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*Title:* Investigation of the Initial Stages of Processing Bi-2223  
Multifilamentary Tapes by Analytical Electron Microscopy

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# Investigation of the Initial Stages of Processing Bi-2223 Multifilamentary Tapes by Analytical Electron Microscopy

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**Abstract**—Analytical transmission electron microscopy (TEM) was used to probe the formation of liquid phases in multifilamentary Bi-2223 tapes. Silver was found to nucleate small amounts of liquid phase early in the processing. However, liquid formation was primarily associated with the 14-24 AEC and time at temperature (induction period) was the major factor determining the amounts of lead-rich liquid phase formation in these tapes. The compositions of the lead-rich liquid phases were measured quantitatively. The data presented is consistent with a mechanism whereby Bi-2223 can precipitate from a liquid phase.

**Index Terms**—high temperature superconductor, lead, liquid phase, TEM, sintering

## INTRODUCTION

LEAD additions are necessary to improve the formation, stability, connectivity, and superconducting properties in the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  (Bi-2223) composite materials [1-3]. The addition of lead to the system results in the formation of a liquid phase at normal processing temperatures. It also results in the formation of several lead-rich secondary phases during processing or under cool down conditions [4-6]. While the addition of lead is necessary for producing conductors from the Bi-2223 phase, it also increases the system complexity.

Currently, the best critical current densities ( $J_c$ 's) in oxide-powder-in-tube (OPIT) tapes are only a fraction of the values obtained in thin films [7-9]. A key area for improving the performance is microstructural characterization of the BSCCO tapes. Two aspects of this structure are important. They are the structure / property relationships in fully processed tapes and the structure / processing relationships that develop during manufacturing. The role of lead in both of these areas is still the subject of much debate [5, 10, 11].

A significant amount of work related to the effects of lead on the transport properties, field performance, microstructure, and compositional variations in fully processed tapes has been published previously [3, 12, 13]. In the current work, the structural changes and formation of the lead-rich liquid phase at the beginning of the processing cycle are examined. The microstructural and compositional aspects of liquid

phase formation were determined by quantitative compositional analysis in the transmission electron microscope.

## EXPERIMENTAL

Bi-2223 multifilamentary tapes were obtained from American Superconductor. The starting composition of the Bi-2223 powder used in the tapes was  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.9}\text{Ca}_{2.0}\text{Cu}_{3.0}\text{O}_y$ . These tapes were processed in a vertical furnace and quenched into an oil bath after processing for 0, 10, 100, 150, and 300 minutes at 827°C in 8% $\text{O}_2/\text{N}_2$ . Quenched tapes were prepared for examination in scanning and transmission electron microscopes (SEM and TEM) in short and longitudinal transverse sections. Quantitative compositional analysis was performed by energy dispersive spectrometry (EDS) in the TEM using Bi-2212 glass and  $\text{Ca}_2\text{PbO}_4$  standards. Details of the quantification method can be found elsewhere [13].

## RESULTS

### A. Rapid Grain Growth

The as-received tape was characterized as having a small Bi-2212 grain size, some alkaline-earth cuprates, and CuO as shown in Fig. 1. The diffraction pattern of Fig. 1 also indicates some deformation-related, c-axis texture of the Bi-2212 relative to the silver sheath interface. The early stages of processing of Bi-2223 tapes are characterized by the rapid growth and development of alkaline-earth cuprates and  $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  (Bi-2212). Shown in Fig. 2 is a SEM backscattered electron image (BEI) of the tape after quenching from the processing temperature at  $t = 0$  minutes. Fig. 2 shows the recrystallization and coarsening of the silver in the sheath and Bi-2212 in the filaments, and the rapid growth of the alkaline-earth cuprates,  $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$  (14-24 AEC) and  $\text{Ca}_{2-x}\text{Sr}_x\text{CuO}_3$  (2:1 AEC). This is typical of the early phase development in the Bi-2223 tapes.

A few grains of the Bi-2223 phase can be found in the samples in the early stages of heat treatment. These grains are located primarily along the silver interface. Bi-2223 grains could be found along the silver interface in all of the samples quenched from 827°C, but not in the filament interiors in agreement with Luo *et al.* [14]. The compositions of the major phases in the quenched samples can be found in TABLE I.

### B. Liquid Phase Formation

A few small pockets of a lead-rich liquid phase start to appear in the microstructure upon reaching the processing temperature. They are easiest to see in the SEM and are

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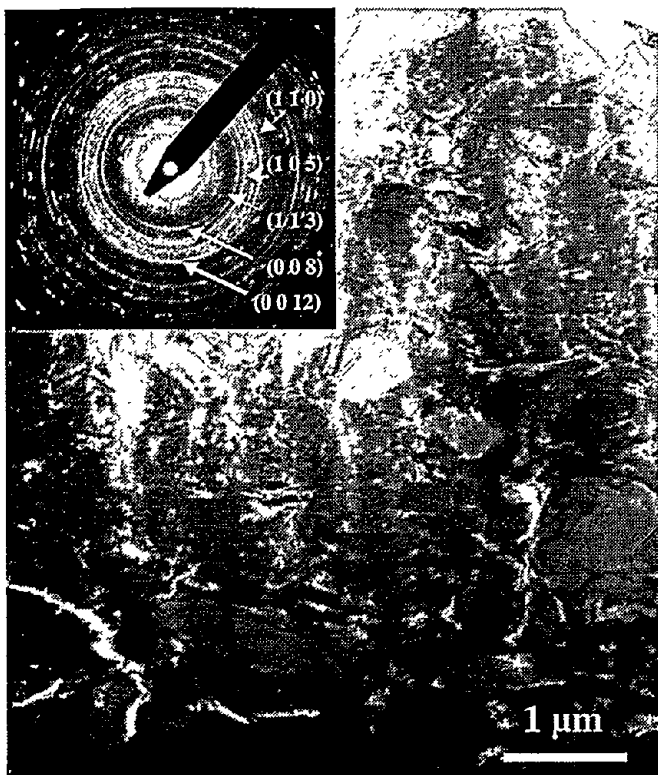


Fig. 1: TEM micrograph of the as-rolled Bi-2223 tape. SAD reveals some texturing of the sample due to the mechanical deformation. The silver/BSCCO interface runs parallel to the top of the micrograph.

marked by the presence of small silver particles in the center of the liquid phases shown in Fig. 3. Shown in Fig. 4a are several TEM micrographs of a sample quenched after 10 minutes at the processing temperature. Only one spot within the area contained a liquid phase. A higher magnification TEM image of the liquid phase/silver microstructure is shown in Fig. 4b. In general, the extent of liquid phase formation in the early stages of processing ( $\leq 10$  minutes) was found to be limited. Although these regions could be seen by SEM in the sample quenched upon reaching  $827^{\circ}\text{C}$ , they were not measured in the TEM due to the difficulty in locating one of these regions in a TEM specimen.

### C. Liquid Phases and Phase Development

Lead-rich, liquid phase formation increases with time at temperature. For samples quenched after 100 minutes, significantly more regions and volumes of amorphous phases were found. These regions of liquid phase formation were primarily connected to the 14-24 AEC phase although a few regions were found connected to the 2:1 AEC. Between 100 minutes and 300 minutes, there is a break in the microstructure as shown in Fig. 5a and b; the liquids are no longer confined to the interstices between grains and they start to play an active role in phase development. As shown in Fig. 5b, Bi-2212 grains appear to be dissolving into the liquid phase in the sample quenched after 300 min at  $827^{\circ}\text{C}$ . The structure along the boundary can vary from a clean interface between the Bi-2212 and liquid as shown in Fig. 5a and a dendritic structure of Bi-2201 between Bi-2212 and the liquid as shown in Fig. 5b. The origin of the latter structure could be related to the dissolution of Bi-2212 or to some precipitation occurring upon quenching into the oil bath.

The microstructural differences between the samples

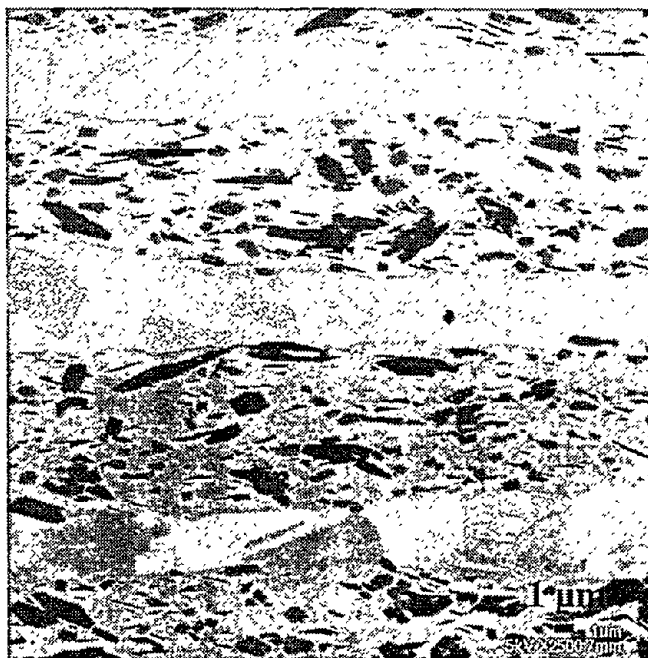


Fig. 2: SEM backscattered electron images of the Bi-2223 tape after ramping to the processing temperature and immediately quenching.

quenched after 100 and 300 minutes suggests a critical amount of liquid phase is needed for Bi-2223 phase development to commence in the filament interiors. This is supported by EDS data in Table I which shows negligible differences in the compositions of the liquid phases in all the samples. There is a certain amount of variability in the composition of the liquid phase due to the presence of small precipitates of Cu-O and/or Ag-Cu. As shown in Table 1, the regions of liquid phase that contained these precipitates were copper deficient relative to the precipitate-free regions of liquid phases.

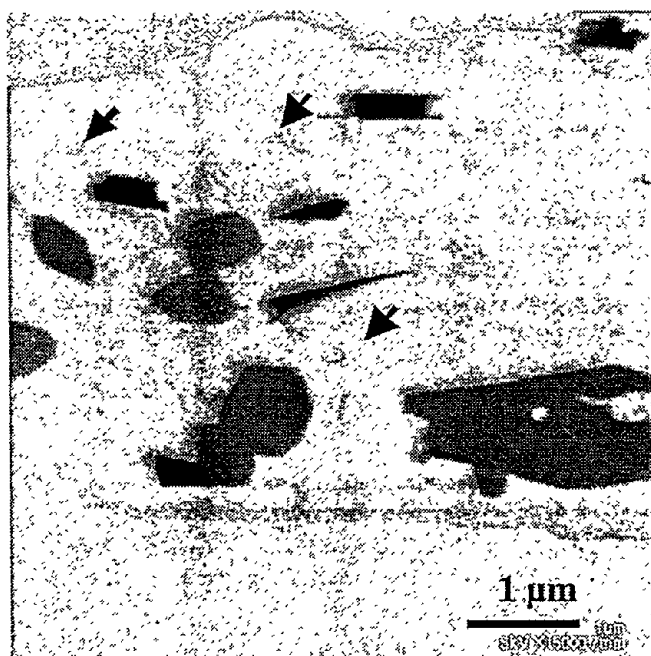


Fig. 3: SEM BEI of a Bi-2223 tape quenched from the processing temperature after 10 minutes. The arrows denote pockets of the amorphous phase containing silver precipitates.

(a)



(b)

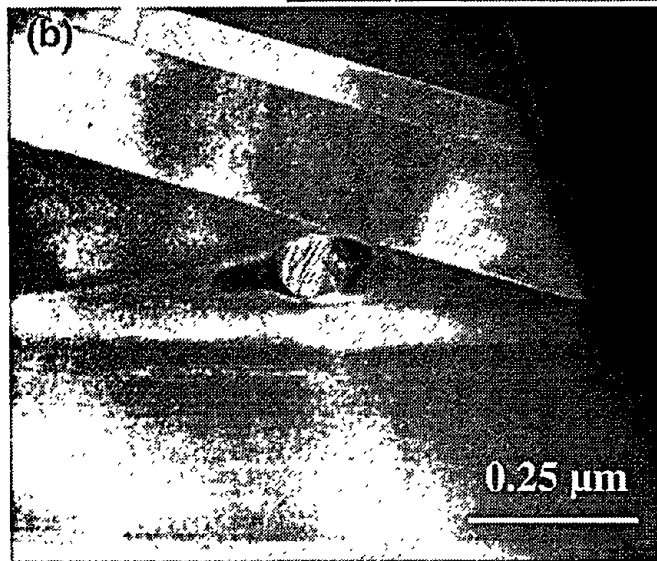


Fig. 4: TEM micrographs taken from a sample quenched after 10 minutes at the processing temperature. In (a), only one region of liquid phase formation was found in the area shown. The sample is comprised primarily of alkaline-earth cuprates, porosity, and Bi-2212. A higher magnification TEM micrograph in (b) shows the pure silver particle that is usually found with the few pockets of the liquid phase in this sample. The composition of the liquid phase was  $\text{Bi}_{1.06}\text{Pb}_{0.91}\text{Sr}_{0.57}\text{Ca}_{0.47}\text{Cu}_{1.99}\text{O}_y$ .

#### DISCUSSION

Despite the rapid formation of Bi-2223 next to the silver

TABLE I  
PHASES AND COMPOSITIONS IN QUENCHED Bi-2223 TAPES

Sample	Phases <sup>†</sup>
Quenched upon reaching 827°C	Bi-2212: $\text{Bi}_{1.81}\text{Pb}_{0.30}\text{Sr}_{1.63}\text{Ca}_{1.14}\text{Cu}_{2.09}\text{O}_y$ 14-24 AEC: $\text{Bi}_{0.25}\text{Pb}_{0.07}\text{Sr}_{0.30}\text{Ca}_{0.02}\text{Cu}_{2.35}\text{O}_y$ 2:1 AEC: $\text{Bi}_{0.00}\text{Pb}_{0.00}\text{Sr}_{0.16}\text{Ca}_{1.92}\text{Cu}_{0.92}\text{O}_y$
Quenched after 10 minutes at 827°C	Bi-2212: $\text{Bi}_{1.80}\text{Pb}_{0.26}\text{Sr}_{1.72}\text{Ca}_{1.20}\text{Cu}_{2.02}\text{O}_y$ Amorphous: $\text{Bi}_{1.06}\text{Pb}_{0.91}\text{Sr}_{0.57}\text{Ca}_{0.47}\text{Cu}_{1.99}\text{O}_y$ 14-24 AEC: $\text{Bi}_{0.23}\text{Pb}_{0.06}\text{Sr}_{0.75}\text{Ca}_{0.53}\text{Cu}_{2.41}\text{O}_y$ 2:1 AEC: $\text{Bi}_{0.01}\text{Pb}_{0.00}\text{Sr}_{0.17}\text{Ca}_{1.89}\text{Cu}_{0.92}\text{O}_y$
Quenched after 100 minutes at 827°C	Bi-2212: $\text{Bi}_{1.75}\text{Pb}_{0.28}\text{Sr}_{1.72}\text{Ca}_{1.14}\text{Cu}_{2.11}\text{O}_y$ Amorphous: $\text{Bi}_{1.25}\text{Pb}_{0.87}\text{Sr}_{0.70}\text{Ca}_{0.45}\text{Cu}_{1.75}\text{O}_y$ Amorphous: $\text{Bi}_{1.57}\text{Pb}_{1.21}\text{Sr}_{0.74}\text{Ca}_{0.38}\text{Cu}_{1.14}\text{O}_y$ 14-24 AEC: $\text{Bi}_{0.28}\text{Pb}_{0.06}\text{Sr}_{0.75}\text{Ca}_{0.09}\text{Cu}_{2.81}\text{O}_y$ 2:1 AEC: $\text{Bi}_{0.81}\text{Pb}_{0.30}\text{Sr}_{1.65}\text{Ca}_{1.14}\text{Cu}_{2.09}\text{O}_y$
Quenched after 300 minutes at 827°C	Bi-2212: $\text{Bi}_{1.88}\text{Pb}_{0.29}\text{Sr}_{1.75}\text{Ca}_{1.04}\text{Cu}_{2.04}\text{O}_y$ Amorphous: $\text{Bi}_{1.25}\text{Pb}_{0.98}\text{Sr}_{0.70}\text{Ca}_{0.43}\text{Cu}_{1.64}\text{O}_y$ Amorphous: $\text{Bi}_{1.48}\text{Pb}_{0.94}\text{Sr}_{0.92}\text{Ca}_{0.57}\text{Cu}_{1.09}\text{O}_y$ 14-24 AEC: $\text{Bi}_{0.23}\text{Pb}_{0.05}\text{Sr}_{0.70}\text{Ca}_{0.37}\text{Cu}_{2.62}\text{O}_y$ 2:1 AEC: $\text{Bi}_{0.00}\text{Pb}_{0.00}\text{Sr}_{0.17}\text{Ca}_{1.88}\text{Cu}_{0.96}\text{O}_y$

<sup>†</sup> Compositions are normalized to 9 cations for Bi-2223, 7 cations for Bi-2212, 38 cations for 14-24 AEC, 3 cations for 2:1 AEC, and 5 cations for quenched liquid phases.

The second listed composition for the liquid phase is for those measurements on quenched liquid phases containing precipitates.

sheath, the bulk of BSCCO filament relies on the formation of the lead-rich liquid phase for Bi-2223 phase formation. The initial formation of the liquid phase around these isolated silver particles may reflect the chemical influence of the silver in lowering the melting points of the Bi-based superconductors. However, the bulk of the liquid phase development was primarily associated with the 14-24 AEC, which is consistent with previous phase equilibria work [15]. Of the 29 five-phase equilibria assemblages examined by Wong-Ng *et al.*, those containing the 14-24 AEC produced some of the lowest melting liquid phases observed in their study. The association of a few 2:1 AEC grains with some of the amorphous phases is also consistent with the latter work. Mixtures containing the 2:1 AEC also produced some relatively low partial melts.

Overall, the formation of a sufficient amount of liquid phase depends upon the time spent at temperature. The results of this work support the earlier work of Luo *et al.* who noted an induction period in the formation of the Bi-2223 phase [16]. Based on the present work, the induction period is the formation time for a sufficient amount of lead-rich liquid phase to form to promote Bi-2223 growth. The ratios and amounts of Bi to Pb in the measured amorphous phases agree with the earlier works on liquid phase formation in these systems [5, 17]. The change in microstructure with the sample that was quenched after 300 minutes suggests that the liquid phase is now aggressively interacting with the Bi-2212 matrix of the filaments. This scenario would support the viewpoint that the Bi-2223 phase formation is enhanced by the addition of lead to form a liquid phase from which the Bi-2223 phase can precipitate during processing [17].

#### SUMMARY

The initial stages of Bi-2223 formation in silver-sheathed tapes were investigated. The initial formation of some lead-

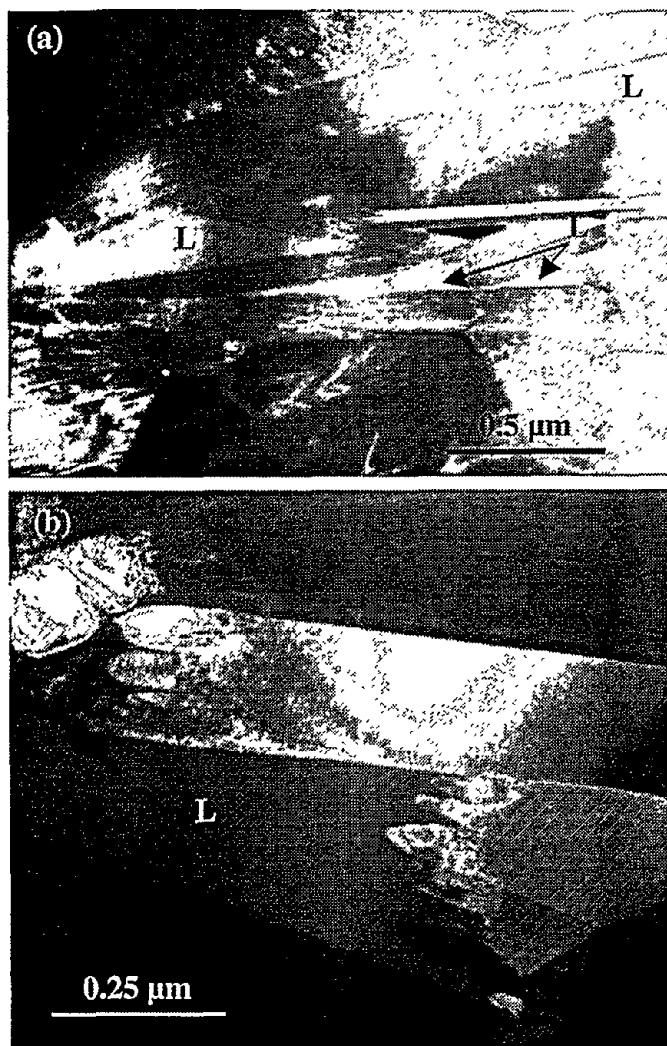


Fig. 5: TEM micrographs of the amorphous regions in Bi-2223 tapes after quenching from 827°C for (a) 100 minutes and (b) 300 minutes. The liquid phase is actively participating in phase development in (b).

rich liquid in the tapes was around isolated silver particles within the filaments. However, the amount of liquid phase that formed was time dependent and associated primarily with the 14-24 AEC. The microstructural development in the early stages of Bi-2223 tape processing is consistent with the scenario of the formation of a lead-rich liquid phase from which the Bi-2223 phase can precipitate.

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