

**Phase Stability and Grain Growth in an Ag/Bi-2223 Composite  
Conductor Prepared Using Fine-Grained Bi-2223 as a Precursor\***

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# Phase Stability and Grain Growth in an Ag/Bi-2223 Composite Conductor Prepared Using Fine-Grained Bi-2223 as a Precursor

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**Abstract**--We have investigated the stability and microstructural transformability of the Bi-2223 phase in a silver-sheathed monofilament composite tape fabricated using fine-grained  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.9}\text{Ca}_{2.0}\text{-Cu}_{3.0}\text{O}_y$  (Bi-2223) as the precursor powder. The fully formed Bi-2223 precursor was prepared using established procedures. The purpose of this study was to explore the prospects for growing textured, large-grain-size Bi-2223 from the fine-grained precursor by process parameter perturbations. These perturbations included thermal ramp up variations, programmed heat treatment temperature and oxygen pressure fluctuations, and parameter manipulations during cool-down. Our results show that the types of heat treatments used in conventional oxide-powder-in-tube (OPIT) processing do not facilitate Bi-2223 grain growth when the precursor powder is preconverted Bi-2223. We also observed that the Bi-2223 partially decomposed during conventional thermal ramp-up in 0.075 atm  $\text{O}_2$ , but that this decomposition can be inhibited by ramping up in a reduced oxygen pressure. A pathway was found for back-reacting the fine-grained Bi-2223 (to Bi-2212, Bi-2201 and nonsuperconducting secondary phases), then reforming large-grained Bi-2223 in a colony microstructure having some distinct differences from that produced during conventional OPIT processing.

## I. INTRODUCTION

The silver-sheathed  $(\text{Bi},\text{Pb})_2\text{Sr}_2\text{Ca}_2\text{-Cu}_3\text{O}_y$  (Ag/Bi-2223) composite conductor in long length multifilament form stands today as the state-of-the-art for practical utilization of high-critical-temperature (high- $T_c$ ) superconductivity in electric

power applications [1-5]. Achieving the levels of current carrying capacity in the Ag/Bi-2223 composite conductor required for such applications has spurred a substantial development effort to optimize processing strategies and to refine processing parameters [6-10]. In order to obtain high  $J_c$  and good in-field properties in these materials, it is essential to have large-grained, textured microstructures with extremely fine secondary phases that can act as pinning centers [11]. In two prior studies, Duo et al. [12] and Parrell et al. [13] also investigated the Bi-2223 decomposition-reformation route. Their work showed that such treatments can influence the microstructure, phase chemistry, and performance properties ( $J_c$  and flux pinning) of Ag/Bi-2223 composites. However, in both cases [12,13], the starting phase assemblage in the tape was Bi-2212 and secondary phases to give an overall Bi-2223 stoichiometry. In our work, the starting phase assemblage is fine-grained 95% pure Bi-2223 with minor amounts of Bi-2212 and secondary phases. We have found a pathway for back reacting this fine-grained Bi-2223 (to Bi-2212, Bi-2201 and secondary phases), then reforming large-grained Bi-2223 in a colony microstructure, distinct in some respects from that produced by conventional OPIT processing.

## II. EXPERIMENTAL PROCEDURE

The monofilamentary OPIT Ag/Bi-2223 composite tapes employed in this research were prepared by methods described in previous publications [6-8]. The precursor powder used in this study had the nominal composition  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.9}\text{Ca}_{2.0}\text{Cu}_{3.0}\text{O}_y$  and was composed of fine-grained Bi-2223 mixed with

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small amounts of Bi-2212 and alkaline earth cuprates. The precursor powder was prepared by a freeze-dry process.

Short samples (ca. 1 inch long) cut from a monofilament tape were either ramp heated (10°C/min up to 800°C and 2°C/min to 825°C) or immersion heated (100°C/min) to an initial processing temperature of 825°C in a 3-zone resistively heated furnace under a  $pO_2$  of either 0.075 atm or 0.046 atm. Temperature excursions either downward to 780°C for 30 minutes or upward to 855°C for 20 minutes were programmed into the anneal cycle after an initial 3000 minute hold at 825°C in 0.075 atm  $O_2$ .  $pO_2$  variations to 0.002, 0.02 and 0.046 atm during annealing at 825°C were also studied. Samples were either quenched or furnace cooled after each heat treatment [14]. They were characterized using scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDS), and x-ray diffraction (XRD) in the manner described by Luo et al. [14] and Merchant et al. [15].

### III. RESULTS AND DISCUSSION

Figure 1 shows two of the types of heat treatment cycles used in the decomposition-reformation studies reported here. XRD measurements on samples annealed under the cycle depicted in Fig. 1a but quenched after 0 minutes at 825°C in 0.075 atm  $O_2$  revealed that as much as 50% of the Bi-2223 phase decomposed to Bi-2212 and secondary phases during the ramp-up to 825°C. A similar decomposition of the Bi-2223 phase was also observed when the samples were immersion heated. However, in subsequent studies we found that this decomposition, could be fully arrested by ramp heating the sample to 825°C under a  $pO_2$  of 0.002 atm. This can be mainly attributed to the fact that the phase stability boundaries of Bi-2223 are crossed during ramp up in 0.075 atm  $O_2$ , but are not in the lower  $pO_2$  of 0.002 atm [15].

Figure 2 shows an SEM micrograph of the transverse cross section of a sample annealed for 6000 minutes in 0.075 atm  $O_2$  at 825°C and furnace cooled. The micrograph shows that layered phase grain growth is essentially nonexistent and that transverse cracks appear with regularity. This, we

believe, is due to the fact that during normal OPIT processing of a tape that has Bi-2223 as the major phase to begin with, no liquid phase is formed during heat treatment to facilitate grain growth. Also, cracks that may have formed during the deformation processing before the annealing cannot be healed due to the persistent absence of liquid phase.

Figure 3 shows an SEM micrograph of a sample annealed using the cycle shown in Fig. 1b, which features a 20 minute excursion to 855°C followed by a 3000 minute recovery treatment at 825°C. It is evident from the micrograph that layered phase grain growth does occur under these conditions. Also, no cracks are visible in the sample, indicating that all cracks formed during the deformation processing are healed, quite possibly due to the presence of a liquid phase. XRD showed that the sample is 80% Bi-2223, 16% Bi-2212, and ca. 4% Bi-2201. It is

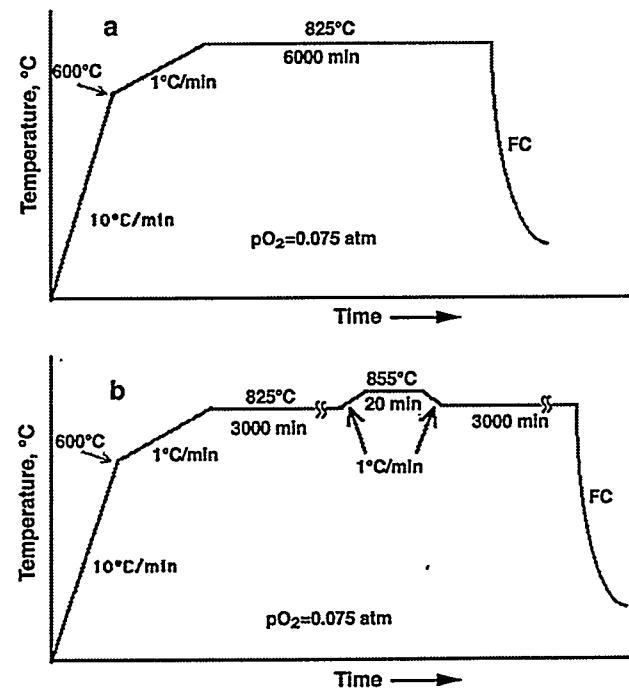


Fig. 1. Heat treatment cycles for Ag/Bi-2223 decomposition/reformation tests: (a) blank run and (b) partial melt simulation procedure.

not clear that annealing the sample for a time longer than 3000 minutes after the

reformed by post annealing at 825°C in 0.075 atm O<sub>2</sub>. Some efforts were also made to manipulate the microstructure via low pO<sub>2</sub> anneal, (e.g., use of 0.02 atm and 0.002 atm O<sub>2</sub> at 825°C); how-

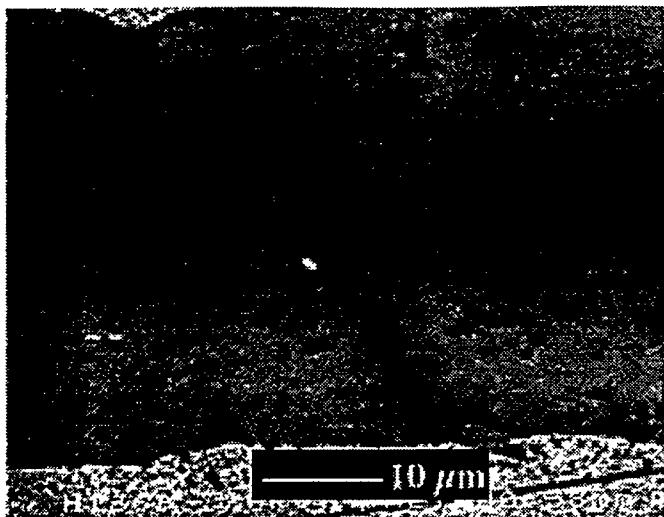


Fig. 2. SEM micrograph in backscatter mode of transverse section of monofilament sample annealed for 6000 minutes at 825°C in 0.075 atm O<sub>2</sub>.

high temperature excursion will necessarily produce complete reformation of the Bi-2223. Alternatively, the excursion temperature and/or time may have to be shortened to limit the decomposition of Bi-2223. It is also noteworthy that the nonsuperconducting secondary phases are really quite small after this decomposition-reformation treatment.

Figure 4 shows a TEM micrograph of a sample that was subjected to the cycle in Fig. 1b. This micrograph highlights a unique microstructural effect of the decomposition-reformation treatment, i.e., the occurrence of large adjacent Bi-2223/Bi-2212 grain colonies near the Ag/superconductor interface that have (001) orientation.

Our efforts during this study to investigate low temperature dips in the anneal cycle e.g., 825°C for 3000 minutes/780°C for 30 minutes/825°C for 3000 minutes in 0.075 atm O<sub>2</sub> had no discernable impact on the Bi-2223 microstructure. Also, attempts to use longer excursion periods (e.g., 855°C for up to 920 minutes) resulted in substantial decomposition of the Bi-2223 layered phase (80%+) with concomitant large secondary phases that could not be

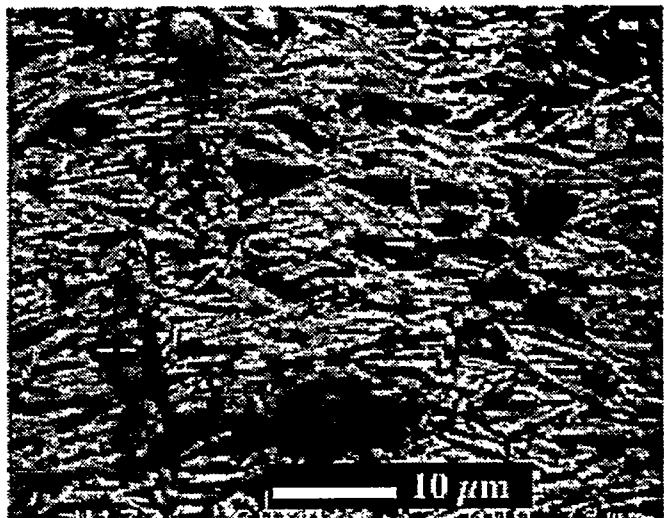


Fig. 3. SEM micrograph in backscatter mode of transverse section of sample annealed using cycle shown in Fig. 1b.

ever, these manipulations led to results similar to the extended high temperature excursions, i.e., substantial decomposition of the Bi-2223 phase (over 80%) that could not be recovered to any significant extent by post annealing.

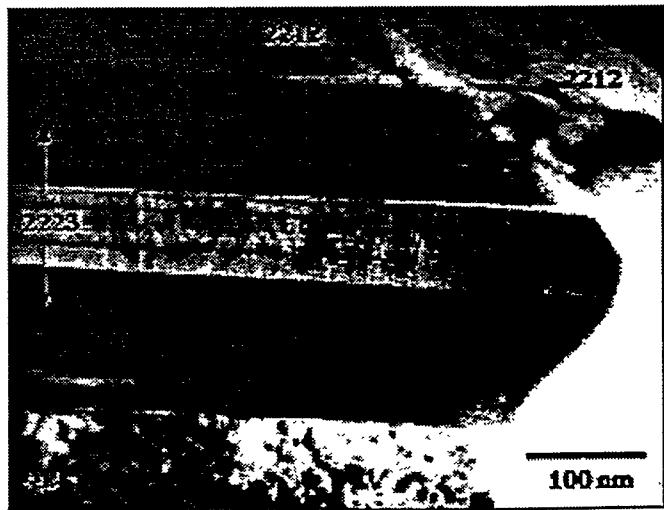


Fig. 4. TEM micrograph of sample subjected to 855°C excursion, showing large colonies of Bi-2223 and Bi-2212 grains.

#### IV. CONCLUSIONS

Preconverted Bi-2223 in a silver sheath backreacts to Bi-2212 plus secondary phases during ramp and immersion heating in 0.075 atm O<sub>2</sub>. This decomposition can be arrested by use of 0.002 atm O<sub>2</sub> during ramp up. Extended heat treatment at 825°C in 0.075 atm O<sub>2</sub> reforms nearly all of the Bi-2223 phase, but does not result in any significant grain growth. Intermittent temperature dipping to 780°C does not have any visible effect on the microstructure of the layered phase. Extended excursions at high temperature (to 855°C in 0.075 atm O<sub>2</sub>) and reduced pO<sub>2</sub> anneal (0.02 atm O<sub>2</sub> and lower at 825°C) led to melting/decomposition of the Bi-2223 phase that can be only partially reformed by annealing at 825°C. Brief temperature excursions to 855°C (0 to 20 minutes) followed by extended anneal at 825°C in 0.075 atm O<sub>2</sub> lead to layered phase grain growth, elimination of cracks and reduced secondary phases. This general type of treatment (decomposition/reformation) represents an interesting and potentially effective technique for improving J<sub>c</sub> and flux pinning in Ag-clad Bi-2223 composite conductors.

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