Analysis of Texture and Impurity Content in $Ag/(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ Composite Superconductor Specimens by High-resolution Transmission X-ray Diffraction

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Introduction

The silver-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Ag/Bi-2223) composite is currently being manufactured in kilometer lengths suitable for the manufacture of prototype motors, generators, transmission lines, and fault current limiters [1]. The methodology used to fabricate long lengths of Ag/Bi-2223 wire is known as the powder-in-tube process [1,2]. A key step in this process is the heat treatment that transforms the ceramic powder mixture (nominally Bi-2212 plus an alkaline earth cuprate mix) enclosed in the precursor billet into the superconducting Bi-2223 phase. Monitoring of this process as a function of relevant process variables (e.g., time, temperature, and oxygen partial pressure) requires direct examination of the samples. The standard methods employed for such examinations are x-ray diffraction (with a laboratory source) and scanning electron microscopy coupled with energy-dispersive spectroscopy [2]. These methods have two drawbacks: first, both methods require destructive sectioning of the sample; second, neither method provides a truly representative measure of either the volumetric impurity content of the filaments or the c-axis texture of the Bi-2223 grains.

In the case of conventional x-ray diffraction (XRD), the analysis is performed by polishing one face of the Ag/Bi-2223 tape specimen to remove silver to the point where a representative number of Bi-2223 filaments are exposed, then mounting the specimen in a diffractometer, such that the incoming x-ray beam only interrogates the exposed ceramic core(s) during the two-theta scan. Also, in the course of the precursor transformation, the Bi-2223 grains form in a colony microstructure with the crystal c-axis perpendicular to the surface of the tape. As a consequence of this texturing and the measurement configuration used when the two-theta scan is taken, the [00L] reflections of Bi-2223 dominate the diffraction pattern, making it extremely difficult to detect impurity phases (mainly unreacted Bi-2212 phase, residual alkaline earth cuprates, and a commonly observed lead-rich impurity known as the "3221" phase) using the conventional XRD approach.

An alternative approach to conventional XRD that avoids the need to abrade away the silver sheath and also, in principle, avoids having to section long lengths of composite wire, is to perform the XRD measurements at x-ray energies high enough to fully penetrate the silver-sheathed composite (i.e., direct transmission of the x-ray beam through the intact silver sheath). In 2001 we showed that this can be done very effectively by working at 25 keV, an energy that lies just below the Ag Kα edge. Using this technique, we were able to gauge the aggregate impurity content of as-rolled, partially heat treated, and fully heat treated Ag/Bi-2223 specimens without damaging them and in a manner that provides a more representative indication of the true volumetric impurity content. Following up on our prior work, we have added new features to the transmission XRD measurement method that have significantly improved the achievable resolution and provided a basis for *in situ* texture analysis.

Methods and Materials

The multifilament Ag/Bi-2223 composite tapes investigated in this study were prepared by the powder-in-tube processing methodology described elsewhere [1]. The tape specimens (4 mm wide, and 0.2 mm thick) were cut into ca. 50 mm lengths. The individual filaments in these tapes (nominally 50 to 60 filaments per tape) were ca. 500 μm wide and ca. 20 μm thick. The measurements were made at the Materials Research Collaborative Access Team (MR-CAT) insertion device beamline (10-ID) using an eight-circle Huber diffractometer. The x-ray energy was 25 keV, corresponding to a wavelength of 0.49594 Å. A silicon (111) crystal analyzer was positioned on the theta arm of the Huber ahead of the detector to enhance the resolution of the many closely spaced diffraction lines exhibited by Bi-2223 and the prevalent impurity phases. The x-ray beam spot on the sample was slit-framed to a 1.5 mm by 1 mm rectangle. Patterns were recorded at ca. 0.1°/minute.

Results and Discussion

The powder-in-tube process for manufacturing long length Ag.Bi-2223 tape comprises three steps, a first heat treatment (HT-1), an ambient-temperature rolling deformation (to remove porosity that develops during the first heat treatment), and a final heat treatment

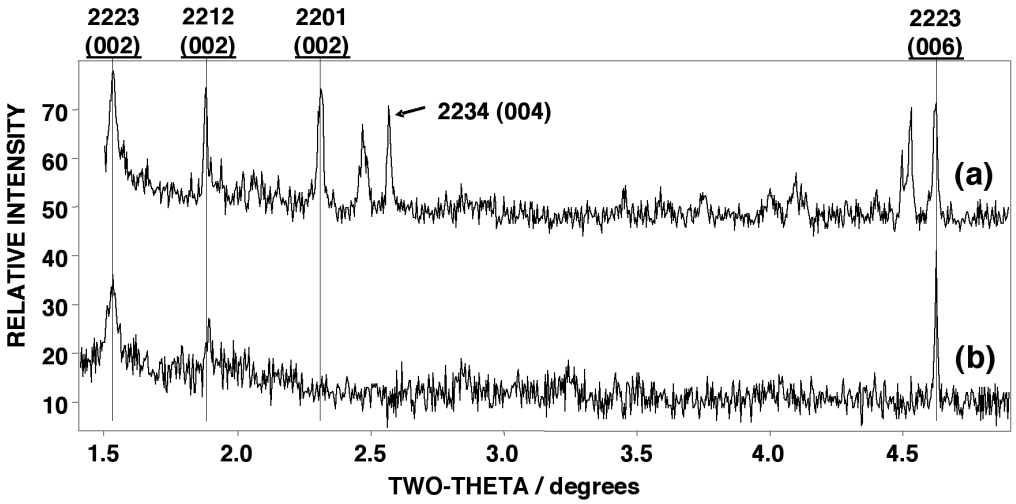

FIG. 1. Low two-theta T-XRD patterns for (a) a pre-FHT Ag/Bi-2223 specimen and (b) a post-FHT specimen.

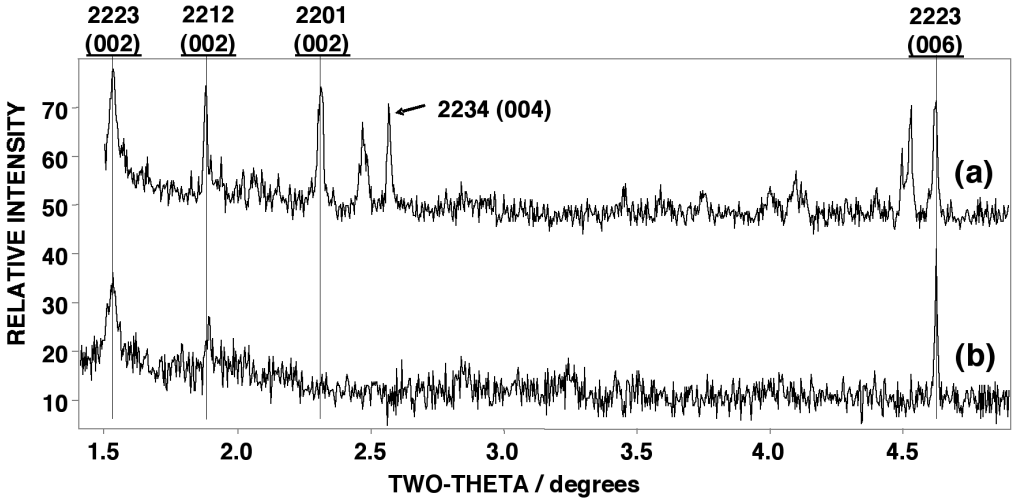

FIG. 2. Mid-two-theta T-XRD patterns for (a) a pre-FHT Ag/Bi-2223 specimen and (b) a post-FHT specimen.

(FHT). The phase evolution during HT-1 has been studied extensively (see [2] and references therein) and is reasonably well understood. The purpose of the FHT is to drive the Bi-2223 formation reaction to completion, such that no residual Bi-2212 or second phases remain in the ceramic filaments to block current flow. Thus, it is understandable that there is considerable interest in the phase transformations occurring during FHT and in being able to quantify the residual impurity content at the end of the FHT. In recent experiments performed on the MRCAT ID line, we have begun to explore these issues by performing transmission XRD (T-XRD) measurements on Ag/Bi-2223 specimens prior to and following FHT.

Figures 1 and 2 show two key regions of the acquired diffraction patterns for a pre-FHT Ag/Bi-2223 tape specimen and a post-FHT specimen. The pre-FHT specimen exhibits a series of diffraction lines at low two-theta values (Fig. 1a) that emanate from Bi-2223 and other layered cuprate superlattice domains remaining after HT-1 (some we can index to known phases, others we cannot). Whereas most of the non-Bi-2223 layered cuprate domains are dissipated by the FHT (Fig. 1b), there is still some residual Bi-2212 that is normally not detectable by the conventional XRD method.

Within the two-theta range covered in Fig. 2, we find evidence that the FHT causes an increase in the relative amount of the “3221” phase compared to the pre-FHT phase state. Using the (00L) lines of Bi-2223 as an internal standard, this increase appears to be in the range of three to four fold. Also, the slight shift in peak

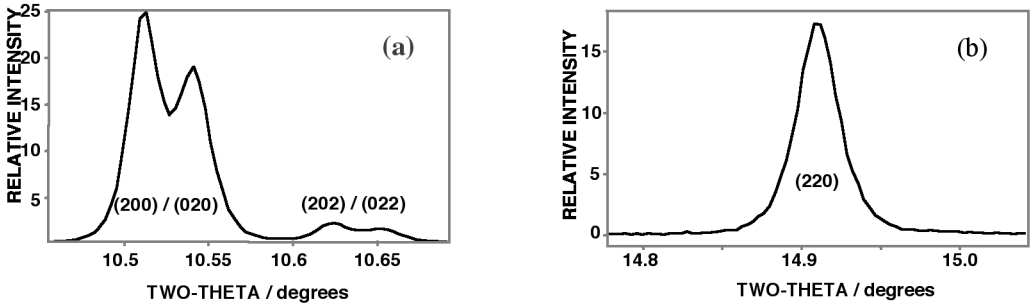

FIG. 3. T-XRD scans of a post-FHT Ag/Bi-2223 specimen in the two-theta range of the (a) (200) / (020) and (202) / (022) pairs and (b) the intense (220) diffraction line.

positions and relative line intensities for the two "3221" lines near two-theta equal to 10° is most probably due to a difference in composition of the pre- and post-FHT "3221." Transmission electron microscopy analysis of similarly prepared post-FHT tape specimens has shown that the "3221" exists in stratified layers that run parallel to the a,b planes of the Bi-2223 grain colonies [3]. These layers of nonsuperconducting material are quite possibly one of the major causes of current transport blocking in the filament microstructure. Furthermore, in addition to the "3221" phase, there is evidence in Fig. 2 of unreacted alkaline earth cuprate (AEC), specifically, (Ca,Sr)2CuO3 (2/1), before and after FHT.

Also noteworthy in Fig. 2 is the observation that FHT appears to create a detectable amount of the quasi-crystalline ("QC") phase reported by Khan [4]. This phase (a Sr- and Ca-deficient version of Bi-2223) is believed to form from an incipient liquid that persists during FHT, wets the Bi-2223 grain boundaries, and quite possibly provides a diffusion path for the cation transport needed to complete the Bi-2223 formation process. *In situ* T-XRD measurements on Ag/Bi-2223 specimens undergoing FHT are planned for the coming year. The goal will be to determine if manipulations of oxygen partial and temperature (similar to those reported in [2]) can be used to completely dissipate the "3221," quasi-crystalline Bi-2223, and AEC phases during FHT.

Insertion of the silicon (111) crystal analyzer in front of the detector appreciably enhanced the diffraction line resolution achieved with the silver-sheathed composite tapes. In the diffraction geometry we now employ for these measurements (the incident x-ray beam being approximately parallel to the Bi-2223 grain colony c-axis), the two most intense diffraction lines are the (200)/((020) pair and the (220) reflection. The splitting of the (200)/(020) pair (see Fig. 3) provides a measure of the orthorhombicity of the Bi-2223. Note in Fig. 3a that this splitting is less than 0.05 degrees in two-theta value — but is clearly resolved by the above described setup. The strong (220) reflection, which is well isolated from other diffraction lines (Fig. 3b), can be easily and rapidly subjected to rocking curve analysis in order to gauge the quality of the Bi-2223 c-axis texture. We are currently engaged in a project with Rigaku MSC to determine whether a silver x-ray tube mounted on a laboratory-grade diffractometer has sufficient power to produce such a rocking curve in an embodiment that could be used as an on-line diagnostic instrument at an Ag/Bi-2223 manufacturing facility.

Acknowledgments

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