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Author(s): Terry G. Holesinger, MST-6

Submitted to: Proceedings of the Fall 2001 Meeting of the Materials Research Society, Boston, MA, November 26-30, 2001.

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The Early Stages of the Microstructural Development of the Colony Structure in Bi-2223 Tapes

T.G. Holesinger

Materials Science and Technology Division, Los Alamos National Laboratory,
Los Alamos, NM 87545 U.S.A.

ABSTRACT

The current protocol for processing $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-x}$ (Bi-2223) multifilamentary tapes involves the *in situ* formation of the primary phase from a suitable mixture of precursor phases. As such, the developments during the first few minutes of heat treatment determine to a large extent the efficiency of primary phase development, competing secondary phase development, texture evolution, and grain-to-grain connectivity. This work documents the development of the liquid phase, secondary phases, defects which may affect alignment and reaction kinetics, and the precipitation of Bi-2223 from the liquid phase.

INTRODUCTION

It is commonly held that most of the transport current in Bi-2223 tapes is carried close to the silver interface. Hence, it is of interest to document this particular microstructure and determine the conditions during processing that shape its development. The overall structure in fully processed tapes has been documented by electron microscopy as well as by *in-situ* neutron and synchrotron x-ray diffraction [1-7]. Only a few of the electron microscopy studies have focused on the through-process microstructure development while *in-situ* XRD and neutron studies suffer from a lack of spatial resolution in tracking phase development within the filaments as a function of position. In this work, phase, microstructure, and composition development in Bi-2223 tapes were examined. An emphasis was placed on detailing the structure and composition of the Bi-2223 development during the initial stages of processing.

EXPERIMENTAL

Multifilament Bi-2223 tapes at various stages of processing were examined by analytical electron microscopy. The starting composition of the Bi-2223 powder used in the 19-filament tapes was $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.9}\text{Ca}_{2.0}\text{Cu}_{3.0}\text{O}_y$. All of the tapes used in this work were processed at 827°C in 8% O_2/N_2 . After ramping up to the processing temperature, the Bi-2223 tapes were held for a short dwell time and then quenched into an oil bath. The dwell times were 0, 10, 100, 300, 400, 500, and 640 minutes. The critical current densities (J_c) of fully processed tapes from this series of samples reached 70 kA/cm² at 77 K and self-field.

These tapes were examined from three principle directions of view in scanning and transmission electron microscopes (SEM and TEM): short transverse section, longitudinal transverse section, and plan view. Final TEM and SEM specimen preparations were accomplished with dimple polishing and ion-milling. Compositional measurements were performed in the TEM using energy dispersive spectroscopy (EDS). Standards consisted of

Figure 1: Comparison of the changes in the microstructure between the as-rolled Bi-2223 tapes, (a) SEM and (c) TEM, and the microstructure of the tapes quenched after ramping up to the processing temperature of 827°C, (b) SEM and (d) TEM.

amorphous Bi-2212 and Ca_2PbO_4 . Details of the compositional quantification method can be found elsewhere [4].

DISCUSSION

The development of the microstructure and alignment in Bi-2223 tapes starts with the initial rolling and ramp up to temperature as indicated by the micrographs in Figure 1. The as-rolled tape consists of several sub-micrometer sized precursor phases of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (Bi-2212), alkaline-earth cuprates (AEC's), and CuO as shown in Figure 1a and c. Interfacial roughness between the silver and BSCCO arises during the rolling stage as shown in Figure 1a,

Figure 2: TEM micrographs of (a) highly-deformed Bi-2212 grains in the as-rolled tapes, (b) the random nucleation and growth of the Bi-2212 phase on the AEC's during the early stages of heat treatment, and (c) formation of crack structures in the filaments of the as-rolled tapes.

but appears to be smoothed out by the rapid grain growth that occurs during initial heating. Figures 1b and d show the resulting microstructure of Bi-2212, $(\text{Sr,Ca})_2\text{CuO}_2$ (2:1 AEC), and $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ (14:24 AEC) that develops during the thermal ramp. The Ca-rich 2:1 AEC phase assumes a needle-shaped morphology that can exceed 10 μm, while the $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ (14:24 AEC) develops as a blocky phase 1-2 μm in size.

Defects that can affect the formation of the Bi-2223 colony structure can arise in these early stages of processing. The rolling process severely distorts and even amorphizes the Bi-2212 phase as shown by the grain bending, basal plane defects, and regions of amorphous material in Figure 2a. This accumulation of damage is one reason for the rapid and somewhat uncontrolled growth of the Bi-2212 phase during the early stages of heat treatment. Rapid grain growth is also observed with the crystallization of amorphous Bi-2212 glasses [8]. The initial texture imparted by the rolling process and the presence of the silver sheath can partially control the development of the Bi-2212 phase. However, other defect structures in the tapes can also affect

the recrystallization of the Bi-2212 phase. The AEC's provide nucleation sites for the alignment and growth of the Bi-2212 phase as indicated in Figure 2b. Since the AEC's are randomly aligned, the nucleation and growth of the Bi-2212 phase from these AEC's can also be expected to be random with respect to the silver sheath. Large crack structures, as shown in Figure 2c, can develop in the matrix of the as-rolled tapes. Although broadly textured (c-axis perpendicular to the silver sheath) by the rolling process, the local alignment of the Bi-2212 grains can be drastically altered in the vicinity of the crack structures. During subsequent processing, this defect structure may lead to the development and growth of Bi-2212 grains that are also misoriented with respect to the silver sheath. These two effects are important to understand as the local development of the Bi-2223 is directed by the local alignment of the Bi-2212 phase.

The formation of the Bi-2223 phase typically involves the presence of a liquid phase. The liquid phase arises from the interaction of the AEC's, CuO, and Bi-2212 phases [9]. The liquid phase forms slowly and is often found with small silver or silver-copper precipitates as indicated in Figure 3a. Hence, small particles of silver trapped within the filaments appear to promote the formation of the liquid phase early in the heat treatment. The composition of the liquid averaged over all the samples was $\text{Bi}_{1.24}\text{Pb}_{0.92}\text{Sr}_{0.70}\text{Ca}_{0.44}\text{Cu}_{1.70}\text{O}_y$. The latter composition did not differ significantly from the individual measurements of the liquid phase as a function of processing time indicating that the liquid phase is thermodynamically stable. The measured composition of the liquid phase is not similar to the nominal Bi-2212 stoichiometry as was suggested by an earlier work [10]. In the present work, the stoichiometry of Bi,Pb-2212, in the presence of the liquid phase, was measured to be $\text{Bi}_{1.88}\text{Pb}_{0.29}\text{Sr}_{1.75}\text{Ca}_{1.04}\text{Cu}_{2.04}\text{O}_y$.

In the early stages of heat treatment, the liquid phase is confined to interstices between grains in the filament. Bi-2223 development does not start until sufficient liquid phase has formed to burst out of its confines, flow through the filament structure, and consume the precursor phases more rapidly as indicated in Figure 3b. This period of time, between 100 and 300 minutes, is analogous to the induction period described in an earlier work [11]. Bi-2223 grains found in the early stages of heat treatment were always associated with a liquid phase in agreement with earlier works [9,12]. The TEM micrograph of Figure 3b shows directly for the first time the formation (white arrow) of the Bi-2223 phase via precipitation from the liquid phase within the filaments. Note that the Bi-2223 phase is assuming the approximate alignment of the existing Bi,Pb-2212 phase. This result confirms the earlier work that showed Bi-2223 precipitating from a lead-rich liquid on the surface of a pressed pellet [12]. Intergrowths of the Bi-2212 phase are commonly found in the converted grains as indicated in Figure 3c. However, they are non-uniformly dispersed and their density is directly proportional to the distance from the adjacent liquid phase suggesting different diffusion rates for the individual components within the liquid phase.

As the Bi-2223 precipitates, a shell of Bi-2223 is formed around the pocket of the liquid phase as indicated in Figure 3b. Since the Bi-2223 phase can be in equilibrium with the liquid phase, such a structure would be stable and would act to confine and inhibit the liquid phase from consuming more of the precursors. Hence the need for an intermediate deformation step to break up these structures and allow the reactions to proceed to completion. Another detrimental effect of the liquid phase is the residual porosity that remains as the liquid phase is consumed to form Bi-2223. The liquid does eventually make its way out of the shell of Bi-2223 leaving behind the triangular shaped porosity that is commonly found in the Bi-2223 tapes. Again, this demonstrates the need for an intermediate reduction to close up the porosity and enhance the grain-to-grain alignment of the Bi-2223 phase.

Figure 3: TEM micrographs of (a) the formation of the liquid phase after 100 minutes at 827°C, (b) the liquid phase and the precipitation of the Bi-2223 phase after 500 minutes of processing, and (c) the non-uniform distribution of Bi-2212 intergrowths in a “Bi-2223” grain from the sample processed for 500 minutes. The black arrows in (a) indicate the silver-copper precipitates found in the early liquid phases. The white arrow in (b) denotes the transition zone for the conversion to Bi-2223. The liquid phase is visible at the bottom of (c).

CONCLUSIONS

The formation of the Bi-2223 and its associated microstructure in silver sheathed tapes was documented. Defects and secondary phases in the as-rolled tape can significantly affect the

alignment and phase development of the intermediate Bi-2212 phase during the initial stages of heat treatment. This is an important point to understand as the local formation of the Bi-2223 follows the local alignment of the Bi-2212 phase. A direct observation of the precipitation of the Bi-2223 phase from an intermediate liquid phase within the Bi-2223 tapes was made and the composition of the liquid phase was measured. Its formation starts at the interface between the lead-rich Bi-2212 phase and surrounding alkaline-earth cuprates. The precipitation process that forms Bi-2223 can also form structures that further inhibit phase conversion and leave behind residual porosity. Both of these aspects point to the need for an intermediate deformation process that closes up porosity and brings the remaining precursor materials into contact to complete the phase transformation to Bi-2223.

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REFERENCES

1. O. Eibl, *Superconductor Science and Technology* **8**, 833-861 (1995).
2. Li-jun Wu, Y.L. Wang, W. Bian, Y. Zhu, T.R. Thurston, R.L. Sabatini, P. Haldar, and M. Suenaga, *Journal of Materials Research* **12** (11), 3055-3073 (1997).
3. Y. Yan, M.A. Kirk, and J.E. Evetts, *Journal of Materials Research* **12** (11), 3009-3028 (1997).
4. T.G. Holesinger, J.F. Bingert, J.O. Willis, Q. Li, R.D. Parrella, M.D. Teplitsky, M.W. Rupich, and G.N. Riley Jr., *IEEE Transactions on Applied Superconductivity* **9** (2), 2440-2446 (1999).
5. T.G. Holesinger, J.F. Bingert, M. Teplitsky, Q. Li, R.D. Parrella, M.P. Rupich, and G.N. Riley Jr., *Journal of Materials Research* **15** (2), 285-295 (2000).
6. E. Giannini, E. Bellingeri, R. Passerini, and R. Flukiger, *Physica C* **315**, 185-197 (1999).
7. H.F. Poulsen, T. Frello, N.H. Anderson, M.D. Bentzon, and M. van Zimmermann, *Physica C* **298**, 265-278 (1998).
8. T.G. Holesinger, D.J. Miller, and L.S. Chumbley, *Journal of Materials Research* **7** (7), 1658-1671 (1992).
9. T.G. Holesinger, A. Ayala, M.B. Ruxandra, and V.A. Maroni, *IEEE Transactions on Applied Superconductivity* **11** (1), 2991-2994 (2001).
10. D.P. Grindatto, J.C. Grivel, G. Grasso, H.-U. Nissen, and R. Flukiger, *Physica C* **298**, 41-48 (1998).
11. J.S. Luo, N. Merchant, V.A. Maroni, D.M. Gruen, B.S. Tani, W.L. Carter, and G.N. Riley Jr., *Applied Superconductivity* **1**, 101-107 (1993).
12. P.E.D. Morgan, R.M. Housley, J.R. Porter, and J.J. Ratto, *Physica C* **176**, 279-284 (1991).