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**PRACTICAL SUPERCONDUCTOR DEVELOPMENT FOR ELECTRICAL
POWER APPLICATIONS**

ANNUAL REPORT FOR FY 1993

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PRACTICAL SUPERCONDUCTOR DEVELOPMENT FOR ELECTRICAL POWER APPLICATIONS

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Abstract

Development of useful high-critical-temperature superconductors requires synthesis of superconducting compounds; fabrication of wires, tapes, and films from these compounds; production of composite structures that incorporate stabilizers or insulators; and design and testing of efficient components. This report describes technical progress of research and development efforts aimed at producing superconducting components in the Y-Ba-Cu, (Bi,Pb)-Sr-Ca-Cu, (Tl,Pb,Bi)-(Ba,Sr)-Ca-Cu, and Hg-Ba-Ca-Cu-O oxide systems. Topics discussed are synthesis and heat treatment of high- T_c superconductors; formation of monolithic and composite wires, tapes, and coils; characterization of structures and superconducting and mechanical properties; fabrication and properties of films; and development of prototype components. Collaborations with industry and academia are documented.

1 Introduction

The superconductor program at Argonne National Laboratory (ANL) includes both bulk and film processing development directed toward improving the properties of high-critical-temperature (high- T_c) superconductors, developing processing methods for production of commercial conductors, and fabricating and testing prototype conductors. Team relationships with industrial and academic partners are integral to this program. The principal objective of the ANL program is to develop methods of fabricating and using structurally reliable high- T_c superconductors for the generation, transmission, and storage of electrical energy. Ceramic processing and joining techniques are being developed to provide useful conductors from one or several of the high- T_c superconductors. Work has focused on superconductors based on yttrium-barium-copper oxide (YBCO), bismuth-strontium-calcium-copper oxide (BSCCO), lead-doped bismuth-strontium-calcium-copper oxide (PBSCCO), pure and lead/bismuth/strontium-doped thallium-barium-calcium-copper oxide (TBCCO), and mercury-barium-calcium-copper oxide (HBCCO).

There are several requirements for monolithic and composite conductors in the form of wires, tapes, films, or other shapes. For most applications, the conductors must be capable of carrying high currents in the presence of high magnetic fields and must be strong, flexible, and chemically and cryogenically stable. Potential applications for such conductors include transmission lines, motors, generators, transformers, magnetic energy storage devices, and electronics (Wolsky et al., 1987). The principal impediments to the use of bulk high- T_c superconductors are low critical current density (J_c) in large applied magnetic fields, poor mechanical properties, and the need for long lengths with uniform properties. Processing methods for the improvement of all conductors have been and continue to be developed. The goals of ceramic fabrication include promoting high conductivity by obtaining phase-pure final materials and imparting favorable grain alignment, maximizing flux pinning through microstructural control, and increasing flexibility and reliability by minimizing microstructural flaws and optimizing the strength and toughness of each material.

This report reviews the technical progress and status of (1) synthesis and heat treatment of high- T_c superconductors; (2) forming of monolithic and composite wires, tapes, and thick films; (3) characterization of superconducting and electrical properties, microstructures, and mechanical properties; (4) fabrication of thin films and evaluations of fundamental properties; and (5) fabrication and testing of prototype superconducting devices. Interactions with industry and academia are also documented.

2 Technical Progress in 1992–1993

2.1 Synthesis and Heat Treatment

2.1.1 Y–Ba–Cu–O System

In previous periods, substantial effort was placed on synthesis of large batches of phase-pure orthorhombic YBCO powders from Y_2O_3 , $BaCO_3$, and CuO precursors. Reduced-pressure calcination at $\approx 800^\circ C$ was used to prepare the superconducting powders (Balachandran et al., 1992). Special care has been taken to keep the carbon content of the powder low. Carbon has an appreciable solubility in YBCO (Lindemer et al., 1990), and its presence can degrade superconducting properties.

Preparation of YBCO powders is a mature technology. YBCO sintering studies were also completed previously. Techniques were developed to produce strong, fine-grained compacts of high density in minimum time (Singh et al., 1992). Controlling O_2 partial pressure (pO_2) has proved to be essential, with faster sintering kinetics coming from reduced pressures (Chen et al., 1989).

The thermodynamic instability of YBCO at low pO_2 (Bormann and Nölting, 1989, Singh et al., 1992) was used recently to create very strong bulk YBCO wires that had adequate J_c values. In brief, plastically extruded wires were sintered in a pO_2 sufficiently low for the superconductor to partially decompose. The decomposition products, primarily $BaCuO_2$ and Cu_2O , formed as discrete solid particles on grain boundaries. They acted to pin boundary motion during sintering. Fine-grained products with densities greater than 90% of theoretical are the result. After sintering, annealing in pure O_2 at $\approx 800^\circ C$ caused the fine decomposition products to react to reform YBCO, and because the temperature was low, virtually no grain growth occurred. Annealing in O_2 produced wires with J_c values of 200–1000 A/cm² at 77 K. Average strengths were 230 MPa, which appears to be a record for YBCO (Goretta et al., 1993a).

2.1.2 Bi–Sr–Ca–Cu–O System

We routinely synthesize powder of the $Bi_2Sr_2CaCu_2O_x$ (Bi-2212) phase that is shown to be phase-pure by X-ray diffraction and differential thermal analysis (DTA). Low-pressure calcination is used to increase reaction kinetics and remove carbon, but higher-pressure O_2 is needed to form the desired Bi-2212 phase (Bloom et al., 1991). Most current work in this system is focused on $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Bi-2223), with $T_c \approx 110$ K.

A so-called two-powder process developed at ANL (Dorris et al., 1993) reproducibly yields powder-in-tube (PIT) specimens of highly pure Bi-2223. The resulting high purity and good reproducibility are expected to facilitate the fabrication of long lengths of superconductor with high J_c . In this process, $CaCuO_2$ and Pb-doped Bi-2212 ($Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{1.0}Cu_{2.0}O_8$) are made separately, then combined and reacted inside an Ag sheath. The Pb-doped Bi-2212 contains a small amount of Ca_2PbO_4 , and $CaCuO_2$ decomposes to $Ca_2CuO_3 + CuO$; thus, the two-powder process involves reaction among four phases: $Bi_{1.8}Pb_{0.4}Sr_{2.0}Ca_{1.0}Cu_{2.0}O_8$, Ca_2PbO_4 , Ca_2CuO_3 , and CuO . Some speculate that Ca_2PbO_4 is important to the formation of Bi-2223, because it participates in melting during heat treatment, which helps to enhance formation of Bi-2223 and heal damage done during mechanical processing (Wong-Ng et al., 1992; Huang et al., 1990; Y. Chen et al., 1992). However, if a large fraction of Pb is present as Ca_2PbO_4 , dissociation of Ca_2PbO_4 may control the formation of Bi-2223, so it is not clear that the presence of Ca_2PbO_4 is desirable.

To study the importance of Ca_2PbO_4 in the two-powder process, PIT processing was done on mixtures containing various amounts of Ca_2PbO_4 . Each mixture was made from the same four phases: Ca_2PbO_4 , Ca_2CuO_3 , CuO , and $Bi_{1.8}Pb_zSr_{2.0}Ca_{1.0}Cu_{2.0}O_8$, where z , the amount of Pb put into the Bi-2212 phase, ranged from 0.0 to 0.4. All mixtures had the

same overall composition, $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{2.0}\text{Ca}_{2.0}\text{Cu}_{3.0}\text{O}_{10}$, but differed in the amounts of the four phases. The amounts of the phases in each mixture are related by the reaction below and are summarized in Table 1.

For $z = 0.0$, all Pb was added as Ca_2PbO_4 ; for $z = 0.4$, all Pb was incorporated in the Bi-2212, as in the two-powder process described above. To study in a more general way how the method for introducing Pb affects Bi-2223 phase development, an additional mixture was made from Pb-free Bi-2212, Ca_2CuO_3 , and CuO; in this mixture, all Pb was added as PbO.

The phases $\text{Bi}_{1.8}\text{Pb}_z\text{Sr}_{2.0}\text{Ca}_{1.0}\text{Cu}_{2.0}\text{O}_8$, Ca_2PbO_4 , and Ca_2CuO_3 were prepared from Bi_2O_3 , PbO, SrCO_3 , CaCO_3 , and CuO for z values of 0.0, 0.1, 0.2, 0.3, and 0.4. The powders were calcined at reduced total pressure of $\approx 4 \times 10^2$ Pa O_2 ($20^\circ\text{C}/\text{h}$ to 750°C , followed by 6 h at 750°C) to ensure complete decomposition of the carbonate precursors. The desired phases were then formed by calcining for 24–48 h at 840°C in CO_2 -free air at ambient pressure. The powders were ball milled in isopropyl alcohol for ≈ 16 h and calcined again at 840°C in CO_2 -free air at ambient pressure. Calcinations were repeated with intermediate ball-milling steps until nearly single-phase materials were obtained. Total calcination times were 24 h for Ca_2PbO_4 , 48 h for Ca_2CuO_3 , and 96–126 h for $\text{Bi}_{1.8}\text{Pb}_z\text{Sr}_{2.0}\text{Ca}_{1.0}\text{Cu}_{2.0}\text{O}_8$.

The mixtures of Table 1 were made by combining appropriate amounts of each phase and ball milling in isopropyl alcohol for ≈ 16 h. They were then processed into tapes by the PIT method described in Dorris et al. (1993). Samples ≈ 4 cm long were cut from the tapes and heat treated for 50 h in 8% O_2 at 815°C , after which they were uniaxially cold pressed at ≈ 2 GPa to reduce thickness by $\approx 20\%$. Following pressing, the tape samples were annealed for an additional 100 h at 815°C in 8% O_2 . This process of pressing followed by annealing was repeated until cumulative heat-treatment times of up to 250 h had been reached. The 77-K J_c of each tape was measured after 50, 150, and 250 h of total heat treatment time.

Table 1. Molar amounts of Ca_2PbO_4 , Ca_2CuO_3 , and CuO mixed per mole of $\text{Bi}_{1.8}\text{Pb}_x\text{Sr}_{2.0}\text{Ca}_{1.0}\text{Cu}_{2.0}\text{O}_8$ in studying the role of Ca_2PbO_4 in the two-powder process

x	Ca_2PbO_4	Ca_2CuO_3	CuO	Comments
0.0	0.4	0.1	0.9	Pb-free Bi-2212
0.1	0.3	0.2	0.8	–
0.2	0.2	0.3	0.7	–
0.3	0.1	0.4	0.6	–
0.4	0.0 ^a	0.5	0.5	Two-powder process
0.0	0.0 (0.4 PbO)	0.5	0.5	Pb-free Bi-2212

^aA small amount of Ca_2PbO_4 is present in $\text{Bi}_{1.8}\text{Pb}_{0.4}\text{Sr}_{2.0}\text{Ca}_{1.0}\text{Cu}_{2.0}\text{O}_8$.

DTA results are shown in Fig. 1a for the $\text{Bi}_{1.8}\text{Pb}_z\text{Sr}_{2.0}\text{Ca}_{1.0}\text{Cu}_{2.0}\text{O}_8$ powders and in Fig. 1b for the mixtures of Table 1. The DTA traces for $\text{Bi}_{1.8}\text{Pb}_z\text{Sr}_{2.0}\text{Ca}_{1.0}\text{Cu}_{2.0}\text{O}_8$ powders consist of a single endotherm whose position decreases by $\approx 7^\circ\text{C}$ as the Pb content, z , increases from 0.0 to 0.4. It has been shown that the substitution of Pb also lowers the melting point of Bi-2223 (Oota et al., 1988), although the melting point of Bi-2223 depends more strongly on the Pb content.

The DTA traces for the mixtures consist of three endotherms; the highest-temperature endotherm is broad and shallow, extending from ≈ 910 – 970°C . This endotherm is positioned well above the normal processing range for Bi-2223 tapes and is thought to result from a reaction involving the cuprate phase and perhaps copper oxide. A second endotherm appears at 877°C , and like the first endotherm, is independent of the mixture composition in terms of size and position. By contrast, the size of the third endotherm depends markedly on composition; the position of the endotherm also depends on composition, but to a smaller degree, decreasing from 850°C for $z = 0.4$ to 846°C for $z = 0.0$.

The third endotherm shrinks noticeably as z increases from 0.0 to 0.4, i.e., as the mixture changes from one in which all Pb is present as Ca_2PbO_4 to a mixture in which essentially all Pb is incorporated in the Bi-2212. (Although no Ca_2PbO_4 is deliberately added to the $z = 0.4$ composition, a small amount is present as a second phase, possibly because the solubility limit for Pb is less than 0.4 (Boekholt et al., 1991). As a result, the $z = 0.3$ and 0.4 mixtures contain nearly the same amount of Ca_2PbO_4 , as confirmed by X-ray analysis. The apparent correlation between the size of the low-temperature endotherm and the amount of Ca_2PbO_4 in the mixture strongly suggests that Ca_2PbO_4 is involved in partial melting at these low temperatures.

Figure 2 compares J_c for tapes made from the different mixtures after total heat-treatment times of 50, 150, and 250 h at 815°C in 8% O_2 . For each heat-treatment time, J_c increases as the amount of Pb incorporated in the Bi-2212 phase increases. After 250 h total heat-treatment time, J_c for $z = 0.4$ is approximately twice that for $z = 0.0$, whether the Pb is added to the $z = 0.0$ composition as PbO or as Ca_2PbO_4 . Incorporation of Pb in the Bi-2212 clearly yields properties superior to those obtained when Pb is added as either PbO or Ca_2PbO_4 .

Photomicrographs taken at the University of Wisconsin-Madison Applied Superconductivity Center (Figs. 3a-3d) show that Bi-2223 phase development varied significantly with mixture composition. Figures 3a and 3d represent $z = 0.0$ composition of Bi-2212; Pb was added as Ca_2PbO_4 in Fig. 3a, but was added as PbO in Fig. 3d. From Fig. 3a to Fig. 3c, increasingly more Pb was added to the Bi-2212 and less Pb was added as Ca_2PbO_4 .

Fig. 1. DTA traces for (a) $\text{Bi}_{1.8}\text{Pb}_z\text{Sr}_{2.0}\text{Ca}_{1.0}\text{Cu}_{2.0}\text{O}_8$ for $0.0 \leq z \leq 0.4$ and (b) mixtures described in Table 1. PbO is present only where noted. In all other mixtures, lead is present either as Ca_2PbO_4 or in the Bi-2212 .

Fig. 2. J_c as a function of Bi-2212 lead content, z , after total heat-treatment times of 50, 150, and 250 h in 8% O_2 at 815°C

Fig. 3. Backscatter electron images of samples heated for 250 h in 8% O_2 at 815°C: (a) $z = 0.0$, $Ca_2PbO_4 = 0.4$; (b) $z = 0.2$, $Ca_2PbO_4 = 0.2$; (c) $z = 0.4$, $Ca_2PbO_4 = 0.0$; (d) $z = 0.0$, $Ca_2PbO_4 = 0.0$, $PbO = 0.4$

Adjacent to the Ag sheath along the edges of each core, several distinct phases are evident in varying amounts. The black, blocky phases and the light-gray needles were identified by energy-dispersive analysis of X-rays (EDAX) as alkaline earth cuprates and Bi-2212, respectively. The dark-gray major phase was identified as Bi-2223. As Pb content in the Bi-2212 phase increased, the amounts of both Bi-2212 and alkaline earth cuprates decreased. For $z = 0.0$, Pb was added as either Ca_2PbO_4 (Fig. 3a) or PbO (Fig. 3d). When Pb was added as Ca_2PbO_4 , both Bi-2212 and alkaline earth cuprates were abundant, with the grain sizes of the alkaline earth cuprates being $\approx 5\text{--}10\text{ }\mu\text{m}$. When Pb was added as PbO, alkaline earth cuprate grains were larger ($10\text{--}25\text{ }\mu\text{m}$) and more abundant, whereas Bi-2212 grains were very fine and sparse. When all Pb was put into the Bi-2212, the second phases were small in size ($<5\text{ }\mu\text{m}$) and concentration; however, in some regions a Bi-rich phase was evident.

These results are reasonable because of the well-known importance of Pb in stabilizing the Bi-2223 phase (Takano et al., 1989; Dou et al., 1989; Pierre et al., 1990). Appreciable concentrations of Bi-2223 do not form in the absence of Pb. In mixtures containing Pb-free Bi-2212, where Pb is added as either PbO or Ca_2PbO_4 , Pb must diffuse into the structure before or during formation of Bi-2223. When Ca_2PbO_4 is the source of Pb, its dissociation is an additional necessary step. These steps are eliminated by incorporating Pb in the Bi-2212 prior to heat treatment. Because Bi-2223 formation competes with the coarsening of Bi-2212, cuprates, and CuO during heat treatment, the elimination of additional, possibly rate-determining steps may be important. By incorporating Pb in the Bi-2212, Bi-2223 formation is made more favorable relative to coarsening of the precursor phases.

2.1.3 Tl-Ba-Ca-Cu-O System

Small batches of high-quality $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Tl-1223) powder are required for conductor work (Kim et al., 1991; Poeppel et al., 1991). Three compositions are now under examination: $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (1223), $\text{Tl}_{0.5}\text{Bi}_{0.5}\text{Ba}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_x$ (Bi-doped 1223), and $\text{Tl}_{0.5}\text{Pb}_{0.5}\text{Ba}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_x$ (Pb-doped 1223). The Bi-doped compound is easiest to synthesize in nearly phase-pure form (Goretta et al., 1992; Ren and Wang, 1993). The Pb-doped compound has a shorter c axis and appears to have better inherent flux pinning than the undoped compound (Kim et al., 1991).

Work on synthesis of the Pb-doped 1223 compound continues in collaboration with staff members of Los Alamos and Sandia National Laboratories. Because Ba and Pb have a strong tendency to form a stable BaPbO_3 compound, the staff at SNL have synthesized by coprecipitation a precursor that contains all of the non-Tl constituents. Also, because the cations are distributed on a very fine scale, subsequent heat treatment promotes formation of complex oxides at the expense of BaPbO_3 . The doped 1223 powders to date are $\approx 90\%$ pure, have T_c values up to 117 K, and have been incorporated into Ag-clad tapes.

The Bi-doped compound is being developed in conjunction with the State University of New York at Buffalo. This compound has the advantages of minimal Ba content and ease of formation. Disadvantages are a somewhat lower T_c of $\approx 107\text{ K}$ and a melting point higher than that of pure 1223. Coprocessing with Ag is, however, not a problem because in air this compound is stable and its melting point is below that of Ag (Ren and Wang, 1993). The first Ag-clad tapes fabricated from Bi-doped 1223 had J_c values superior to those made from pure 1223.

Many possible dopants will be of use in Tl-1223. Reduction of the c-axis length and increased conductivity along the c-axis are two current goals. We have begun with Prof. Z. Z. Sheng of the University of Arkansas to explore use of novel compositions of Tl-1212 and Tl-1223. Among the dopants now under study are Bi, Nd, V, and Cr (Z. Y. Chen et al., 1993). Identification of the most promising alloys is expected by mid-1994.

2.2 Bulk Conductor Production

2.2.1 Monolithic Conductors

Wires, Rods, and Bars

Plastic extrusion can yield long lengths of high- T_c superconductors that may be used in low-field, low- J_c applications such as current leads (Poeppele et al., 1991; Wu et al., 1991). Cold isostatic pressing of YBCO has also been used recently. YBCO rods 1 m long and 10 mm in diameter have been fabricated. Because this process requires relatively little addition of organic material, heat treatments are simpler and more reliable. A minimum performance criterion of 50 A/rod in a 40 G ambient magnetic field was adopted, and a set of rods was produced for a current-lead assembly. This assembly functioned successfully at 1000 A of continuous current.

Because of its T_c of 110 K, Bi-2223 may be superior to YBCO at 77 K. Monoliths 1 m long have been made by cold isostatic pressing. J_c values in zero applied field have reached 1.6×10^3 A/cm². Hot deformation in air at 845°C has produced bars with J_c values to 8×10^3 A/cm² (N. Chen et al., 1993). For both, critical current (I_c) has exceeded 200 A. The hot-deformation process is now being scaled up to produce lengths to 20 cm.

Pellets

Work has continued on low-temperature melt-growth processing to fabricate thick pellets for flywheel applications. Low-temperature processing was made possible by addition of submicrometer-sized Y₂BaCuO₅ (211) particles to YBCO powder before melt processing. The YBCO pellets fabricated by this technique are used in prototype flywheel units (Weinberger et al., 1991).

Fine 211 precipitates in a YBCO matrix increase flux pinning (Murakami et al., 1989; Shi et al., 1989; Sengupta et al., 1992) and hence levitation forces. We have worked to optimize pinning through controlled additions and to improve levitation by enhanced grain growth and texture via SmBa₂Cu₃O_x crystal seeds. These seeds do not melt at the processing temperature and promote favorable nucleation and growth of YBCO upon cooling from the partially molten state. Levitation forces in liquid N₂ have reached 84 Pa.

2.2.2 Composite Conductors

Processing high-temperature superconductors in Ag tubes has resulted in several reports of J_c values greater than 10^4 A/cm² at 77 K and greater than 10^5 A/cm² at 4.2 K (Jin and Graebner, 1991). Advantages of PIT processing include obtaining high green densities, which obviate use of high sintering temperatures; protection of the superconductor from atmospheric exposure; and possible stabilization of the superconductor by the metallic sheath. Ag or Ag alloys are used as the sheath because of their chemical compatibilities with high- T_c superconductors (Meyer et al., 1989).

Wires and Tapes

At ANL, research has included swaging, drawing, pressing, cold-rolling, and hot-rolling operations and tape casting (Poeppel et al., 1991 and 1992). Recent efforts have focused on three compounds: Bi-2212, for high-field, low-temperature applications; Bi-2223, for moderate-field, high-temperature or high-field, moderate-temperature applications; and Tl-1223 for high-field, high-temperature applications.

Ag-clad Bi-2212 tapes continue to be fabricated by drawing and cold rolling (Wu et al., 1993). The highest transport J_c at 4.2 K has reached 1.5×10^5 A/cm². This result, a slight improvement over previous results, was obtained through greater total reduction of the core during rolling. Recent efforts in collaboration with Prof. J. Schwartz have focused on warm and hot rolling of Bi-2212 (Guo et al., 1993). Initial results indicate that, because of the high hardness of all nonsuperconducting phases in the Bi-Sr-Ca-Cu-O system, the superconductor core must be highly phase-pure to produce good final microstructures. In addition, transport J_c values increase with rolling temperature. Work is underway to modify the rolling mill so that temperatures greater than 450°C can be reached.

We have fabricated Ag-clad Bi-2223 tapes from multiphase powders that reactively sinter in-situ to form Bi-2223. The kinetics of Bi-2223 phase formation and its relationship to microstructure and electrical properties were studied previously (Koyama et al., 1988; Kaufman et al., 1993). Recent work has focused on improved final microstructures (Dorris et al., 1993) and fabrication of longer lengths and prototype coils.

The presence of a liquid phase during PIT processing of Bi-2223 is thought to be critical. It may enhance the kinetics of formation for Bi-2223 (Hatano et al., 1988; Aota et al., 1989; Tsuchiya et al., 1989; Oh and Osamura, 1991), facilitate grain growth and alignment, and heal damage by mechanical processing (Yamada et al., 1991). For example, Aota et al. (1989) reported that Bi-2212 undergoes partial melting during formation of Bi-2223 and that its partial-melting temperature can be lowered by decreasing pO_2 in the processing atmosphere. Tsuchiya et al. (1989) found that Bi-2223 can be produced if the melting point of Bi-2212 is lower than that of Bi-2223; they claim that the use of Ca-rich Bi-2212 enhances formation of Bi-2223. Phase evolution and microstructural development of Ag/Bi-2223 wires produced by the two-powder method continue to be investigated in the core program.

In the most recent study, three wires (B-13, T-13, and B-17) were the main focus. All three wires were prepared from a blend composed of Pb-doped Bi-2212 + Ca_2CuO_3 + CuO, with the nominal stoichiometry $Bi_{1.8}Pb_{0.4}Ca_{2.0}Cu_{3.0}O_x$. The principal difference between the three wires was that the B-13 and T-13 powder constituents were prepared at ANL, whereas the B-17 constituents were purchased from Seattle Specialty Ceramics, Inc. (SSC) of Bothell, WA. The kinetics of Bi-2223 phase evolution was studied between 790 and 855°C in 7.5% O_2 for equilibration times of 10 to 5400 min. Because only a limited amount of B-13 was fabricated, the most extensive studies were carried out on T-13 and B-17.

The optimal processing temperatures for B-13, T-13, and B-17 were 815, 815, and 820–825°C, respectively, based on rate of conversion, second-phase particle-size control, and absence of Bi-2201 in the final product. Conversion of the powder to Bi-2223 in the as-rolled wires approached 100% in times of several thousand minutes. In a series of equilibrations carried out for 1500 min, there was very little conversion at temperatures below 810°C. The second phases (determined by SEM and EDAX) were predominantly

(Ca,Sr)₂CuO₃ and CuO at temperatures below 840°C. The B-17 wire contained detectable quantities of (Ca,Sr)₁₄Ca₂₄O₄₁ (14/24) at all temperatures (the amount generally increasing with temperature), whereas B-13 and T-13 showed very little evidence of the normally deleterious 14/24 phase. T-13 showed some Sr-rich phases that were generally not seen in B-17.

The results of a series of 1500-min equilibrations on B-13 and B-17 are shown in Fig. 4. Although B-17 appears to react more slowly than B-13 up to the 1500-min point, it also showed 100% conversion to Bi-2223 when equilibration time was extended to 4000 min. The similarity in the shapes and positions of the two sets of data in Fig. 4 may be attributed to the fact that the powder stoichiometry, phase chemistry, and PIT processing parameters were essentially identical. The slight difference in overall reaction time to achieve 100% conversion to Bi-2223 may be attributed to differences in powder properties (ANL-prepared in one case and SSC-prepared in the other).

Figure 5 shows an Arrhenius plot of the initial eight data points for B-17 given in Fig. 4. The ordinate in this plot is derived by the Avrami-Erofe'ev formalism for analyzing phase transformation kinetics (Luo et al., 1993a and 1993b). The break in the activation plot near 818°C has been observed for other similarly prepared Bi-2223 wires (Carter et al., 1993; Luo et al., 1993b) and is believed to be due to a transition from an all-solid-state reaction process occurring below 818°C to a liquid-phase-controlled process in the 818-to-835°C range. The sharp decrease in reaction rate above 835°F (see Fig. 4) is a consequence of crossing the Bi-2223 stability line and entering the temperature domain in which Bi-2223 undergoes decomposition to Bi-2201, Bi-Bi-2212, (Ca,Sr)₁₄Ca₂₄O₄₁, and other phases, such as (Ca,Sr)CuO₂ and (Ca,Sr)₂CuO₃ (Luo et al., 1992).

For temperatures ≥840°C, the conversion of Bi-2212 to Bi-2223 decreased. Bi-2201 and (Ca,Sr)CuO₂ were the major second-phase compounds, with B-17 also showing increased amounts of 14/24. Typical second-phase particle sizes ranged from 1–3 μm for B-13 and T-13 samples processed at ≥840°C, and 5–10 μm for B-17. Scanning electron micrographs also gave evidence of partial melting at processing temperatures ≥840°C for both wires. At higher temperatures (≥850°C), the alkaline earth cuprate (AEC) second phases in B-13 and T-13 were elongated rectangular crystals that appeared to be growing from a molten phase. For B-17 samples, the AEC second phases were found to have an aspect ratio close to unity, and the area fraction of second phases was always larger in B-17 than in similarly treated T-13 samples.

The results for B-13, T-13, and B-17 to date show that two-powder Ag/Bi-2223 wires can exhibit substantial differences in phase evolution and microstructural properties, even when there are small differences in the powder preparation method. In the case of B-13, T-13, and B-17, we are examining (1) the details of the powder preparation procedures employed by ANL and SSC, (2) the characteristics of the two as-prepared powders, and (3) the wire fabrication procedure used at ANL. Additional research is in progress to connect differences in these details with the differences in phase evolution and microstructural properties of the processed wires discussed above.

A study has been made of the effect of post-annealing on the critical temperature, T_c , exhibited by Ag/Bi-2223 wires in which the conversion to Bi-2223 was close to 100% prior to the annealing. A 5-cm length of an Ag/Bi-2223 wire prepared by the single-powder method was equilibrated at 825°C in 7.5% O₂ for 400 h. X-ray diffraction on a peeled specimen showed essentially complete conversion to Bi-2223. Other specimens

Fig. 4. Percent conversion to Bi-2223 as a function of heat-treatment temperature

Fig. 5. Activation energy plot for conversion to Bi-2223

were subjected to post-annealing at 450°C for 1000 min in a series of pO_2 levels ranging from ≈ 0 to 100%. The results (Fig. 6) indicated that the maximum T_c (≈ 109 K) occurred at a pO_2 of 7.5%. The results also confirm that even Ag-sheathed Bi-2223 decomposes rapidly in very low pO_2 , and that atmospheric-pressure O_2 was not optimal for post-annealing of Ag/Bi-2223 wires.

Fig. 6. T_c versus annealing atmosphere at 450°C

A study of Pb loss in Ag/Bi-2223 wires has been completed. In this study, 2-cm-long specimens of a single-powder wire were subjected to extended heat treatment at 825°C in 7.5% O₂. One series of specimens was treated in the as-rolled condition, while in a second series each specimen was peeled open to expose the core during treatment. Specimens from each series were equilibrated for various lengths of time and examined by X-ray diffraction. The series of as-rolled specimens exhibited a normal conversion-versus-time profile (see Fig. 7), with complete conversion reached after about 2000 min and no evidence of Bi-2223 decomposition for times out to ≈30,000 min. Peeled specimens never achieved more than 50% conversion to Bi-2223 (see Fig. 7), even for heat-treatment times as long as 20,000 min. These results indicate that fully sheathed Bi-2223 powders are apparently stable to prolonged heat treatment, provided that the temperature and pO₂ are in the range where Pb-doped Bi-2223 is the stable phase. The lower conversion and erratic behavior during extended heat treatment of the peeled specimens are attributed to Pb loss from the exposed powder. Conversely, the Ag sheath surrounding Ag/Bi-2223 wires appears to be an effective barrier to Pb loss.

Electromotive force (EMF) measurements are underway to determine oxygen fugacity as a function of oxygen stoichiometry and temperature in the Pb-doped Bi-2223 system. A coulometric titration technique employing an yttria-doped ZrO₂ electrolyte is being used to investigate the thermodynamic behavior of the Bi-2223 system as a function of pO₂, oxygen stoichiometry, and temperature. There are very little data concerning (1) the dependence of pO₂ and temperature on the behavior of the Bi-2223 and Bi-2212 systems, and (2) the effect of oxygen stoichiometry variation on phase relationships and stability in these systems. Such data could prove useful in determining optimal processing conditions for producing Ag/Bi-2223 wires capable of carrying high critical currents. Measurements on a Bi-2223 powder sample prepared at ANL have been completed and work is in

Fig. 7. Percent conversion to Bi-2223 as a function of time for closed and open tapes

progress on a Bi-2223 powder sample received from Ames Laboratory. X-ray diffraction analysis of the as-received Ames sample showed only single-phase Bi-2223, whereas the ANL sample appeared to be a mixture of Bi-2212 and Bi-2223.

The results of EMF measurements at 815°C are shown in Fig. 8, where calculated oxygen partial pressures are plotted as a function of x in $(\text{Bi,Pb})_2\text{Sr}_2\text{Cu}_2\text{Cu}_3\text{O}_x$. It is seen that the shapes of the isotherms are similar for both the Ames and ANL samples, i.e., large changes in $p\text{O}_2$ occur as x approaches the lower plateau region ($p\text{O}_2 \approx 0.3\%$). Thermodynamic assessments of the partial molar quantities indicate that the lower plateau region is close to that of the diphasic $\text{CuO-Cu}_2\text{O}$ system. It is also noteworthy that the $p\text{O}_2$ measurements as functions of x were reversible in the single-phase region, but irreversible in the lower plateau region (i.e., plateau back to single-phase region). The results of our studies to date indicate that processing or annealing Pb-doped Bi-2223 at 750–815°C and at $p\text{O}_2$ ranging from ≈ 2 –20% should tend to preserve Bi-2223 as essentially single-phase material.

In addition to phase development, we also examined the effects of thermomechanical treatment and Ag additions on Ag-sheathed Bi-2223 tapes made by a PIT technique. The process included packing Ag tubes with superconductor powder, followed by swaging, drawing, and rolling to form thin tapes. Subsequently, the tapes were subjected to repeated thermomechanical treatment of pressing (at ≈ 1000 MPa for 5 s) and sintering (835°C in a 10% flowing oxygen atmosphere for 50 h) to enhance texture and J_c .

Figure 9 shows the variation of J_c with number of thermomechanical cycles. The variations at 77 K and 4.2 K with number of thermomechanical cycles are similar. J_c increases with increasing number of thermomechanical cycles and reaches a peak value in

Fig. 8. $\log p_{O_2}$ versus oxygen coefficient, x , in $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ for powders prepared at ANL and Ames Laboratory

the tapes after the fifth pressing and sixth sintering (at 4.2 K, J_c increases from 31,000 to 124,000 A/cm²). This increase with thermomechanical cycle is believed to be due to (1) increase in grain size and alignment, (2) increase in Bi-2223 phase fraction, and (3) possibly improved density of the superconducting core (Joo et al., 1993). X-ray diffraction analysis and SEM confirm these suggestions.

Further thermomechanical treatment (sixth pressing and seventh sintering) results in a corresponding decrease in J_c . This decrease may be related to the formation of defects such as an irregular interface between superconducting core and Ag sheath. In addition, the decrease in J_c may also be partly due to reduced presence of a liquid phase (after a large number of thermomechanical cycles); the liquid helps to heal microcracks/cracks induced during mechanical treatment (Hellstrom, 1993; Flükiger et al., 1991).

Fig. 9. Dependence of J_c on number of thermomechanical cycles for Ag-sheathed Bi-2223 tapes

Effects of Ag additions on the Bi-2223 core in Ag-sheathed tapes and on superconducting properties were also evaluated. Ag-sheathed tapes with 15 and 25 vol.% particulate Ag additions were subjected to thermomechanical treatments as discussed before. Dependence of J_c on Ag content and number of thermomechanical cycles is shown in Fig. 10, which indicates that the J_c variation of the Ag-sheathed Bi-2223/Ag composite tapes is quite similar to that of the monolithic Ag-sheathed tapes. However, the measured value of J_c for the Bi-2223/15 vol.% Ag composite tapes is slightly higher than that of the monolithic Bi-2223 tapes. As proposed by Singh et al. (1993b), a slightly higher J_c for Bi-2223/15 vol.% Ag composite tapes is due to (1) slightly better texturing and increased Bi-2223 phase content, (2) improved grain connectivity, and (3) higher density. These improvements are believed to be due to enhanced diffusional kinetics that result from the lowering of the melting temperature of the Bi-2223/15 vol.% Ag composite core by Ag additions (Singh et al., 1989 and 1993a; Joo et al., 1993). However, higher Ag contents (25 vol.%) in Bi-2223/Ag composite tapes results in a decrease in J_c , probably because of a relatively large reduction in the volume fraction of superconducting phase. The addition of 15 vol.% Ag appears to be optimal for maintaining high J_c .

To evaluate the effects of Ag powder morphology in Bi-2223/Ag core, tapes were processed with addition of Ag flakes. The resulting J_c variation was similar to that in composites with equiaxed Ag particles. However, the highest J_c obtained for Bi-2223/Ag (flake) tapes was $\approx 30\%$ higher than that obtained for Bi-2223/Ag (particle) tapes. X-ray diffraction analysis indicated that the relative content of Bi-2223 was similar in both types of tape. The degree of texturing was higher in the tapes with Ag flakes than in the tapes with equiaxed Ag particles. It is believed that the two-dimensional morphology of the flakes helps to orient the Bi-2223 grains, resulting in improved J_c (Singh et al., 1993b). In addition, as reported previously (Poeppel et al., 1992), Ag particles significantly improve the strain tolerance of Ag-sheathed tapes.

Fig. 10. Variation of J_c with number of thermomechanical cycles for Ag-sheathed Bi-2223 tapes with various Ag contents

The Bi-2223 Bi-Sr-Ca-Cu-O superconductor also forms the basis of a joint program between ANL and Intermagnetics General Corporation (IGC). The goal of this program is to produce long uniform lengths of high-quality composite conductors exhibiting excellent mechanical and physical properties for commercial operation at or above 35 K in applied fields up to 2 T. The initial focus of the program was to extend PIT processing to yield conductors with practical levels of current densities in lengths up to 10 m. The current focus is on developing manufacturing technology for conductor lengths >100 m for incorporation into large-scale energy-related applications. This research encompasses all phases of conductor fabrication from powder synthesis to wire/tape forming by the powder-in-tube technique to identification of heat-treatment conditions in order to optimize superconducting properties.

Substantial progress has been made in fabricating long lengths of flexible Ag-clad Bi-2223 tapes by the PIT method. Tapes with high J_c that are attractive for electrical-power and high-field magnet applications have been produced. The multiphase precursor powders used in our PIT processing are prepared from Bi_2O_3 , PbO , SrCO_3 , CaCO_3 , and CuO by calcining at 800–850°C for ≈ 50 h (Balachandran et al., 1988). For some of the best results, the Bi:Pb:Sr:Ca:Cu ratio was 1.8:0.4:2:2.2:3. Several other variants from the stoichiometric composition have also been used with appropriate heat treatments. The partially reacted precursor powders were packed by mechanical agitation into Ag tubes. The packed tubes were lightly swaged, drawn through a series of dies, and then rolled to a final thickness of ≈ 0.1 mm. Tapes of ≈ 100 m long have been produced by this technique.

Short lengths of tapes were cut and heat treated at 830 to 860°C in air with intermittent uniaxial pressing. High J_c values in short tapes have been achieved by the combination of uniaxial pressing and heat treatments. Although the combination of uniaxial

pressing and heat-treatment cycles induced uniform orientation and densification by providing homogeneous compression, this procedure is not amenable to fabrication of long lengths of tape. To fabricate long-length tapes successfully, a practical approach such as rolling, without uniaxial pressing, is needed. Using a two-step rolling with an intermediate and final heat treatment, we have processed Ag-clad Bi-2223 tapes that are more than 30 m long and ≈ 0.1 mm thick. These long conductors carried a critical current of 16 A at 77 K in self-field (corresponding to $J_c > 10^4$ A/cm²).

Shown in Fig. 11 are J_c values of short samples as a function of applied field at 77 K and, in pumped liquid N₂, at 64 K. These measurements were made at Brookhaven National Laboratory by M. Suenaga. There is a considerable increase in J_c (≈ 4 kA/cm²) in a field of 1 T (H//c) at 64 K compared to the values at 77 K. J_c values as high as 20 kA/cm² were achieved at 64 K in a field of 1 T applied parallel to the a-b plane. These results show that practical devices can be made with Bi-2223 tapes operated at temperatures obtainable by pumping liquid N₂ (Balachandran et al., 1993).

Although the Bi-2223 tapes do not exhibit high J_c in high applied fields at 77 K, at lower temperatures (<40 K), they outperform the NbTi and Nb₃Sn superconductors in very high fields (≥ 15 T). Figure 12 shows J_c measurements taken at liquid helium (4.2 K) and liquid neon (27 K) temperatures in applied magnetic fields up to 20 T. These tests were performed at the Francis Bitter National Magnet Laboratory at the Massachusetts Institute of Technology by Y. Iwasa. The J_c data were taken for short, pressed-and-heat-treated tapes with the field applied parallel (H//ab) to the flat direction of the tape and also in the perpendicular (H//c) direction. At 4.2 K, field-independent behavior is observed for both directions in applied fields up to 20 T; this is consistent with previously reported results (Sato, 1991). At 27 K, however, we report for the first time that applied fields in the perpendicular direction tend to drive the conductor to the normal state in fields > 15 T. As seen in Fig. 12, the samples carry $\approx 10^5$ A/cm² in low fields at 4.2 and 27 K. At 40 K and above, the J_c dropped drastically when magnetic fields were applied in the perpendicular direction.

Long lengths of rolled Bi-2223 conductors were tested by winding them into pancake coils. One to six tapes were cowound in parallel on Al₂O₃ formers with ceramic insulation (used to separate each turn) and heat treated by the wind-and-react approach. The J_c of coils containing one and two 1-m lengths of conductors approached 10^4 A/cm² at 77 K in self-field and exceeded 10^4 A/cm² at 4.2 K in fields up to 13 T. The J_c values of the coils are ≈ 60 –80% of the short, rolled sample results at 77 K. The difference in J_c values is probably due to inhomogeneities and microcracks along certain regions of the tapes. Moreover, the coils are subjected to large self-fields during testing, whereas the short linear tapes do not generate much self-field.

Figure 13 shows an example of a wind-and-react pancake coil that was wound from three lengths of 10-m-long conductor tapes onto a 2.5-cm-diameter mandrel, resulting in a coil with 7.65 cm outside diameter. The total number of turns in this coil is 57. With a 1- μ V/cm criterion, the critical current for this coil was determined to be ≈ 22 A at 77 K and ≈ 280 A at 4.2 K. The coil exhibited ≈ 1250 ampere-turns at 77 K and $\approx 16,000$ ampere-turns at 4.2 K. The generated fields were 33 mT (77 K) and 420 mT (4.2 K). We fabricated six such pancake coils, each containing three 8.5-m lengths of rolled Bi-2223 tapes (Haldar et al., 1993). These six pancake coils were stacked together, connected in series, and tested at 4.2 and 27 K as a function of applied magnetic fields up to 14.5 T. The total length of rolled conductor tapes in this stack of coils was 153 m.

Fig. 11. J_c versus applied magnetic field for short lengths tested at 77 and 64 K

Fig. 12.
 J_c versus applied magnetic field for short lengths at 4.2 and 27 K

Fig 13
Pancake coil couvound with three 10 m
lengths of Bi 2223 tape

Figure 14 presents plots of the central field generated by the test magnet versus background field at 4.2 K and 27 K. Because each pancake coil performed differently, data corresponding to the minimum and maximum critical currents are plotted. The maximum corresponds to the highest critical current of the assembly, while the minimum represents the coil with the lowest critical current. The magnet generated a maximum field of 1.03 T at 4.2 K in zero background field and 0.61 T in a background field of 14.5 T. At 27 K, these values correspond to 0.76 and 0.42 T, respectively. At 4.2 K, the stack carried a maximum critical current of 170 A and a minimum of 118 A in self field, and 100 A (maximum) and 60 A (minimum), in a field of 14.5 T. At 27 K, the maximum and minimum critical currents were 125 A and 78 A in zero applied field and 69 A and 42 A in an applied field of 14.5 T. Recently, we assembled a test magnet containing 10 pancake coils, each coil contains five 9.5 m long tapes. The total length of tape in this test magnet was 475 m. This magnet generated a maximum field of 1.65 T and a minimum of 1.30 T at 4.2 K. At 77 K, the maximum and minimum fields were 0.25 T and 0.17 T, respectively. These results indicate that high T_c materials are promising for high field magnets and electric power devices operating below 30 K; operation above 4.2 K could improve refrigeration efficiency and reliability substantially.

Work on Ag clad Tl 1223 tapes has expanded and has been integrated with thick film work on Tl 1223. It is discussed in Section 2.5 of this report.

2.3 Properties of Bulk High- T_c Superconductors

2.3.1 Characterization Methods

Ceramic superconductor samples produced in ANL projects are characterized to help guide improvement of the chemical formulations and the forming and processing procedures. High T_c products fabricated for application by others also are characterized to evaluate product performance. The property of primary interest is the DC transport

Fig. 14. Maximum and minimum values of test magnet center field versus background field at 4.2 and 27 K

critical current (I_c) of the sample, measured as a function of the intensity of an applied magnetic field. Selected samples are tested to determine T_c , AC resistance, strength of the diamagnetic response, remanent field strength, magnetic shielding performance, presence of structural defects or changes in structural properties, or mechanical properties.

2.3.2 Electrical Characterization of Superconductors

DC Characterization

Critical current tests have continued at an average rate of 128 new samples each month. Substantial differences among batches of bulk material or formed products necessitated continual screening. The standard four-point resistance method was used with a $1\text{-}\mu\text{V}/\text{cm}$ criterion. Sample types consisted primarily of BSCCO-Ag tapes under development for magnetic coil applications and YBCO-Ag or BSCCO bars and rods for use in current leads. Results are discussed below and elsewhere in this report.

Major advances in the performance of individual superconductors at high currents during this reporting period were supported by the 1000-A pulsed current facility described in the previous annual report (Poeppl et al., 1992). Prior to recent developments, the I_c values in single bars or rods at 77 K were about 200 A or less and typically fell 30% or more in ambient magnetic fields near 50 G. Much higher I_c values at that sample temperature have now been observed with BSCCO rods and bars made by melt-casting, multistage isostatic pressing, or sinter forging; e.g., a 13-mm-diam, 75-mm-long, melt-cast BSCCO rod displayed an I_c of more than 700 A, together with a much reduced sensitivity to applied magnetic fields of intensities typical of those in current-lead service.

The validity of results obtained with 0.2-s square-wave current pulses was shown by comparison with results of continuous DC tests. An assembly of 1-m-long YBCO-Ag rods connected in parallel for a 1000-A transport-current demonstration had been successfully produced by ANL and evaluated by pulse testing. The assembly was retested with DC to determine whether the assembly's performance would become degraded by, for example, a slowly propagating heating effect. A 1000-A DC facility was made available by Superconductivity, Inc. (Middleton, WI). The pulse test results were confirmed, and no degradation was evident with DC applied for up to 45 min. Temperature was 77 K for both tests.

AC-Loss Apparatus Upgrade and Results

A low resistance to AC flow is displayed by high- T_c superconductors, even at currents well below the DC critical current, as reported previously. This resistance is associated with the magnetic hysteresis of the material. As found here earlier, the energy loss per cycle of current is rather independent of the AC frequency up to at least 400 Hz. In tests of selected 1-mm-diameter YBCO wires, AC dissipation was equal to that produced by DC at the 1- μ V/cm critical level when a 50-Hz test current was 67-80% of the DC critical value.

In more recent work, AC power loss in superconductors was studied in collaboration with Prof. M. Marinelli of the University of Genoa, Italy. Magnetic hysteresis measurements were made in polycrystalline nontextured YBCO and YBCO-Ag produced by ANL; results were found to correlate well with those of AC transport current tests and to support the previous findings. A theoretical analysis was developed through use of a phenomenological critical-state model with two phases that accounted quantitatively very well for the results of the two kinds of measurements. The model suggests that AC loss may be reduced if superconductor diameter is reduced and the reduction is compensated by the use of several parallel superconductors.

Recently, the effect of diameter was tested as the study was extended to melt-cast Bi-2212 rods at 77 K. Two samples obtained from Hoechst-Celanese were used. Initial results are shown in Figs. 15 and 16. The required derating factor for the use of AC increased with diameter, as expected, for power loss equivalent to that of DC at the critical level. Further, a comparison of the Figs. 15 and 16 shows that a given AC transport current can be more efficiently transported by a parallel array of small-diameter rods than by a large-diameter conductor. Finally, the losses in the Bi-2212 tested were sufficiently small for practical use of the material in applications such as AC downlinks operated at power-line frequencies.

Other Electrical and Magnetic Studies

Dissipation induced by DC currents at values near and above I_c is being studied in a Kalamazoo College/ANL collaboration. Empirical knowledge of correlations between composition, microstructure, and observed types of dissipation is useful for the engineering of devices that can withstand quenching and for the design of current limiters that depend on a sharp transition from superconductive to dissipative properties as current is increased.

The dissipation behavior of sintered YBCO differs greatly from that of melt-textured YBCO. The data in Figs. 17 and 18 (Askew et al., 1993) illustrate the striking differences possible with different microstructures.

Fig. 15. Energy loss per cycle for unit length of a 13.1-mm-diameter, melt-cast Bi-2212 rod at 77 K, versus current at two frequencies; DC I_c was 715 A

Fig. 16. Energy loss per cycle for unit length of a 7.75-mm-diameter, melt-cast Bi-2212 rod at 77 K, versus current at three frequencies; DC I_c was 330 A

Fig. 17. Dissipation in randomly oriented YBCO pellet

Fig. 18. Dissipation in melt-textured YBCO pellet

Each sample was subjected to a "sawtooth" current pulse that rises linearly with time and is measured on the right vertical axis. When the rising current exceeds the critical current (5.8 A in Fig. 17 and 1.75 A in Fig. 18), a nonzero voltage is observed and is measured on the left axis. The cross sections of the two samples are small, so the observed J_c values were 1400 A/cm² in Fig. 17 and 2000 A/cm² in Fig. 18. Voltage curves are shown for currents that reach four times J_c in zero field, and more than 10 times J_c in the applied fields indicated. The sample composed of unoriented YBCO (Fig. 17) shows a type of dissipation that quickly converges onto a family of straight lines that indicate ohmic

behavior. Curves of this type are a confirmation of the "summation model" (Bungre, 1991), which holds that the flowing current is effectively the sum of a lossless supercurrent (field dependent) and a lossy, resistive current with a field-independent resistivity.

Completely different behavior is observed for grain-aligned samples, such as that shown in Fig. 18. Considerable effort is required to prevent noticeable heating of the sample during such high levels of dissipation. The required pulse technology is evolving from techniques developed to measure just the onset of dissipation in order to find J_c . The present effort is directed toward measurements of this type on much larger samples (carrying correspondingly larger currents) that are more typical of parts likely to find application in actual devices. Figure 19 illustrates a recent measurement of this type on a 10-mm-diameter YBCO-Ag composite rod with an I_c of 151 A at 77 K.

The indicated linear regions suggest that deep in the sample, near the axis of the cylinder, a supercurrent may still be flowing. This has motivated efforts to attempt measurement of the internal magnetic fields of large polycrystalline superconductors.

A small, high-sensitivity Hall probe has been developed for this purpose. The probe will fit into a 2-mm-diameter hole, and has a field resolution of about 0.05 Oe. YBCO preforms were fired with longitudinal holes drilled at various positions. The internal field in the probe hole could then be measured while the current through the sample was pulsed deep into the dissipative regime. The probe does not measure the actual internal field in the sample because of shielding and demagnetization effects, but these can be estimated and subtracted from the data. Results are shown below (Fig. 20) for two probe positions: one was 1/3 of the distance out from the axis to the edge of the cylinder, and the other 2/3 out.

In the 2/3 position, one can see the penetration of the self-field of the current develop at about the value of the critical current (87 A at 77 K). Beyond this point, a trapped field remains in the sample after the current is removed. This trapped field eventually saturates at about 5 Oe while the penetrating self-field of the current continues to grow. Field penetration at the 1/3 position is not seen until much higher currents, indicating that the local J_c in the central regions of the sample is probably still quite large. Further measurements of this type should help indicate exactly how the self-field penetrates high-current conductors and lead to geometrical and material designs with enhanced supercurrent capacities.

2.3.3 Contact Resistances

Past work has shown the low resistance of Ag-to-superconductor interfaces made by applying Ag powder to 0.5 cm² surfaces of YBCO/Ag conductors prior to the sintering of the conductors. The overall resistance at 77 K of one lapping pair of such contacts conducting 80 A, including a thickness of solder between them, was only 0.5 $\mu\Omega$; and the specific interfacial resistivity, derived by subtracting the contributions of the metallic layers and accounting for the configuration and size of the two interfaces at the joint, was 64 n Ω -cm². In comparable tests on similar samples of YBCO-Ag, the overall resistances were greater but were within a factor of 2 of that noted.

Resistivities of bulk BSCCO-to-Ag interfaces at 77 K were tested in this reporting period. Values below 100 n Ω -cm² were found for Bi-2212 that was melt-cast to Ag, and below 10 n Ω -cm² for Bi-2223 that was pressed to Ag during sinter forging.

Fig. 19. Electric field versus current for 10-mm-diameter YBCO rod. Indicated linear regions suggest that deep in the sample, near the axis of the cylinder, a supercurrent may still be flowing.

Fig. 20. Internal field in YBCO cylinder

2.3.4 Mechanical Properties

Mechanical-property research has continued. Recent efforts have focused on Bi-2212 and Bi-2223. Effects of Ag additions, texture, and plastic deformation have been examined.

Properties of Monolithic Bi-2212 and Bi-2223

The strength and fracture toughness (K_{IC}) of highly textured, nearly fully dense monolithic Bi-2212 and Bi-2223 were measured. The specimens were fabricated by sinter forging (Blondo et al., 1992; Chu et al., 1992) and exhibited very strong c-axis textures. Strength for both materials was 140 ± 10 MPa; K_{IC} for both materials was 3.0 ± 0.2 MPa(m)^{0.5}. These values are higher than those obtained for comparable YBCO bars.

Elastic-moduli studies of sinter-forged Bi-2212 were conducted in collaboration with the University of Bath. Longitudinal waves were used to determine a value of 118 GPa in the plane of the bar (largely a-b crystal planes) and 44 GPa perpendicular to the plane (largely c axes). These values are very close to those measured for single crystals (Wang et al., 1989). They reflect the extremely good texture and density of the polycrystalline sample and indicate the importance of texture on properties. For example, a goal of 0.2% strain to failure for Ag-clad tapes will be difficult to attain, because

$$\sigma = e E, \quad (1)$$

where σ is the strength, e is the strain, and E is the modulus. A strain of 0.2% implies a strength of ≈ 236 MPa, which is very high. Compressive residual stresses on the superconductor core imparted by the Ag sheath may help to reach this level (Kupperman et al., 1989; Singh et al., 1993a).

Effects of Ag Additions on Strength and Toughness

Effect of Ag additions on the mechanical and superconducting properties of sintered bulk YBCO, Bi-2212, and Bi-2223 have been evaluated. To eliminate the effect of density and grain size on mechanical properties, monolithic and composite specimens with similar grain size and relative density were fabricated by controlling the sintering temperature and time. The density and grain size of YBCO and its composites were $\approx 94\%$ and ≈ 4 μm , respectively, whereas those of the Bi-Sr-Ca-Cu-O monoliths and composites were $\approx 90\%$ and ≈ 10 μm in length, respectively. These specimens were evaluated for their mechanical and superconducting properties (Joo et al., 1993).

Figures 21 and 22 show the effects of Ag additions on mechanical properties of sintered YBCO and BSCCO bars. Strength and K_{IC} of YBCO and BSCCO bars increased with increasing Ag content up to 30 vol.% Ag. Addition of 30 vol.% Ag increased strength of YBCO from 87 to 136 MPa and K_{IC} from 1.82 to 3.9 MPa(m)^{0.5}. Similarly, the strength of Bi-2212 increased from 58 to 107 MPa and that of Bi-2223 increased from 41 to 90 MPa with 30 vol.% Ag additions. The corresponding increase in K_{IC} was from 1.89 to 2.79 MPa(m)^{0.5} and from 1.09 to 1.94 MPa(m)^{0.5}, for Bi-2212 and Bi-2223, respectively. These high values of BSCCO/30 vol.% Ag composites are comparable to those of dense Bi-2212 made by sinter forging, hot pressing, and hot isostatic pressing (Nash et al., 1990, Chu et al., 1992, and Goretta et al., 1993).

Fig. 21. Dependence of strength on Ag content for specimens shown

Fig. 22. Dependence of fracture toughness on Ag content for specimen shown

As discussed by Singh et al. (1989 and 1993a), the improvements in strength and K_{IC} by addition of Ag are believed to have several causes. First, the presence of Ag between superconducting grains in composites may provide a plastic-flow region that allows for relaxation of undesirable residual stresses resulting from the grain anisotropy of superconductors. Second, the presence of Ag may induce compressive stresses in the superconducting matrix due to the thermal-expansion mismatch between superconductors and Ag

particles. The compressive stresses in the superconducting matrix can pin crack tips and impede crack propagation. For YBCO/Ag composites, compressive strains in the YBCO matrix as high as $\approx 0.1\%$ due to addition of 20 vol.% Ag have been measured by neutron diffraction (Kupperman et al., 1989; Singh et al., 1990). Because the thermal-expansion coefficients of Bi-2212 and Bi-2223 (Arendt et al., 1991 and 1992) are higher than that of Ag, compressive stresses are expected in these superconductor matrices also. Third, Ag particles may resist crack propagation by deflecting and bridging the crack and pinning the crack tip (Singh et al., 1993a).

The hardness of YBCO and Bi-2212 and Bi-2223 were observed to decrease with increasing Ag contents because of the lower hardness of Ag. On the other hand, addition of Ag showed no adverse effects on superconducting properties (J_c and T_c) of YBCO and Bi-2212 and Bi-2223 superconductors (Joo et al., 1993).

High-Temperature Deformation

Additional high-temperature-deformation studies (N. Chen et al. 1992) were completed for Bi-Sr-Ca-Cu-O. Previous work confirmed that for low stresses, diffusional flow occurred in Bi-2212 when the specimens were compressed at 780–835°C. The activation energy for the deformation was 990 ± 190 kJ/mole, which is quite similar to that for YBCO. No effect of deformation on pO_2 was found (Routbort et al., 1992).

The most recent work focused on use of higher stresses. Dense polycrystalline Bi-2201, Bi-2212, and Bi-2223 specimens were compressed in air at 730–835°C. All of the materials exhibited an apparent steady-state creep response. Strain rate was proportional to stress to the 3.1–3.8 power. Apparent activation energies for the deformation processes were 520 ± 50 kJ/mole for Bi-2201, 630 ± 210 kJ/mole for Bi-2212, and 960 ± 210 kJ/mole for Bi-2223. Transmission electron microscopy (TEM) revealed substantial generation and propagation of basal-plane dislocations during deformation; few nonbasal-plane dislocations were observed. Intergranular fracture was evident in all deformed samples, and intragranular fracture was evident along the basal planes of some grains. It was interpreted that the kinetics of fracture were determined by dislocation motion within the grains (Goretta et al., 1994). These results indicate that plastic deformation can be used to form dense superconductors, but that cracking may be a problem.

2.3.5 Nondestructive Evaluation

Ultrasonic Examination of $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_x/Ag$ Tapes

An ultrasonic technique is being explored to detect and monitor incongruent melting during fabrication of Bi-2223/Ag and other superconducting tapes. It is believed that control of a liquid phase is essential in achieving proper phase development, grain alignment, and subsequent optimization of electrical properties. The end of a sintering cycle should be determined by the disappearance of the liquid. At present, there is little information on when the liquid phase forms during sintering and, more important, when it disappears. An ultrasonic technique is being evaluated to measure the velocity of sound in the tape, which appears to be sensitive to the amount of liquid present.

Tapes about 250 μm thick, 4 mm wide, and 5 cm long were prepared by the PIT method. The tapes were sintered in air at 845°C while the velocity of sound was monitored to detect the appearance and disappearance of liquid. A magnetostrictive transducer launches a 140 kHz wave in a 2-mm diameter remendur rod that is welded to an Inconel

rod that, in turn, is attached to the superconductor by a ceramic cement. Clear echoes are evident from the tape/rod interface and from the end of the tape. The round-trip transit time for the tape, which is entirely inside the furnace, is monitored. Transit time (Δt) increases with temperature as the tape expands and the material composite elastic modulus decreases. DTA curves indicate when incongruent melting occurs. As the temperature of the ribbon rises, there is a relatively rapid increase in Δt over the temperature range where liquid is expected to form. The rise in Δt implies that the velocity dropped, as expected, when the liquid was mixed with Ag and Bi-2223 solid. This result suggests that the velocity measurement can be used to determine when liquid is present.

A simple analytical model can be used to predict, approximately, the experimental observations and to better understand the type of wave that propagates in the tape (longitudinal, shear, or lamb wave). As discussed below, the assumption that the long and narrow tape can be treated as a thin rod appears to be valid and allows calculation of the Young's modulus (E) of the Bi-2223, including E as a function of temperature, from the density and velocity of sound data from a pure Ag tape and a Bi-2223/Ag tape. From the assumption that the tape can be treated as a thin rod, it follows that

$$E = \rho V^2, \quad (2)$$

where ρ is density and V is the longitudinal velocity of sound. The second assumption, which also appears to be valid, is that the Reuss model (constant stress in the two constituents of a composite) applies to the calculation of velocity of sound and E for waves traveling along the superconductor tape. Then,

$$1/E = f/E_{HTCS} + (1-f)/E_{Ag}, \quad (3)$$

where f is the volume fraction of the superconductor (HTSC), $(1-f)$ is the volume fraction of Ag, E_{HTCS} is the Young's modulus of the HTSC, and E_{Ag} is the modulus of the Ag (Lees and Davidson, 1977). The room-temperature modulus of 70.91 GPa, measured experimentally for the Ag, is consistent with literature value of 71 GPa. The value of 53.43 GPa, measured experimentally for a Bi-2223/Ag tape with a standard pulse-echo technique for determining sound velocity, can be used to calculate the modulus of the Bi-2223 at room temperature (Eq. 3). The predicted value is 30.71 GPa. This number is consistent with the experimentally determined values of 25 ± 5 GPa for Bi-2223 by Tritt et al. (1991) and 35 GPa by He et al. (1989).

We have also measured the temperature-dependent velocity of sound (thus E), which decreases monotonically for a pure Ag tape and drops only about 15% from room temperature to 900°C. In view of the Ag data, the sharp decrease in longitudinal velocity of sound in the composite tape at high temperature is attributed to the sharp drop in the modulus of the Bi-2223 caused by the presence of a liquid phase (and subsequent loss of a shear contribution to the total modulus) and the resultant changes in microstructure.

In Fig. 23, the transit time, shown as a fractional change relative to 700°C, is plotted against temperature for three different tapes. A reference tape formed from Al_2O_3 and Ag is compared with Bi-2223 and Tl-1223 tapes. No liquid forms in the Al_2O_3 tape. The formation of the liquid at different temperatures in the Bi-2223 and Tl-1223 tapes is clearly evident from the rise in $\Delta t/t$, where t is the echo transit time in the tape and Δt is $t - t_{700}$. This result is particularly important for Tl-1223/Ag tapes, because the volatility of Tl makes DTA-reliable data very difficult to generate. The drop in $\Delta t/t$ before the sharp rise is the result of densification before the liquid phase. The dip indicates a higher

Fig. 23. Ultrasonic echo transit time, shown as fractional change relative to 700°C, vs. temperature for three tapes. A reference tape formed from Al_2O_3 and Ag is compared with Bi-2223 and Tl-1223 tapes. Formation of liquid at different temperatures in the Bi-2223 and Tl-1223 tapes is clearly evident from the rise in $\Delta t/T$. The dips in the curves, before the liquid forms, indicates a higher velocity resulting from increased density.

velocity which is associated with increased density. Initiation of this microstructural change is clearly evident when Bi-2223 and Tl-1223 curves are compared with the Al_2O_3 curve.

In Fig. 24, a Bi-2223/Ag tape heated in air is compared with one heated in 8% oxygen. Again, $\Delta t/t$, where t is the echo transit time in the tape and Δt is $t - t_{700}$ is plotted against temperature T . The shift in temperature of a few degrees for the formation of liquid can be seen.

The effect of oxygen content on the onset of the liquid phase was also studied for Tl-1223/Ag ribbons. Generally, the transit time, shown as a fractional change relative to 700°C, is plotted against temperature. Sometimes a comparison of samples is more relevant if the slopes of the t vs. T curves are presented. The derivative of the curve of ultrasonic echo transit times vs. temperature, from 700°C, for Tl-1223/Ag samples heated in 100, 10, and 1% oxygen atmospheres, are presented in Figs. 25-27. The 10% and 100% samples show similar trends with the liquid phase onset at 905°C for the 100% atmosphere and 890°C for the 10% atmosphere, a change consistent with expectations. The data for the 1% atmosphere have a different character, making it difficult to determine a distinct temperature for the formation of the liquid phase. This is the result of decomposition and complicated changes in the microstructure of the Tl-1223 when heated in a low-oxygen atmosphere.

Fig. 24. Bi-2223/Ag tape heated in air compared with one heated in 8% oxygen. Data are plotted as $\Delta t/t$ vs. T , where t is echo transit time in the tape, Δt is $t - t_{700}$, and T is temperature.

These curves show the sensitivity of the ultrasonic technique to temperature-dependent variations in microstructure of the ceramic superconductor. The data are useful for setting the temperature for fabricating superconducting wires from this material and monitoring the quality of the wire during the heating and cooling cycles. This information is currently being used by another laboratory to optimize the fabrication of its TI-1223/Ag wires.

X-ray Imaging of Ag-Clad Tapes

High-spatial-resolution microfocus-based X-ray imaging technology, both real-time and film, has been used to study the thickness variation in the oxide core of Ag-sheathed BSCCO tapes produced by the PIT method (Ingerly et al., 1993). This thickness variation (also called work instability or sausaging) occurs during incremental rolling and degrades the J_c values of the tapes. Using X-ray image data, we determined the onset and severity of sausaging. Onset occurred at a thickness of 203 μm , and the severity increased with subsequent rolling reductions. SEM was used to confirm the X-ray image data. X-ray imaging provides several advantages over more traditional methods of characterizing the superconductors, such as optical or scanning electron microscopy; it provides nondestructive information about the entire width of the ribbon, with far greater speed, lower cost, and more flexibility than do the traditional techniques.

X-ray image data reveal changes in sample thickness or changes in density of an imaged part. Each tape is actually a composite, i.e., an Ag sheath around a Bi-2223 powder core. The Ag—with a density of 10.5 g/cm³—will absorb more X-rays for a given unit thickness than will Bi-2223 powder (density = 5.1 $\pm$ 0.8 g/cm³). When sausaging occurs

Fig. 25. Derivative of curve of ultrasonic echo transit time vs. temperature, from 700°C, for a Tl-1223/Ag sample heated in 100% oxygen

Fig. 26. Derivative of curve of ultrasonic echo transit time vs. temperature, from 700°C, for Tl-1223/Ag sample heated in 10% oxygen

Fig. 27. Derivative of curve of ultrasonic echo transit time vs. temperature, from 700°C, for Tl-1223/Ag sample heated in 1% oxygen

during the rolling reduction, the ratio of Ag thickness to Bi-2223 changes in a given cross section. This change is detected by differences in X-ray attenuation, which is displayed as a difference in gray scale on the images.

Figure 28 shows X-ray images of four tapes of different thicknesses: 394, 254, 203, and 102 μm . Gray-scale plots from the center of the X-ray images shown in Fig. 28 were constructed. The X-ray image of the 394- μm tape shows a uniform powder core with gray-scale peak changes of 250 gray-scale values or less. The X-ray image data for the 254- μm tape shows a small amount of sausaging. Changes in gray-scale peak values were typically up to 300, with a few of the largest peaks reaching 450. There is a strong transition from no sausaging to significant sausaging between the 254- and 203- μm ribbons. This seems to be the thickness range during rolling where onset of sausaging takes place. X-ray image data for the 203- μm tape show significant gray-scale changes, with peaks in the 500 range. The X-ray image data for the 102- μm tape show that sausaging increases as the rolling reduction continues. Changes in gray-scale peak values for the 102- μm ribbons commonly reached 1000, with a maximum of 1300. SEM photos of cross sections of each tape confirm the X-ray image data.

A total of five sets of tapes, each from different starting tubes, were examined. All samples were examined by both SEM and X-ray imaging methods. The SEM results confirmed the X-ray image data in all cases. It was also shown during these studies that X-ray imaging can be used to find and examine other types of processing defects.

Fig. 28. X-ray images of tapes of thickness (a) 394 μm , (b) 254 μm , (c) 203 μm , and (d) 102 μm

2.4 Applications and Devices

Application research and development are focused on production and testing of components, analysis of performance (Cha et al., 1993a-c; Niemann et al., 1993a-d), and design of new systems (Lorimer et al., 1993; Schoenung et al., 1993; Weinberger et al., 1993)

2.4.1 Current Leads

Current leads employed for the transfer of electrical energy from ambient-temperature devices to cryogenic-temperature devices (Wu et al., 1991) continue as a viable near-term application of high- T_c superconductors. Such high- T_c superconductor current leads offer the advantage of reduced low-temperature refrigeration loads because they eliminate Joule heating and reduce thermal conduction along the lead. Suitable bulk high- T_c superconductor materials are available with current densities at 77 K of 100–1000 A/cm², which results in thermally efficient and reasonably compact current-lead assemblies at acceptable cost (Hull, 1993a).

Near term applications include superconducting magnets for particle accelerators, magnetic energy storage, superconducting motors, and space-based cryogenic devices. The objective of our development program is commercialization with U.S. industry of high- T_c superconductor current leads. The program includes development of conductors, analysis of performance, design and fabrication of leads, and evaluation of lead performance.

The conductor development program considers current characteristics, AC losses, mechanical strength, fracture toughness, thermal shock and cycling, and ceramic-conductor-to-metal transitions. The emphasis of the program has shifted from YBCO to Bi-2212 and Bi-2223 because of their ability to maintain acceptable current density at moderate-to-high magnetic fields. Typical properties for Bi-2223 in bulk rod form are $J_c = 10^3\text{--}10^4$ A/cm² at 77 K and 60 mT, flexural strength = 140 MPa, and $K_{IC} = 3.0$ MPa(m)^{1/2} (N. Chen et al., 1993).

Component design and fabrication considers lead performance, reliability, safety, manufacturability, and cost. 100-A capacity leads have been designed, fabricated, and are undergoing performance evaluations. Ongoing and future activities include lead assemblies utilizing YBCO bulk rod, Bi-2223 bulk rod, and Bi-2223 powder-in-tube high- T_c superconductors. The design, in collaboration with industry, of a 1500-A lead (Niemann et al., 1993a-d) for micro-SMES applications has been completed and is shown in Fig. 29. The lead is in the final stages of construction and will be evaluated in an actual commercial micro-SMES system (Hull, 1993b).

Performance evaluation experimentally considers the performance of high- T_c superconductor leads and their components in the areas of critical current, heat input, voltage drop, pressure drop, connection resistance, and transient response. A 100-A current-lead heat-leak measurement facility with low background heat leak continues to be in operation. Measurements continue with leads of different design and operating mode. Component evaluations include the performance of demountable electrical connections (Niemann et al., 1993a) and of the transition assembly between the conventional upper stage lead and the high- T_c lower stage lead, as shown in Fig. 30. Results of such evaluations are applied to component design and performance analysis.

Fig. 29.
Current-lead design

Fig. 30.
Transition assembly for high T_c
lower-stage current lead

2.4.2 Analysis of Current Flow in Composite Conductors

Analytical study of current distributions in composite conductors, such as Bi based high- T_c superconductors made by PIT processing, was carried out (Cha et al., 1994). In a model that was constructed, it was assumed that the Ag sheath is continuous and that there are periodic discontinuities in the superconductor. Closed form solutions were obtained, and the results showed that the solution depends on only one dimensionless parameter, $\lambda_s L/2$, which is equal to the square root of the ratio of the resistance of the Ag to the interfacial resistance between the Ag and the superconductor core.

Figure 31 shows the average current in a Bi 2223 core (I_{B3} / I_o , where I_o is the total current) as a function of the parameter $\lambda_s L/2$. Results of this analysis can be employed to predict the effect on J_c of transverse cracks generated by axial strains. Figure 32 shows the variation of the current density with the interfacial parameter $(RA)_i$ and the half distance $L/2$ between two transverse cracks (in Fig. 32, d_{pw} is equal to the cross sectional area of the superconductor, R is the interfacial resistance, and A is the interfacial area between the superconductor and the Ag sheath). The results in Fig. 32 indicate that J_c decreases with increasing distance between transverse cracks, which is in agreement qualitatively with the experimental observations reported by Ekin, et al. (1992). It is important to note that even with through cracks, voltages of less than 1 μV can be generated by the current shunting across the Ag sheath.

2.4.3 Superconducting Magnetic Bearings

A rotating permanent-magnet bearing assembly can be stably levitated above a stator component composed of high- T_c superconductor (HTSC) elements without the need for position sensors and the elaborate feedback control systems required for conventional active electromagnetic bearings. Significant advances were made during FY 1993 in the development of very low-friction magnetic bearings based on the unique levitation

Fig. 31. Average current in Bt-2223 core versus dimensionless parameter defined in Section 2.4.2

Fig. 32. Variation of current in core as function of interfacial resistance parameter

characteristics of HTSC materials. The major accomplishments included one-order-of-magnitude scale-up in bearing size and demonstration of friction coefficients ($\mu < 10^{-6}$) that were more than three orders of magnitude lower than those of the best commercial bearings (Poeppel et al., 1992).

A collaborative effort with Commonwealth Research Corporation was initiated in FY 1993 to demonstrate that low-loss bearings can be scaled to sizes of interest for flywheel energy storage (FES) applications (Weinberger et al., 1993). The project task elements included:

1. HTSC Stator Materials - develop HTSC materials with improved crystalline structure and a higher density of effective flux-pinning centers.
2. Permanent Magnet Materials - develop improved materials and designs for permanent magnet elements used in flywheel rotor/HTSC bearing applications.
3. HTS Bearing/Flywheel Rotor - develop HTSC magnetic bearing designs for enhanced levitation force and stiffness characteristics, and fabricate and test prototype units.
4. Design of HTSC Bearing/Flywheel Test Apparatus - for bearing scale-up tests, representing the next generation beyond the current bell-jar test-rig experiments.
5. Procurement and Assembly of Test Apparatus - with the capability for testing large FES rotors.
6. System Checkout and Preliminary Rotor Tests - to verify scale-up characteristics of low-friction bearing systems.
7. FES Power Input/Output Design - assessment of design alternatives for achieving high-efficiency power transfer (greater than 90% round trip) from rotational energy to 110 V/60 Hz power.

Efforts during FY 1993 focused on Tasks 1-4 and 7, with Tasks 5 and 6 scheduled for early FY 1994. In addition, laboratory investigations of HTSC bearing phenomena were continued throughout FY 1993 in the 30-cm-diameter bell-jar test apparatus (Poeppel et al., 1992).

Bulk YBCO elements sufficient to cover a surface area of $\approx 655 \text{ cm}^2$ were processed at ANL for use in HTSC bearing experiments. Improved melt-processing techniques and incorporation of small single-crystal seeds have resulted in improved levitation characteristics for the YBCO stator component of HTS bearings. Detailed assessment of the impact of azimuthal inhomogeneities, and other characteristics of rare-earth permanent magnets, on rotor performance was continued. A close working relationship was established with industry to develop improved rotor magnets.

A series of bell-jar experiments was performed to delineate the potential source of losses in the HTSC stator and the bearing rotor components. A large 91.4-cm-diameter high-vacuum test chamber, illustrated schematically in Fig. 33, was designed for bearing scale-up tests; fabrication and assembly are scheduled for completion early in FY 1994. The project goal is to utilize this test apparatus to develop larger prototype FES units that use HTSC magnetic bearings with energy dissipation rates $< 0.1\%/h$.

Fig. 33. Schematic diagram of vacuum chamber for testing prototype flywheels

2.5 Lower Anisotropy Materials: Grain-Aligned Tl-1223 Development

Lower anisotropy materials, such as Tl-1223, have clear advantages for intrinsic flux pinning at high temperatures and fields (Kim et al., 1991), but they can be used effectively only if conductors with well-connected grains can be made. The need for good grain alignment for high J_c values in polycrystalline HTSC is well-documented, and the first reports of high J_c in Tl-1223 were in thick deposits made at General Electric; these materials showed a high degree of c-axis grain alignment (DeLuca et al., 1991, 1992, 1993). Unfortunately, Tl-1223 does not possess the favorable mechanical properties of BSCCO that aid grain alignment in PIT processing. Therefore, our program also addresses alternative methods to achieve such alignment in a viable process for a practical conductor.

2.5.1 Technical Progress

Thick-Film Processing

The pursuit of grain alignment in conductors has been motivated in large part by reports of record critical currents in thick films of Tl-1223 prepared at General Electric (GE) Corporate Research and Development (Tkaczyk et al., 1992). Work has been conducted at both GE and ANL. To foster this collaboration, GE shipped one of its two-zone reactors to ANL and has provided consultation on its use. In addition, many samples have been exchanged between the two institutions.

Processing at GE focused on use of a static reactor, in which Ti_2O vapor was not flowed, to prepare 3- μm -thick, highly textured, superconducting films of pure Ti-1223 on yttria-stabilized ZrO_2 (YSZ) substrates. The films were formed by thalliation in an O_2 environment of precursor films heated to 860°C . The precursor films were prepared by spray depositing a Ba-Ca-Cu-Ag nitrate solution on a heated substrate, followed by decomposition of the nitrates in O_2 . A post-growth annealing on the films in O_2 improved J_c by factors of 2-5. Films were prepared with $T_c \approx 105\text{ K}$, J_c at $77\text{ K} = 10^4 - 2 \times 10^5\text{ A/cm}^2$, and the expected high irreversibility line (DeLuca et al., 1993; Kim et al., 1991). Key development needs for this process addressed at GE are (1) film homogeneity; (2) maintaining good superconducting properties in films thicker than $4\text{ }\mu\text{m}$, (3) process chemistry optimization; (4) preparation of high-quality films on flexible substrates; (5) understanding of film growth and post-growth annealing mechanisms, and (6) process scale-up.

(1) Film homogeneity. In our general experiments, we found a pronounced spatial variation in the J_c characteristics of the films, which was deduced to be due to decomposition of the nitrates. Working from this hypothesis, we prepared precursor films, with 5% Ag, on YSZ substrates by three methods: Deposition #1 - (a) the amount of precursor needed for a 3-4 μm film was deposited, (b) the film was heated rapidly in air to 650°C , and (c) the film was cooled to 500°C and then heated in O_2 to 850°C in 30 min. Deposition #2 - the film was prepared with four depositions, each of which was subjected to heat treatment 1(b), and finally the fully deposited film was subjected to heat treatment 1(c). Deposition #3 - the amount of material required was deposited, the sample was heated in air to 500°C , and then heated very slowly in O_2 to 850°C . All precursor films were thalliated under the same conditions and were then patterned with a 4 mm x 2 mm test bridge consisting of four 1 mm test segments. Listed below for each deposition test is the mean J_c at 77 K in zero applied field, the ratio of the standard deviation to the mean, and the number of segments.

Deposition #1: 16,000 A/cm^2 , 1.21, 44.

Deposition #2: 38,000 A/cm^2 , 0.54, 56.

Deposition #3: 40,000 A/cm^2 , 0.32, 20.

Clearly, deposition processes #2 and #3 are superior to process #1, which was used in the earlier work (DeLuca et al., 1991 and 1992). Microstructural analysis indicated that processes #2 and #3 produced more homogeneous films than did process #1.

(2) Thicker films. Because of the favorable J_c results and because deposition process #3 takes less time than #2, it was used to prepare films with final thicknesses of 7-10 μm . Thalliation times were adjusted accordingly. J_c results, expressed in the format above, were:

Thicker films: 10,500 A/cm^2 , 0.85, 28.

Inspection of the films revealed the presence of a surface morphology much rougher than observed in the thinner films, as well as microcracking in many samples. These results clearly indicate that maintaining good J_c with increasing film thickness is not straightforward.

(3) Process chemistry optimization. Oxide precursors with Ba:Ca:Cu:Ag stoichiometry of 2:2:3:0.37 were used in most tests. This composition is designated 5 mole% Ag. Previous experience has shown that Ag contents in excess of 10 mole% have a pronounced deleterious effect on film properties. In an effort to determine the optimal Ag level, we used deposition process #3 to prepare films with Ag concentrations of 0.5, 2, 5, and 8 mole%. These experiments were marred by an unexpected adhesion problem in the 2 and 5 mole% samples; this problem did not become apparent until electrical testing. The limited data obtained indicate that 5 mole% does appear to be nearly optimal. These experiments revealed a problem inherent to deposition process #3 that did not manifest itself in the initial tests. The Ag-concentration experiments will be redone.

(4) Flexible substrates. The work at GE includes studies of films prepared on rigid and flexible ceramic substrates, metals, and barrier-layer-protected metals. In collaboration with ANL, Tl-1223 films were prepared on Ag substrates. Excessive film cracking occurred on 250- μ m-thick Ag. This problem was minimized by use of 25 μ m Ag. Substantial interaction between the film and substrate was indicated by the formation of excess liquid phase during thalliation. Subsequent chemical analysis revealed that the Ag contents of the films increased from 5 mole% to $\approx$ 10 mole%. Of 10 samples prepared on the 25 μ m substrates, only a few were suitable for measurement. The best of these exhibited a T_c of 105 K, a J_c at 77 K of 10,000 A/cm², and the good pinning characteristics of the films prepared on YSZ.

(5) Film growth mechanism. Microstructural examinations were made of several films, some of which had been quenched from a processing temperature. The observation indicate that a liquid phase is responsible for the accelerated growth of the Tl-1223 films in the Ge process. Studies indicated that the simultaneous presence of Ba, Ca, Cu, Ag, and Tl is required for the phase to form. Liquid formation occurs at different sites in the film as the Tl oxide vapor reacts with it and the liquid dissolves the surrounding oxides. The Tl-1223 phase grows out of the liquid, which advances through the film as addition Tl oxide is incorporated. The final microstructure is the result of intergrowth of many growth fronts.

(6) Process scale-up. It became apparent in early 1993 that the low mass transport rates and the Tl oxide pressure gradients inherent in the static reactor are potential limitations not only for scaling the process up, but also for control of conditions in many types of thick-film processing. Consequently, we redesigned the two-zone system to accommodate a flow-through reactor in which O₂ flows over the Tl oxide source boat and establishes a forced mass transport of the Tl₂O vapor to the sample. Appropriate hardware was also supplied to ANL for modification of its reactor. Although the basic process is viable under forced-flow conditions, details are sufficiently different that a systematic determination of optimal processing condition is required. This work is underway.

ANL structural analyses of several GE films, by X-ray diffraction and electron back-scattered patterns (EBSP), has confirmed a high degree of c-axis alignment, but little in-plane texture in these GE films. Cross-sectional TEM revealed overlapping layers reminiscent of a brick-wall structure (Fig. 34). Although the field dependence of J_c is consistent with that observed in other brick-wall structures (i.e., BSCCO), we cannot unambiguously identify the conduction path. From these and other measurements, however, it seems clear that a high degree of c-axis grain alignment is necessary to achieve high J_c (Miller et al., 1993a and 1993b).

Fig. 34. TEM image of grains in Tl-1223 thick film

In collaboration with GE, we have used coatings made by magnetron sputtering or laser ablation to investigate the effect of precursor density on film quality. After thalliation and annealing at GE, our coatings showed a high degree of *c* axis texture and $J_c \approx 10,000$ A/cm² at 77 K and zero field, thus demonstrating our ability to use dense precursors with the GE process. With GE, we have also begun fabrication of Tl-1223 coatings 15-200 μ m thick made by organic ink precursor techniques, which are easily scalable for production. Preliminary deposits, up to 25 μ m total thickness, showed *c* axis orientation by X-ray diffraction and T_c up to 107 K; however, SEM examination revealed that only a 2- μ m-thick layer adjacent to the substrate was platelike. Assuming that the current flows entirely in the 2 μ m surface layer, J_c at 77 K in zero field was again $\approx 10,000$ A/cm².

We are also exploring alternative grain alignment methods. We have grown large (10-20 μ m), platelike, Sr-substituted Tl-1223 grains that are expected to be amenable to alignment by magnetic techniques. In addition, this process yields in situ texturing within enclosed Ag tubes, offering the possibility of the direct formation of grain aligned PIT tapes.

Powder-in-Tube Tapes

To develop grain alignment in PIT wires, we have studied the effects of in situ reactions and thermomechanical processing on the microstructure and properties of Ag clad Tl-1223 wires. If microstructures in Tl-1223 can be made to be similar to those in Bi-based superconductors, high J_c in high magnetic field should result. Analogous to that in Bi-2223 superconductors, the effect of the starting-phase assemblage on grain growth and crystallographic alignment was studied for Ag-clad Tl-1223 tapes.

Three separate powders of the Tl-1223 stoichiometry were synthesized. Powder 1 was nominally phase-pure Tl-1223. Powder 2 was an assemblage of Ca₂CuO₃, BaCuO₂, and Tl₂O₃ phases. Powder 3 was a mixture of 80% Powder 1 and 20% Powder 2. Separate

tapes were made from these powders by a standard PIT process (Hellstrom, 1993). Annealing temperatures were selected on the basis of DTA and acoustic velocity results. Previous work showed that Tl-1223 melts incongruently in O_2 at $\approx 870^\circ C$ in the presence of Ag. Tapes were heat treated between $800^\circ C$ and $870^\circ C$ for up to 80 h. After each heat-treatment step, J_c was measured at 77 K with a voltage criterion of $1 \mu V/cm$. Phase development and microstructures were studied by X-ray analysis and SEM.

J_c was measured for all tapes as a function of annealing temperature and time. Tape 2 had inferior properties to Tapes 1 and 3 for all heat-treatment conditions. Lower J_c values were because of greater number of impurity phases. The J_c of Tape 3 was monitored as a function of soak temperature for times of ≤ 1 h (Fig. 35). For Tape 3, maximum J_c was achieved by heat treating at $865^\circ C$, slightly below the incongruent melting temperature of the Tl-1223/Ag system. J_c increased as temperature increased from $800^\circ C$ to $865^\circ C$. The decrease in J_c at $870^\circ C$ was attributed to excessive reaction with the Ag sheath. In addition, J_c was monitored as a function of soak time at $865^\circ C$ (Fig. 36). Microstructural data suggest that J_c is decreased as the concentration of secondary phase increased.

In summary, Tl-1223 powders with varied phase distributions were used to fabricate tapes by the PIT process. Powders consisting primarily of phase-pure Tl-1223 were superior to a phase assemblage of Ca_2CuO_3 , $BaCuO_2$, and Tl_2O_3 powders. No texturing in the microstructure was observed for any of the annealing times or temperatures. Critical current densities of more than $5,000 A/cm^2$ were measured at 77 K, and J_c degraded as the number of impurity phases increased. Further work will focus on use of other phase assemblages in the starting powder to determine if improved grain growth and alignment can be achieved in Ag-clad Tl-1223.

Additional studies of tapes made with doped Tl-1223 powders are in progress. In collaboration with staff members of Sandia and Los Alamos National Laboratories, we have examined use of $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$.

The powder is produced by combining Tl_2O_3 with a precursor provided by Sandia. Work is still in progress, but the initial results are promising. A tape from ANL/Sandia powder that was fabricated at ANL and Los Alamos achieved, in short sections, transport J_c values at 77 K well in excess of $20,000 A/cm^2$. The cross section was rather irregular, and it was difficult to ascribe a single J_c to the tape.

Using SEM and TEM, we have examined high- J_c Tl-1223-based tapes (Tl-Sr-Ba-Ca-Cu-O powders with either Pb or Bi additions) prepared at SUNY-Buffalo. Pressed and rolled wires exhibited $\approx 35\%$ higher J_c than totally rolled ones. The overall wire structures were very uniform, suggesting excellent control of mechanical working. Although there were no easily identifiable differences in texture or grain size between the rolled and pressed tapes, it seems that isostatic pressing is least damaging to the development of grain alignment and, therefore, leads to higher J_c . Transport measurements indicate a higher irreversibility line, likely owing to the higher T_c due to Sr and Pb additions, but the highly nonlinear I-V curves made any definitive comparisons difficult. Tapes from $Tl_{0.5}Bi_{0.5}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_x$ have been produced at ANL, and heat treatment and characterization are underway.

We have made one Ag-clad wire from the new superconductor $HgBa_2CuO_x$ (Hg-1201, with $T_c = 96$ K). Highly pure powder was provided by J. L. Wagner and D. G. Hinks of ANL (Wagner et al., 1993). Interest in the Hg-based compounds stems from their structural similarity to the Tl-compounds and their higher T_c values (Gao et al., 1993). The

Fig. 35. J_c of Tape 3 heat treated for ≤ 1 h

Fig. 36. J_c of Tape 3 heat treated at 865 °C

HgBa₂Ca₂Cu₃O_x (Hg-1223) compound may have a T_c of ≈ 150 K, but has yet to be synthesized in pure form. Heat treatment of the Ag-clad Hg-1201 wire revealed strong interaction between the superconductor and Ag at temperatures as low as 500 °C. Little sintering could be induced at temperatures from 500 to 900 °C, and Hg loss became severe at the highest temperatures. J_c values at 77 K were less than 100 A/cm².

2.5.2 Status

We will continue to study the development of texture in thick films and PIT wires and tapes by concentrating on the fundamental relationship between microstructure and

properties. In addition, phase formation by *in situ* reaction, which has been successfully developed for BSCCO, will be given significant attention.

Thick Films

Efforts at GE will focus on establishing a benchmark flow-type reactor that is capable of producing films comparable or superior to those produced in the static reactor. Based on considerable experience, deposition process #2 (described above) will be used. Once a new standard process is established, systematic studies will be initiated on the effects of Ag concentration, growth of films on flexible substrates, and preparation of thicker films. This work will benefit significantly from experience gained in the static reactor. In addition, work will continue on understanding the film growth mechanism. Efforts will also be initiated to understand better and optimize the post-growth annealing, which is used to improve J_c .

The goal of the thick-film program at ANL will be to convert the entire precursor-ink thickness to dense, well-aligned Tl-1223 with improved superconducting properties. We will also examine Sr, Pb and Bi substitutions. In collaboration with GE, we have recently converted our annealing furnace to a gas-flow reactor for improved thalliation uniformity and for testing scale-up concepts. In collaboration with Prof. Jui Wang, SUNY-Buffalo, we will study thalliation in precursors of varying density. Based on these results, very fine precursor powders will be used in the inks. We plan to explore use of commercially viable substrates, such as YSZ buffer layers on metallic tapes.

Phase assemblage in the precursor is doubtless an important facet of this work, as illustrated by the important role of Sr in preferentially promoting the Tl-1223 phase (but its negligible effect in powders annealed with the GE vapor-transport technique). We will try to identify the key intermediate phases that lead to the eventual formation of the Tl-1223 phase and thus optimize *in-situ* reactions for PIT.

We continue to have great interest in Hg-based cuprates. Bulk materials have been almost exclusively studied elsewhere. We plan to use precursors, made by pulsed laser deposition and thick-film ink techniques, to form the Hg-1223 compound which has a reported T_c of 136 K. If successful in sealed tubes, we will then explore the possibility of using the GE vapor-transport method developed for Tl compounds. Additional studies of the reaction path by which Hg is incorporated will also be carried out using laser-ablated and bulk precursors.

Powder-in-Tube Tapes

Work on PIT tapes will continue to focus on comparisons of pure Tl-1223 with various doped compounds. Concentration is likely to be on the Pb/Sr doped compound under joint study with Sandia and Los Alamos and on the Bi/Sr doped compound under joint study with SUNY-Buffalo. Both compounds have produced better phase purity and higher J_c values than the pure Tl-1223.

Although grain alignment appears to play a critical role in transport behavior, variations from sample to sample in PIT wires cannot be easily explained on the basis of texture and phase purity and are likely to be strongly influenced by grain-boundary coupling. We will employ analytical TEM to study the grain boundaries in Tl-1223 wires. In collaboration with SUNY-Buffalo, we will examine the effect of rolling, cold pressing, and hot pressing on grain size and grain-boundary connectivity in order to further identify

the reasons for improved critical currents in pressed wires. In addition, the effect of defects introduced during deformation will be evaluated.

Fabrication of grain-aligned PIT conductors using platelike, Tl-1223 grains will continue. In collaboration with GE, magnetic alignment will be used to orient the large platelike grains we have been able to produce. Key to this will be avoiding damage to the platelike grains and/or their alignment during further mechanical and heat treatments. Studies will determine appropriate sintering processes. We will also prepare a PIT wire from these powders using techniques which have been found, by microstructural characterization of mechanically worked samples, to be less damaging. We will also pursue in-situ reactions that may help to eliminate mechanical damage yet provide seeds for nucleation and growth of aligned grains. Finally, we will prepare thick films by direct reactions in Ag tubes.

2.6 Grain-Boundary versus Flux-Pinning Contributions to Dissipation

The ability to evaluate the relative importance of grain-boundary effects compared to flux depinning in practical wire configurations is clearly important because it can provide specific guidance for synthesis and processing to improve the current-carrying capacity of wires (Hettinger et al., 1992b). The most likely prospect for this is by evaluating the current-voltage characteristics, $I(V)$. Starting from a systematic understanding of $I(V)$ for materials with no grain boundaries and materials dominated by a single or a few well-defined grain boundaries, procedures will be undertaken to interpret these in complicated configurations of grain boundaries with unknown individual characteristics.

2.6.1 Technical Progress

Epitaxial Materials

We understand vortex motion at low currents in materials that are free of grain boundaries in terms of extrinsic pinning and the intrinsic Josephson coupling between Cu-O bilayers. For larger J , we recently found a crossover from strong to weak pinning at higher temperatures and fields; the crossover is defined by the appearance of a nonlinear $I(V)$, i.e., power-law greater than 1. This crossover in the strength of the pinning seems to mimic the dimensionally crossover of the vortices. We noted this behavior in a number of Tl-based cuprates, some of which have been made in collaboration with GE. We conclude that above this crossover point, random pinning sites are ineffective at large J . In addition, these results allow us to determine the intrinsic intragranular dissipation (by vortex motion) so as to distinguish it from grain-boundary effects in polycrystalline materials.

Polycrystalline Materials

In polycrystalline materials, J_c versus magnetic field first shows a sharp reduction in small fields, then a flat portion, and finally a dramatic drop above the irreversibility field. Compared with that in epitaxial materials, J_c is always lower, except in very large fields where the values are comparable. Thus, pinning is comparable and the reduction in J_c at intermediate magnetic fields is no doubt due to dissipation at grain boundaries. This idea is further supported by $I(V)$ curves on polycrystalline materials that show a characteristic curvature out to magnetic fields much higher than the dimensional crossover of the vortices.

Grain Boundaries

Single-grain boundaries, made by epitaxial growth on specially fabricated substrates, were studied. Examples include a 36.8° bicrystal boundary in YBCO made at Westinghouse and YBCO step-edge devices provided by TRW. The $I(V)$ curves for each, shown in Fig. 37, indicate a smaller, linear low-current resistivity as the coupling energy increases. Because a low-current linear resistivity is often not observed in polycrystalline materials, these grain boundaries must be much more strongly coupled than the individual, high-angle grain boundaries, implying that they are mostly low-angle grain boundaries.

Ion Irradiation

To study the ultimate pinning potential, we have irradiated many polycrystalline and epitaxial samples with 615 MeV Xe ions, which make strong-pinning, columnar damage tracks (Kirk, 1991). Considerable care has been taken to ensure that the incident ion beam profile is uniform and that the ion current is well below levels where heating occurs. The uniformity of the beam was improved to $>10\%$ by scattering it through a gold foil, as confirmed by use of variously sized apertures and a Faraday cup. A TEM image of typical defects is shown in Fig. 38. For epitaxial YBCO, the irreversibility line was substantially enhanced.

2.6.2 Status

Grain Boundaries vs. Pinning from $I(V)$ Analysis

To obtain a single parameter defining the current-carrying capacity requires fitting the $I(V)$ to a model that can reproduce a suitable portion of the actual $I(V)$ with that single parameter. Although in general this is a difficult task, it can be done for the limiting cases of samples dominated by either a single weak-link or Josephson junction, or by pure depinning of flux. An example of the former is shown in Fig. 37. However, the shape of the curves alone cannot uniquely differentiate between these extremes, and some insight is necessary as to the potential magnitude of the effects. For example, the added dissipation associated with weak-link effects in polycrystalline materials can be obtained by directly comparing with similar measurements on epitaxial or single crystalline materials.

Standardization of J_c Values

The consistent determination of J_c is likely our most important basic-research result (Hettinger et al., 1992a). To simplify proper comparisons between laboratories and with industrial partners and evaluations of these results, it is advisable to have more-standardized procedures and interpretations. In collaboration with Los Alamos National Laboratory, we will collect $I(V)$ data from willing participants within the program to help uniformly evaluate the procedures, interpretations, and results, and solicit ideas and advice on the following issues: magnetization and transport techniques and their comparison; definition of J_c and standardized nomenclature; and the ability to distinguish grain-boundary from flux-depinning effects in practical polycrystalline conductors.

Ion Irradiation

Preliminary results indicate that pinning is increased by ion irradiation, even when the vortices are two-dimensional. However, in the two-dimensional region, the pinning depends on the orientation of the magnetic field with respect to the defect tracks, in

Fig. 37. $I(V)$ curves for YBCO step edges

Fig. 38.
TEM image of defects in YBCO
induced by 615 MeV Xe ions

contrast to low-field results reported elsewhere. Studies of the samples with ion damage will determine the role of the vortex dimensionality in the pinning by this type of defect. These studies will yield important information on the value of the $I(V)$ characteristic in determining whether dissipation is occurring by flux motion or at grain boundaries in polycrystalline materials.

2.7 Additional Interactions

The project with American Superconductor Corporation (ASC) has been expanded to include phase-equilibrium and microstructure studies of Ag/Bi-2223 wires prepared by the ANL two-powder method and ASC's metal-precursor process. This project remains an integral part of the wire development group collaboration that includes Oak Ridge National Laboratory, Los Alamos National Laboratory, and the University of Wisconsin-Madison, as well as ASC and ANL. Highlights of ANL contributions to this activity during the past year include determination by a combination of TEM and EDAX of the liquid-phase composition in ASC-produced PIT wires. The liquid composition is approximately $\text{Bi}_{2.2}\text{Pb}_{1.7}\text{Sr}_{1.3}\text{Ca}_{1.0}\text{Cu}_2\text{O}_2$ (Luo et al., 1993c). TEM studies on a series of PIT wire specimens processed for various lengths of time in 7.5% O_2 at 825°C revealed that (1) Bi-2212 is initially in direct contact with the Ag sheath, with (001) planes parallel to the interface; (2) an amorphous layer appears between the Bi-2212 and the Ag sheath during the induction period prior to the onset of Bi-2223 formation (first few hundred minutes); and (3) Bi-2223 is fully formed at the Ag/Bi-Bi-2212 interface several hours before it begins to appear in the regions of the core away from the interface.

The collaboration between Superconducting Products Company (SPC) (of Batavia, IL) and ANL has involved fabrication of Ag-clad wires. A process for continuous forming of tapes from Ag plate or sheet has been developed. This process obviates muzzle loading and tube working and has no inherent length limitation. A U.S. patent application is being prepared, and SPC is attempting to scale up the process.

We continue to work with SSC, Inc. (Bothell, WA) on powder synthesis. Use of SSC precursor powders for Bi-2223 and Tl-2223 appears to be very promising.

We have continued to work with Illinois Superconductor Corporation (ISC) of Evanston, IL, to improve the fracture resistance of bulk superconductors. Previous work at ANL and in collaboration with ISC demonstrated the benefits of Ag additions (Singh et al., 1989; Kupperman et al., 1989), 211-coated ZrO_2 additions (Goretta and Kullberg, 1993), and low-pressure sintering (Goretta et al., 1993). Recent work on hot-deformed Bi-2223 has demonstrated that dense, highly textured bars have reproducible strengths and fracture toughnesses of 150 MPa and $3.0 \text{ MPa(m)}^{0.5}$, respectively. In addition, thick films of Bi-2223 and Tl-2223 were examined for several possible uses.

ANL is working with Ceracon Industries (Sacramento, CA) and Lawrence Livermore Laboratory to consolidate high- J_c melt-textured YBCO. Samples were shocked at pressures up to 12.6 GPa at orientations favorable to cause slipping along the basal planes. Samples shocked at <11 GPa were recovered in one piece, whereas those shocked at higher pressures were fractured. Optical microscopy indicated that microfracturing increased with increasing pressure. Magnetization measurements showed that superconducting currents were decoupled across these fractures. TEM revealed that amorphous materials existed between these fractures, even in material shocked at only 2 GPa. Stacking-fault defects and dislocations were pervasive throughout grains whose basal planes were oblique to the shock wave (Nellis et al., 1993). Work is in progress to understand the effects of high defect densities on flux pinning in these materials.

Levitation-melting of YBCO studies with Intersonics of Northbrook, IL, were completed. It was demonstrated that spheres $\approx 2.5 \text{ mm}$ in diameter could be levitated and then melted by a CO_2 laser. Rapid cooling produced metastable structures that can be used as

precursors for melt-texturing. Intersonics is weighing the decision to scale up the process so that commercial quantities of this unique material can be made.

Work continues with BASF (Asheville, NC) on producing YBCO fibers with well-aligned grains, without having to resort to melt-processing. In this approach, YBCO grains with platelike morphology are aligned at BASF by a proprietary fiber-spinning process. The green aligned samples are then heat treated at ANL in reduced O₂ pressure to remove the organics without decomposing the YBCO.

We have continued collaboration with Ames Laboratory on examination of phase equilibria of the Bi-2223 compound. Ames staff makes extensive use of high-temperature X-ray diffractometry to perform studies similar to those on the Bi-2212 compound (Polonka et al., 1991).

Amorphous precursor powders for Bi-2223 have been prepared by a freeze-drying process that incorporates a splat-freezing step. Critical parameters affecting the drying process were studied. The freeze-dried powders have high reactivity and lead to essentially phase-clean Bi-2223 formation in 12 h. The grain boundaries of the Bi-2223 grains appear to be clean, leading to good intergrain contact between grains (Krishnaraj et al., 1993).

Additional ongoing university collaborations include high-resolution electron microscopy studies with Prof. V. Dravid of Northwestern University, primarily on YBCO grain boundaries; work with Prof. D. L. Johnson of Northwestern University on heat treating YBCO by microwave energy; collaboration with Prof. J. A. Lewis of the University of Illinois at Urbana-Champaign on use of magnetic fields to align YBCO and BSCCO powders in the green state; texture analysis of bulk YBCO and BSCCO with Prof. J. S. Kallend of the Illinois Institute of Technology; creep testing of superconductors with Profs. A. Dominguez-Rodriguez and A. R. de Arellano-López of the University of Seville; and tape forming of Li-doped Bi-2212 with Prof. J. Schwartz of the University of Illinois at Urbana-Champaign.

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