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Practical Superconductor Development for Electrical Power Applications

Annual Report for FY 1998

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**PRACTICAL SUPERCONDUCTOR DEVELOPMENT FOR ELECTRICAL
POWER APPLICATIONS**

ANNUAL REPORT FOR FY 1998

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PRACTICAL SUPERCONDUCTOR DEVELOPMENT FOR ELECTRICAL POWER APPLICATIONS

ANNUAL REPORT FOR FY 1998

Abstract

Development of useful high- T_c 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 FY 1998 technical progress of research and development efforts aimed at producing superconducting components in the Bi-(Pb)-Sr-Ca-Cu and Y-Ba-Cu oxide systems. Topics discussed are synthesis and heat treatment of high- T_c superconductors, formation of monolithic and composite conductors, characterization of structures and superconducting and mechanical properties, and fabrication and testing of prototype components. Collaborations with industry and academia are documented.

1 Introduction

The superconductor program at Argonne National Laboratory (ANL) includes bulk and film processing directed toward improving the properties of high- T_c superconductors (HTSs), 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 to fabricate and use structurally reliable HTSs for 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 HTSs. Work has focused on superconductors based on bismuth-strontium-calcium-copper oxide (Bi-2212), lead-doped bismuth-strontium-calcium-copper oxide (Bi-2223), and yttrium-barium-copper oxide (Y-123).

Monolithic and composite conductors in the form of wires, tapes, films, or other shapes must meet several requirements. 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. The principal impediments to the use of bulk HTSs are low critical current density (J_c) in high applied magnetic fields, relatively poor mechanical properties, and need for very long lengths with uniform properties. Processing methods for the improvement of all of these conductors have been and continue to be developed. The goals of fabrication include promoting high conductivity by obtaining phase-pure final materials with 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 (a) Bi-based HTS wires and tapes; (b) Y-123 superconductors in bulk and tape form; (c) characterization of superconducting and electrical properties, microstructures, and mechanical properties;

(d) investigations of fundamental properties; and (e) fabrication and testing of prototype superconducting devices.

2 Technical Progress in 1997–1998

2.1 Bi–Pb–Sr–Ca–Cu–O Superconductors

2.1.1 Phase Development

Monofilament Conductors

By increasing the sintering temperature of Bi-2223 powder-in-tube (PIT) samples by 20–25°C, to near the Bi-2223 stability limit, we have increased critical current density (J_c) from 1 to 10 kA/cm² in samples with a Pb content of Pb_{0.20}, and from ≈6 to 15 kA/cm² in samples with a Pb content of Pb_{0.25}. For samples with higher Pb content (≥Pb_{0.30}), an increase in the sintering temperature raised J_c only modestly (≈5–10%), despite noticeably increasing density and improving grain alignment. Microscopy showed that impurity phases in samples processed at the higher temperatures tended to spread in thin layers along the Bi-2223 grain boundaries. With this type of morphology, a small amount of impurity phase can cover a large portion of the Bi-2223 grain boundaries and significantly affect performance. Therefore, minimizing second-phase content may be crucial to realizing improved connectivity from the higher density and better grain alignment that are a result of processing near the Bi-2223 stability limit.

One reason that second phases are present in Bi-2223 tapes may be that the overall composition of the tape does not lie within the Bi-2223 single-phase field. When the composition of Bi-2223 grains in fully processed tapes was measured by energy-dispersive analysis of X-rays (EDX), we found that our standard composition, Bi_{1.8}Pb_{0.3}Sr_{2.0}Ca_{2.0}Cu_{3.1}O_x, was slightly rich in calcium and copper relative to the composition of the Bi-2223 grains. Therefore, in an attempt to reduce the second-phase content of our Bi-2223 tapes, calcium- and copper-deficient Bi-2223 powders were prepared. The compositions of the powders, determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), are shown in Table 1. Although Powder 1 was intended to have our standard composition and serve as our reference, ICP-AES showed that it was in fact slightly calcium- and copper-deficient relative to the standard composition. Powders 2 and 3 were progressively more deficient in calcium relative to Powder 1, whereas Powders 4 and 5 were deficient in copper. Monofilament PIT tapes were made from each of the powders, and then short lengths (≈3 cm) of tape were heat treated over a range of temperatures. The microstructures of the heat-treated tapes were examined by scanning electron microscopy (SEM) to identify the composition and overall concentration of impurity phases. Critical current density was also measured.

Table 1. Composition of Bi-2223 powders in terms of stoichiometric coefficients, as determined by ICP-AES

Powder No.	Bi	Pb	Sr	Ca	Cu
1	1.83	0.28	1.97	1.91	3.00
2	1.85	0.27	1.97	1.83	3.00
3	1.85	0.27	1.97	1.76	3.00
4	1.83	0.27	1.98	1.90	2.95
5	1.84	0.26	1.96	1.90	2.88

The Bi-2223 powders were prepared by first making Pb-doped 2212 powders, $\text{Bi}_{1.8}\text{Pb}_{0.3}\text{Sr}_{2.0}\text{Ca}_x\text{Cu}_y\text{O}_8$, in which the calcium content x varied from 0.76 to 0.91 and the copper content y varied from 1.88 to 2.00. Powder mixtures with appropriate amounts of Bi_2O_3 , PbO , SrCO_3 , CaCO_3 , and CuO were first calcined at a reduced total pressure of ≈ 400 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 carbonates. After calcining at reduced pressure, the Bi-2212 phase was formed by further calcining for 24 h at 840°C in CO_2 -free air at ambient pressure. The powders were then ball milled in isopropyl alcohol for 12-16 h and calcined again for 24 h at 840°C in CO_2 -free air at ambient pressure. Calcinations in ambient air were repeated with intermediate ball milling until near-single-phase materials were obtained. X-ray analysis showed that Bi-2212 was the dominant phase in each of the powders, but the most calcium- and copper-deficient compositions also contained small amounts of Bi-2201. Bi-2223-precursor powders were prepared by mixing each of five Pb-2212 powders with an equimolar amount of CaCuO_2 , then ball milling in isopropyl alcohol for 12-16 h and calcining at ≈ 400 Pa ($60^\circ\text{C}/\text{h}$ to 720°C , followed by 3 h at 720°C) to eliminate carbon introduced by milling. PIT tapes were prepared from the Bi-2223-precursor powders.

Samples (≈ 3 cm long) were cut from the tapes and heat treated in 8% O_2 in the temperature range of 823 - 850°C . Thermomechanical processing of the tapes began by annealing for 50 h at the chosen heat-treatment temperature, after which the tapes were uniaxially cold pressed at ≈ 2 GPa. After pressing, the tapes were annealed for an additional 100 h at the selected heat-treatment temperature. The process of pressing and then annealing was repeated until cumulative heat-treatment times of 250 h had been reached. The J_c of each tape was measured by the four-probe method at 77 K in zero applied field with a $1 \mu\text{V}/\text{cm}$ criterion.

Figure 1 shows J_c as a function of temperature for samples heat treated in 8% O_2 for 250 h with two intermediate pressings. These data are for tapes made from Powder 1, but tapes made from the other powders showed similar trends. The sharp decrease in J_c above 842°C suggests that Bi-2223 may be partially decomposing above this temperature. X-ray diffraction patterns from tapes annealed at $\geq 846^\circ\text{C}$ show the presence of Bi-2201, a finding that indicates partial melting of Bi-2223. The increase in J_c up to 842°C is consistent with earlier results, which showed that Bi-2223 is stable in tapes in 8% O_2 up to $\approx 845^\circ\text{C}$. As in the earlier study in which our standard composition was used, the density increased, grain alignment improved, and size of second-phase particles increased from <5 to 5-10 nm as heat-treatment temperature increased from 822 to 842°C .

Figure 2 shows J_c values of the five compositions after processing for 250 h in 8% O_2 at 842°C ; J_c is plotted as a function of calcium or copper deficiency relative to Powder 1, whereas Powder 1 represents "zero" deficiency. The J_c drops significantly when either calcium or copper content is decreased relative to Powder 1. These results may suggest that decreasing the calcium and/or copper content of Bi-2223 powder is not beneficial in terms of J_c or phase purity; however, it should be remembered that Powder 1 was itself deficient in calcium and copper relative to our standard composition. Preliminary examination by SEM qualitatively shows that the amount of second phase in the tapes increases as the composition becomes more deficient in either calcium or copper. In the future, the amount of second phases will be quantified and the second phases will be cataloged. In addition, compositions with calcium and copper contents between those of our standard composition and the composition of Powder 1 may be prepared and tested.

Fig. 1.
 J_c at 77 K vs. temperature for $\text{Bi}_{1.83}\text{Pb}_{0.28}\text{Sr}_{1.97}\text{Ca}_{1.91}\text{Cu}_{3.00}\text{O}_x$ (the standard composition) heat treated in 8% O_2 for 250 h with two intermediate pressings.

Fig. 2.
 J_c at 77 K vs. calcium deficiency and copper deficiency relative to standard composition $\text{Bi}_{1.83}\text{Pb}_{0.28}\text{Sr}_{1.97}\text{Ca}_{1.91}\text{Cu}_{3.00}\text{O}_x$. Samples were heat treated for 250 h in 8% O_2 at 840°C, with two intermediate pressings.

Multifilament Conductors

A major focus of our collaboration with American Superconductor Corporation (ASC) has been on optimization of phase chemistry and microstructure in Ag/Bi-2223 composite conductors. ASC's development work in this area has moved along two related paths. One path has involved optimization of the oxide powder (OP) approach, wherein the precursor is a blend of metal oxides; the second path utilizes a metal powder (MP) precursor. The methodologies for fabricating Ag/Bi-2223 conductors from OP and MP precursors are similar. The principal differences between the OP and MP approaches are related to the facts that MP composites are subjected to most of their mechanical deformation (by drawing and rolling) while the precursor powder is still in the metallic state and that after drawing and rolling, MP composites require a special thermal treatment to convert the metallic precursor into oxide phases before the series of heat treatments that transform the precursor powder into Bi-2223 is initiated.

We have addressed several key aspects of phase and microstructure development during heat treatment of multifilament Ag/Bi-2223 tapes. The composition of the precursor powders used to manufacture the OP tapes included in this report was $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.9}\text{Ca}_{2.0}\text{Cu}_{3.0}\text{O}_y$. The MP precursors were slightly richer in Cu. Heat treatments were initiated by immersing 20-mm-long tapes into a preheated furnace that contained, in most cases, 7.5% O_2 in N_2 . After heat treatment for 10-6000 min, the tapes were quenched in an oil bath. We used the immersion-heating procedure ($\approx 80^\circ\text{C}/\text{min}$) to

minimize the time spent below the desired heat-treatment temperature. Similarly, we used a rapid quench at the end of the heat treatment to inhibit phase transformations that occur during the usual types of postheat-treatment furnace-cooling procedure that are employed with Ag/Bi-2223 conductors. These two special procedures (immersion heating and quenching) have allowed us to examine phase formation and kinetics along the isothermal heat-treatment plateau without the complicating effects of normal ramp-up and cool-down protocols used in the manufacture of Ag/Bi-2223.

In this report, we present results for 361-filament MP wires and for 361-, 85-, and 19-filament OP wires to provide an MP-vs.-OP comparison at the 361-filament level and to examine the effects of filament count and filament architecture on OP composites. In the course of this work, we explored the effect of oxygen partial pressure, pO_2 (0-0.13 atm), heat-treatment temperature (790-845°C), and time (0-6000 min) on the kinetics of Bi-2223 formation and conductor microstructure.

Our accumulated experience with the effect of pO_2 on the phase transformation behavior of Ag-sheathed Bi-2223 precursors continues to suggest that a pO_2 of ≈ 0.08 atm is optimal. To check this for the multifilament composites examined in the present study, we obtained phase-conversion data at 815°C for 361- and 85-OP wires at pO_2 between 0 and 0.13 atm, with a processing time of 6000 min. The results of this study (Fig. 3) indicate that a pO_2 of 0.075 atm (the value used in much of our prior work) will support high conversions of the precursor to Bi-2223 for both the 361- and 85-OP composites; but it should be noted that the optimal range is decidedly broader for the composite with the higher filament count. Results included in Fig. 3 for the same two composites at a lower temperature (790°C) illustrate how the Bi-2223 content (even after 6000 min) drops off sharply at temperatures slightly below 800°C. These results support the choice of 0.075 atm O_2 as the base-case pO_2 for subsequent studies.

Further information about the effect of temperature on the Bi-2223 formation rate for MP and OP composites is presented in Fig. 4, where we show the fractional conversion of Bi-2212 to Bi-2223 for selected specimens processed for 1000 min in 0.075 atm O_2 . This time interval was carefully selected so that no specimens reached 100% conversion before the quench, which allowed us to map the relative reaction rates at all test temperatures. The results in Fig. 4 for the 85-, 19-, and monofilament OP composites were obtained with specimens that exhibited identical powder stoichiometry (base case) and phase chemistry. Results are also shown for two 361-filament MP composites with an unknown preheat-treatment phase chemistry because of the as yet unresolved consequences of the post-rolling oxidation step used to convert the MP precursor to a predominantly oxide form before heat treatment. Putting this uncertainty aside, it is clear that the 85- and 19-filament OPs exhibited a broader lower-temperature-shifted reaction profile than the monofilament OP, and that the 361-filament MPs exhibited an even broader profile and appreciably enhanced kinetics.

Measurement of the length of the Ag/ceramic powder interface and the cross-sectional area of typical filaments (obtained from SEM images), which essentially define the surface-area-to-volume ratio of these filaments, provides a correlation for the results shown in Fig. 4. The interface-to-cross-section ratio of the OP monofilament is 40 mm^{-1} , whereas the ratios of the 85- and 19-filament OPs are 112 and 102 mm^{-1} , respectively.

Fig. 3.

Fractional conversion of Ag/Bi-2223 precursor to Bi-2223 in 85- and 361-filament OP composites at 815 and 790°C for various values of pO_2 .

Fig. 4.

Fractional conversion of precursor to Bi-2223 in selected MP and OP Ag/Bi-2223 composites after 1000 min in 0.075 atm of O_2 . Number after slash is filament count.

The ratio for the two 361-filament MPs is difficult to measure (for reasons that will become apparent later), but the value of this ratio is $\approx 300 \text{ mm}^{-1}$. We believe that increased proximity of the precursor powder to the Ag sheath is the principal reason why the peak reaction rate increases, the overall profile broadens, and the peak of the profile seems to shift to a lower temperature as the filament count increases. This result is consistent with our earlier monofilament work, which showed that in the initial stages of heat treatment, Bi-2223 formation proceeds more rapidly at the Ag/ceramic powder interface than in the bulk of the specimen. In fact, the earlier results implied that the reaction was complete at the interface before it even started in the midcore region of a given filament.

Another series of measurements was conducted to explore the fractional conversion of Bi-2212 to Bi-2223 as a function of time at the base case ($pO_2 = 0.075 \text{ atm}$) and several selected temperatures in peak regions of the reaction profiles shown in Fig. 4. In Fig. 5, we show conversion-vs.-time results obtained at 810°C from one of the 361-filament MP composites presented in Fig. 4. The results in Fig. 5, and similar results from other MP and OP composites, were analyzed by the model developed independently by Avrami and Erofe'ev. In this much-simplified presentation, the fractional conversion to Bi-2223, F , is equated to time by the relationship $\ln(1-F) = kt^n$, where k is a rate constant, t is time, and

Fig. 5.
 Fractional conversion of
 precursor to Bi-2223 in 361-
 filament MP composite heat
 treated at 810°C for various
 times in 0.075 atm of O₂.
 Results of Avrami-Erofe'ev
 analysis are also summarized.

n is the exponent of time. In our work, we express F as being equal to $B/(\alpha A + B)$, where A is the XRD peak intensity of the (008) reflection of Bi-2212, B is the intensity of the (0010) reflection of Bi-2223, and α is a coefficient to correct for differences in XRD scattering factors and other related effects. A value of 0.44 for α has been generally recommended, but to account for the fact that the expression for F in terms of A and B ignores the fugacity of secondary phases in the reacting ceramic powder, α can be taken as 0.88. In the past, we have treated our results as if α were equal to 1.0, and have found that the key conclusions to be drawn from analysis of results like those in Fig. 5 are not appreciably affected by this choice for the value of α .

The results of the Avrami-Erofe'ev modeling are presented in Table 2. Whereas the value of k tends to vary widely, depending on wire type (MP or OP), filament count, and temperature, the value of n at temperatures near the peak of the reaction profile (820-830°C) is consistently in the range of 1.5 ± 0.3 , regardless of whether we use $\alpha = 1.0$ or $\alpha = 0.88$. Values of n in this range imply general conformance to several mechanisms, including one that is fully consistent with many observations in the published literature about phase evolution and microstructure development in Ag/Bi-2223 composite conductors, namely, diffusion-controlled, two-dimensional (platelike) growth under conditions of steady to decreasing nucleation rate. At temperatures near the onset points of the reaction profiles in Fig. 4, the value of n often drops below 1.0 (see, e.g., Table 2), possibly indicating a different Bi-2223 formation mechanism at temperatures below the temperature region of the most rapid kinetics.

Table 2. Summary of fitting parameters from Avrami-Erofe'ev^a analyses of OP and MP kinetic data

Temperature (°C)	Filament Type/Count	Fitting Parameters			
		a	n	k	1-Sigma
810	MP/361	1.00	1.19	7.6E-05	0.026
	MP/361	0.88	1.16	1.0E-04	0.028
	OP/85	1.00	0.94	8.4E-04	0.040
	OP/85	0.88	0.93	9.9E-04	0.042
825	OP/19	1.00	1.60	1.4E-05	0.050
830	MP/361	1.00	1.71	1.2E-05	0.086
830	MP/361	0.88	1.69	1.4E-05	0.086
830	OP/85	1.00	1.76	1.3E-06	0.075
830	OP/85	0.88	1.67	2.6E-06	0.083

^aFit to $\ln(1-F) = -kt^n$ for $F = [\text{Bi-2223}] / (a [\text{Bi-2212}] + [\text{Bi-2223}])$.

The principal microstructural differences between the monofilament and multifilament conductors examined in this study are related to the overall cross-sectional area of individual superconducting filaments and the ratio between the volume of each filament and its surface area. Both of these properties tend to decrease with increasing filament count for composites with the same transverse dimensions. When the cross-sectional area of the filaments is reduced, the largest nonsuperconducting secondary phases (usually copper oxide or alkaline earth cuprates that can be as large as 10 μm in major dimension) can begin to occupy a significant fraction of the cross-sectional current path and possibly cause major blockages of the current path. When the Ag/powder interface area is increased relative to the powder volume (a general consequence of increasing the filament count), the proximity of superconducting material to Ag is increased, as discussed above.

Figure 6 shows SEM images of 19-filament OP composite specimens after immersion heating to 800°C in 0.075 atm O₂ and instantaneously quenching (Image a in Fig. 6), and after immersion heating to 825°C in 0.075 atm of O₂ then heat treating for 300 and 4000 min (Images b and c in Fig. 6, respectively). With data like those in Fig. 5 for this particular 19-filament conductor as a guide, the instantaneously quenched sample should contain no Bi-2223, the 300-min specimen should contain $\approx 10\%$ Bi-2223, and the 4000-min sample should contain $>90\%$ Bi-2223. These results show that second-phase crystallites (the dark particles in Fig. 6) are present in the immersion-heated OP specimens during the initial stages of Bi-2223 formation. The results also reveal how grain growth progresses as the Bi-2223 formation reaction moves toward completion. The size and relative abundance of the secondary phases and their progressive dissipation as the reaction to form Bi-2223 proceeds are also noteworthy.

The broader processing window for multifilament composites, indicated by the reaction profiles in Fig. 4, raises questions about the influence of heat-treatment temperature at temperatures where the Bi-2223 formation kinetics are sufficiently rapid to allow complete conversion to Bi-2223 in ≈ 100 h. In Fig. 7, we show results for two 85-filament specimens processed in 0.075 atm of O₂ for 4000 min at 830 or 810°C. The percent conversion of Bi-2212 to Bi-2223 was $\approx 90\%$ at 830°C and $\approx 85\%$ at 810°C, but the

Fig. 6. SEM images (transverse view) of 85-filament Ag/Bi-2223 OP composite specimens processed in 0.075 atm of O_2 for (a) 0 min at 800°C, (b) 300 min at 825°C, and (c) 4000 min at 825°C before quench.

Fig. 7. SEM images (transverse view) of 19-filament Ag/Bi-2223 OP composite specimens processed at 830 and 810°C in 0.075 atm of O₂ for 4000 min.

microstructures differed significantly. The specimen heat treated at 830°C contained a Bi-2223 grain structure that was better developed, but also contained domains of appreciable second-phase growth (dark regions) and exhibited numerous platelike protrusions of Bi-2223 grains into the Ag sheath. The Bi-2223 grain structure in the specimen that was heat treated at 810°C was not nearly as well developed, but the second phases were smaller and there were no platelike growths into the Ag sheath. It was subsequently determined that a heat-treatment temperature of 820°C produced the best critical-current properties for fully processed versions of this particular composite.

The microstructure of Ag/Bi-2223 multifilaments produced by the MP processing route was unusual. Images obtained by SEM of a 361-filament MP composite, as-received and at two stages of heat treatment, are shown in Fig. 8. In all three transverse views, it is difficult to distinguish one filament from another, in that all of the filaments seem to run together. Several possible causes can be proposed for this filament-blurring effect, e.g., (1) virtually all of the mechanical deformation on an MP wire occurs before heat treatment,

Fig. 8. SEM images (transverse view) of 361-filament MP composite specimens (a) as-received with 0% Bi-2223 and processed at (b) 810°C/300 min/0.075 atm O₂/33% Bi-2223, and (c) 830°C/1500 min/0.075 atm O₂/100% Bi-2223.

and blurring is perhaps a consequence of the close match of the mechanical properties of the Ag sheath and the mostly metallic precursor powder; (2) formation of liquid metal phases that partially dissolve the Ag sheath during the special oxidation step that is used to convert the metallic precursor powder to an oxide before what we refer to herein as heat treatment. Specific influences of each of these factors on the microstructure observed in Fig. 8 need more detailed study.

The 361-filament MP composites exhibited the broadest reaction profile of any sample examined in this study, as can be seen in Fig. 4. Within the broad temperature window shown in Fig. 4, we found two noteworthy effects, which are illustrated by the SEM results in Fig. 9. Comparing XRD data for the two specimens processed at 820 and 840°C for 1500 min (in 0.075 atm of O₂), we find that the percent conversions to Bi-2223 are essentially the same (76% and 79%, respectively). As can be seen in Fig. 9, the microstructures are also much the same in terms of the size, content, and spatial distribution of second phase. However, a comparison of the SEM results for the two specimens processed at 820°C for 1500 and 4000 min indicates that second-phase growth at the longer processing time is significantly greater. The determination that the specimen processed for 4000 min at 820°C is >80% converted to Bi-2223 (relative only to Bi-2212), together with the appearance of large regions of second-phase growth in the corresponding SEM image, suggests that there may be an optimal heat-treatment time for MP composites beyond which Bi-2223 phase content begins to drop off because of decomposition.

Energy-dispersive X-ray analyses performed in conjunction with the SEM measurements revealed that the second-phase material seen in Figs. 8 and 9 is mostly CuO, with some (Ca,Sr)₂CuO₃ (2/1 alkaline earth cuprate). In particular, most of the dark phases near the Ag/ceramic interfaces and in the bulk Ag are CuO. The microstructures seen in Figs. 8 and 9 (before and after heat treatment) were investigated in greater detail by transmission electron microscopy (TEM). The image in Fig. 10 shows a longitudinal view of a typical filament in a 361-MP specimen after the MP oxidation step but before heat treatment. This view reveals the severe sausaging that was commonly observed in the MP composites prepared for this study.

Finally, some information about texture development in high-filament-count Ag/Bi-2223 conductors was gained from XRD measurements on specimens of 361-OP and 361-MP composites that were heat treated under conditions that favored nearly complete formation of Bi-2223. XRD can be used to probe the extent of texturing of the Bi-2223 phase in Ag/Bi-2223 composites, and, in the case of the 361-OP and 361-MP specimens prepared for this particular investigation, we found that the 361-MP composite exhibited significantly better texture than the 361-OP composite after heat treatment at 820°C in 0.075 atm of O₂ for 4000 min. This result is illustrated in Fig. 11, which shows XRD patterns for the 361-OP and the 361-MP specimens. The higher count levels and stronger (001) texturing of the 361 MP are clearly evident. The ceramic filament cores in heat-treated 361-MP specimen were less porous in both transverse and longitudinal SEM views than any of the OP multifilaments we investigated. This observation can be appreciated by comparing the images in Figs. 6 and 7 with the ones in Figs. 8 and 9. The superior texturing of 361-MP composites appears to be a beneficial consequence of their compact microstructure.

Fig. 9. SEM images (transverse view) of 361-filament MP composite specimens processed at (a) 820°C/1500 min/0.075 atm O₂/76% Bi-2223, (b) 840°C/1500 min/0.075 atm O₂/79% Bi-2223, and (c) 820°C/4000 min/0.075 atm O₂/88% Bi-2223.

Fig. 10. TEM image (longitudinal view) of as-received 361-filament MP composite, illustrating a commonly observed region of sausaging.

Imaging Raman Microscopy Studies

Raman microspectroscopy and imaging Raman microscopy have proved to be powerful tools for studying the evolution and spatial distribution of chemical phases in the bismuth- and thallium-based families of high- T_c superconducting ceramics. These techniques, in conjunction with SEM and EDX spectroscopy, have been applied to compressed/sintered powders and silver-clad composite conductors. Many important insights have been gained about the identity, size, shape, orientation, and spatial distribution of the various nonsuperconducting secondary phases (NSPs) that form and dissipate during heat treatment of the silver-clad tapes.

The results have allowed us to determine key mechanistic features that control/influence the formation of the superconducting phases as heat treatment progresses, including the location of Pb-rich NSPs and identification of the constituent phases in certain NSP agglomerations that tend to resist dissipation as high- T_c phase formation proceeds to completion. Results of recently completed studies on samples are summarized below.

In a published study in which magnetization and XRD methods were used, we reported some observations concerning the influence of bismuth substitution on liquid formation in heavily strontium-doped Ag/M-1223 composite conductors, in which $M = \text{Tl} + \text{Bi} + \text{Pb}$. An extension of this study that included samples doped with both bismuth and lead produced a series of samples that we have investigated. For this particular series of samples, the

Fig. 11. XRD patterns for (a) 361-filament OP and (b) 361-filament MP composites, heat treated for 4000 min at 820°C in 0.075 atm of O₂.

ceramic powder stoichiometry was $Tl_aBi_bPb_cBa_{0.4}Sr_{1.6}Ca_{2.0}Cu_{3.0}O_x$, where $a + b + c$ was kept at 1.1. Three composite wires with varied thallium and bismuth content, and two wires with varied thallium, bismuth, and lead content were heat treated at 840°C for 20 h in 0.08 atm of O₂. Specimens from all five wires were mounted in epoxy, polished, and examined by the two Raman microscopy techniques to determine phase content. The remaining segments of the five wires were subjected to a second heat treatment at 870°C