superconductivity programs.

A coordinating committee consisting of the three pilot center directors and the DOE Headquarters cognizant program manager for Superconductivity Systems was formed in FY 1992. The committee is chaired by the ORNL Superconducting Technology Program manager. ORNL works with the other program laboratories to address issues such as communication among program participants, workshop and meeting implementation, planned competitive solicitations and pilot center collaborative agreements, and coordination of technical and economic assessments. ORNL manages the Energetics support services contract and will assist, through the coordinating committee mechanism, in developing a program annual operating plan.

ORNL cosponsors and participates in a wide variety of symposia, meetings, and workshops each year to enable exchange of technical progress. These activities include the Fall MRS Meeting, the Joint U.S./Japan Workshop on HTS, the MRS/ISTEC Meeting, the Advanced Motors and Drives Workshop, the DOE Wire Development Workshop, and annual reviews of EPRI, the Texas Center for Superconductivity (University of Houston), and the Defense Advanced Research Projects Agency (DARPA).

Cooperative agreements ensure that technology is developed jointly with industry. The Office of Guest and User Interactions and Patent Counsel work together to place these agreements. Where appropriate, these efforts are coordinated with DOE Office of Energy Research-funded projects within ORNL as well as Work for Others and ORNL Director's R&D Fund projects. Effective funds-out to industry is used to supplement industry cost share. In FY 1992 over $1.6 million in funds-out to industry was provided through cooperative agreements and subcontracts. These technology transfer mechanisms are augmented by Cooperative Research and Development Agreements, user agreements, and licensing activities in order to keep industry involved from the start of the program and to ensure commercialization potential.

In this program, responsiveness to American industry has high priority. An ORNL ad hoc technical review committee, consisting of the Superconducting Technology Program manager, scientific coordinator, manager for conductor development, and manager for applications development, reviews all inquiries from industry and recommends a project for possible funding. This review ensures that the proposed work fits the program mission, that the work is collaborative, that there is legitimate commercial interest, and that the work is feasible. Substantial cost-share is required on cooperative agreements.

3.3 RESULTS OF TECHNICAL ASSESSMENT

In a collaborative project with EPRI, a technical assessment of the potential impact of superconductivity on power quality enhancement was conducted. Electric power quality problems are estimated to cost U.S. industry $26 billion per year in lost production. During the last 10 to 15 years, the use of electronically controlled equipment, which is often sensitive to even slight voltage aberrations, has increased dramatically. This increased vulnerability of all segments of the economy to momentary voltage variation has resulted in increased emphasis on power quality.

While several phenomena are present in the overall power quality problem (viz., voltage spikes, frequency variation, voltage surges, and harmonics), it is now well established that the vast majority of the problems (85 to 90%) are caused by voltage "sags" (brief momentary depression of voltage below 80% lasting 5 to 30 cycles). These conclusions were derived from a variety of studies by the utilities, the Bell System, IBM, Digital Equipment Corporation, and more recently the Power Electronics Applications Center of EPRI. The next major problems (5%) are momentary outages lasting from 0.5 to 2 s. An initial survey of users, manufacturers, and utilities seemed to indicate that longer outages were a problem; however, further evaluation and data collection now support the above results. Users apparently confuse the duration of the equipment down time with loss of electric service, which is generally not the case. The use of superconducting magnetic energy storage devices (SSDs) as the stored energy source for an uninterruptible power supply (UPS) system has recently been commercialized by Superconductivity, Inc. In the event of a voltage sag, energy stored in the superconducting coil is discharged, under the control of a voltage regulator, through an inverter to provide precise voltage and current to the critical ac load. A cost-benefits analysis comparing battery-based UPS with SSD-based UPS shows that the SSD is cost-competitive above the 750-kVA power level (see Fig. 10).

ORNL-DWG 93M-5334R

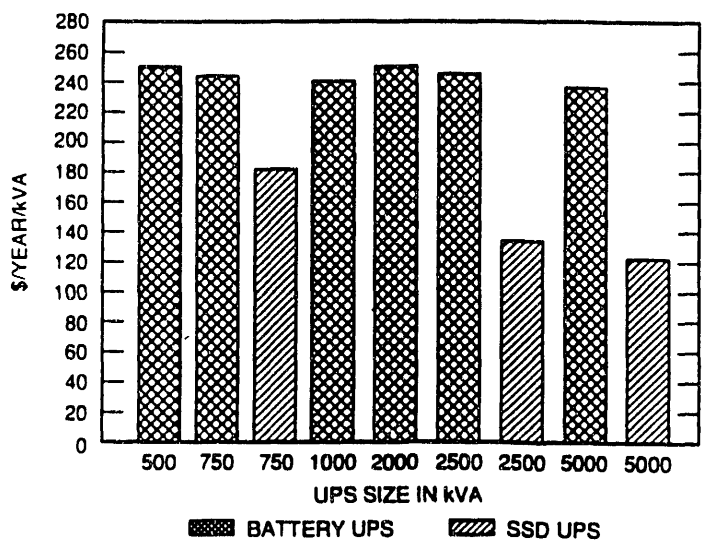

Fig. 10. Levelized uninterruptible power supply vs superconducting magnetic energy storage device costs for turnkey systems including operation and maintenance costs.

3.4 PROGRAM MEASURES

Four new cooperative agreements were executed during FY 1992: Astronautics Corporation of America, American Superconductor Corporation, and two agreements with Intermagnetics General Corporation. Seven new Statements of Work were negotiated, and cooperative agreements were extended an additional year for the following: American Superconductor, General Electric, IBM, Neocera, Inc., State University of New York at Buffalo, Superconductivity, Inc., and Westinghouse Electric. Four new cooperative agreements are pending with the following organizations: Electric Power Research Institute, Reliance Electric, Saphikon, and the University of Wisconsin—Madison.

Eight new invention disclosures were submitted by ORNL or industry principal investigators working on the program. A complete list of invention disclosures is shown in the following table:

ESID	Subject of disclosure	Submitted by
935-X	"Method for Fabricating Continuous Ribbons of High Temperature Superconductors"	Vinod K. Sikka and Charles E. Dunn
1018-X	"Improved $Y_1Ba_2Cu_3O_7$ Superconductor"	A. D. Marwick and L. Civale (IBM), and J. R. Thompson
964-X	"Chemically Compatible Substrate/Jacket Alloy for Oxide Superconductors"	Donald M. Kroeger, Fred A. List III, and Jorulf Brynestad
1039-X	"Method for Preparation of $(Bi\text{-}Pb)_2Sr_2Ca_2Cu_3$ Oxide Powders"	Donald M. Kroeger, Jorulf Brynestad, and Huey S. Hsu
1040-X	"Method for Preparing Superconducting Wires from Oxide Powders"	Donald M. Kroeger and Huey S. Hsu
1058-X	"Rolled Current Density, High Temperature Ribbon Superconductors from Stacked Predeposited Strips"	Graham A. Whitlow and Jeffrey C. Bowker (Westinghouse) and Donald M. Kroeger and Fred 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]	Vinod 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]	Donald M. Kroeger and Frederick A. List

[a]Numbers in parentheses are cooperative agreement numbers under which the work was conducted.

The program resulted in numerous publications, presentations, and reports (see Fig. 11).

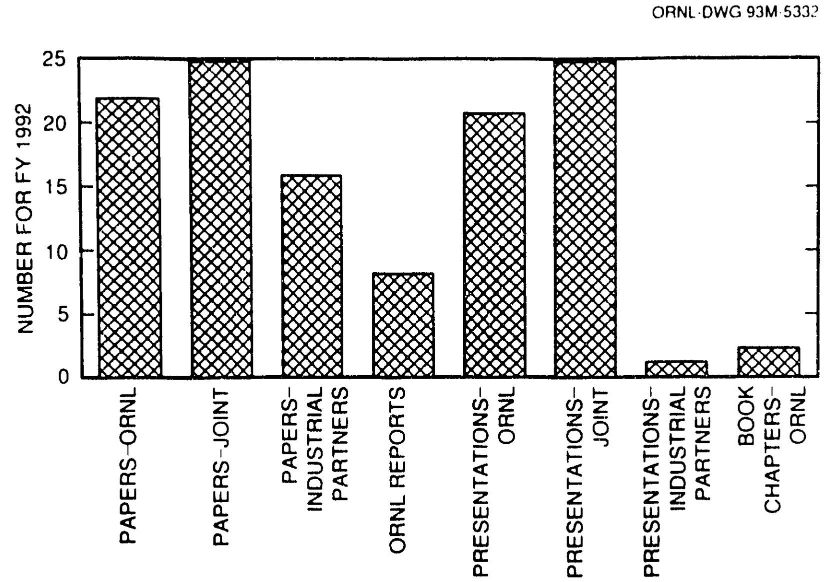

Fig. 11. Publications and presentations during FY 1992.

3.5 HIGHLIGHTS OF INDUSTRY PROGRESS IN FY 1992

Additional highlights from FY 1992 showing progress made jointly with American industry toward fabrication of wire and wire products follow:

- ORNL organized and chaired the major DOE program "Wire Development Workshop" for FY 1992 held in Richmond, Virginia (February 1992).
- In May 1992 an industrial partner, American Superconductor Corporation (ASC), announced that they had been awarded a Department of Commerce Advanced Technology Program contract. For the 3-year effort, ASC and ORNL will jointly develop and test "racetrack" high-temperature superconducting coils for electric motors. Reliance Electric will build and test the motor.
- Record high J_c values in Bi-2223 tapes were measured by Intermagnetics General Corporation (IGC) in a cooperative agreement partially supported by ORNL. At self-field and 77 K, J_c = 40,000 A/cm^2 ($H \parallel ab$); J_c = 20,000 A/cm^2 at 40 K and 6 T.
- ASC demonstrated the ability to fabricate 67 m of HTS wire that conduct 9000 A/cm^2 in self-field at 77 K.
- The newly refurbished variable temperature cryostat at ORNL was used for the first time in joint experiments with U.S. industry. The HTS coils, provided by ASC and IGC, were tested at temperatures from 4.2 to 107 K in magnetic fields up to 6 T. In one experiment the field was varied to evaluate ac losses in the coils. A proprietary coil design from IGC showed no undue losses in ramped fields at temperatures 20 to 77 K.
- Critical currents in wires produced jointly by ORNL and Westinghouse exceeded 550 A in self-field at 4.2 K.

- Seven U.S. industry or university collaborators took advantage of an opportunity to expose HTS films and wires to heavy ion irradiation at ORNL's Holifield Facility. The 600-MeV silver ions produced linear damage tracks in the superconductor, which resulted in enhanced current conduction in the presence of technologically useful magnetic fields.
- In a cooperative agreement with ORNL, Neocera, Inc., developed and commercialized a computer-controlled, multitarget laser ablation deposition system for growing thin and thick superconducting films. Neocera also applied for a copyright on the system control software developed under this agreement.
- In a cooperative agreement with ORNL, CPS Superconductor Corporation reported a YBCO wire, 40-cm long, with performance resembling niobium-titanium wire, but at liquid nitrogen temperatures. The dc transport critical current density of the wire was measured by ORNL to be in excess of 10^5 A/cm^2 in an 8-T magnetic field.
- World-record critical current densities for polycrystalline HTS thick films (Tl-1223) were reported by General Electric researchers. In a 2-T field oriented parallel to the film, critical current densities exceeded 10^5 A/cm^2 at 40 K and 10^4 A/cm^2 at 77 K. The proprietary two-zone reactor, in which sample temperature and thallium oxide vapor pressure are controlled independently, was developed after some pioneering joint work between ORNL and General Electric researchers. This work involved synthesis of thallium films using gaseous Tl_2O.
- In a cooperative effort partially supported by ORNL and DARPA, General Electric researchers demonstrated critical current densities approaching 10^4 A/cm^2 at 77 K in self-field for Bi(2223)/silver tapes.

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