Nondestructive Analysis of Residual Second Phases in $Ag/(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ Composite Superconductor by Transmission X-ray Diffraction

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Introduction

Since the discovery of high-critical-temperature superconductivity in selected families of layered cuprate ceramics in the late 1980s, considerable progress has been made in the development of embodiments of these materials that have potential for practical application in the electric power industry. The most advanced embodiment available today is the silver-sheathed $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (Ag/Bi-2223) composite conductor, which can now be manufactured in kilometer lengths suitable for devices such as motors, generators, transmission lines, and fault current limiters. The technique used to fabricate long lengths of Ag/Bi-2223 wire is known as the powder-in-tube process.[1] A key step in this process is the heat treatment that transforms the ceramic powder mixture enclosed in the precursor billet into the superconducting Bi-2223 phase. Monitoring of this process as a function of process variables, such as time, temperature, and oxygen partial pressure, requires direct examination of the samples. The primary methods employed in virtually all cases today are x-ray diffraction (with a laboratory source) and scanning electron microscopy coupled with energy dispersive spectroscopy. With both of these methods, the sample must be sectioned and the silver polished away to expose the superconducting ceramic cores, i.e., both methods involve destructive sectioning of the sample.

In the case of conventional x-ray diffraction (XRD) analysis of Ag/Bi-2223 composite wires, the sample is polished to remove silver to the point where several filaments are exposed, mounted in a diffractometer with the x-ray beam centered on the exposed ceramic core(s), and subjected to a $\theta/2\theta$. During heat treatment of Ag/Bi-2223 composites, the superconducting phase forms in a grain colony microstructure with the crystallographic c-axis perpendicular to the rolling direction. As a consequence of this texturing and the measurement configuration used when the conventional $\theta/2\theta$ scan is taken, the [00L] reflections of the layered cuprate phases (Bi-2212 and Bi-2223) dominate the diffraction pattern. It has prove very difficult to detect impurity phases, such as the 2201 phase, certain alkaline earth cuprates, and a lead-rich/copper-deficient cuprate phase known as the "3221" phase, using the conventional XRD approach.

As an alternative to the conventional XRD method that avoids the need to abrade away the silver and also, in principle, avoids the need to section long lengths of composite wire, we are investigating transmission XRD at x-ray energies high enough to fully penetrate the silver-sheathed composites. We have found that this can be done very effectively by working at 25 keV (0.49594 Å), an energy that lies just below the silver kα edge. Using this technique, we have been able to determine the bulk second phase content of as-rolled, partially heat treated, and fully heat treated Ag/Bi-2223 specimens without any damage to the specimen itself. This allows us to investigate the same specimen at progressive stages of the deformation/heat treatment process.

Materials and Methods

The fully processed 51-filament Ag/Bi-2223 composite wires investigated in this study were prepared by the powder-in-tube processing methodology described elsewhere.[1] The specimens were 50 mm long, 4 mm wide, and 0.2 mm thick. The average width and thickness of an individual filament were 500 μm and 20 μm, respectively. 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 beam spot on the sample was slitted to a 2 mm × 1 mm rectangle. Patterns were recorded at about. 1° min.

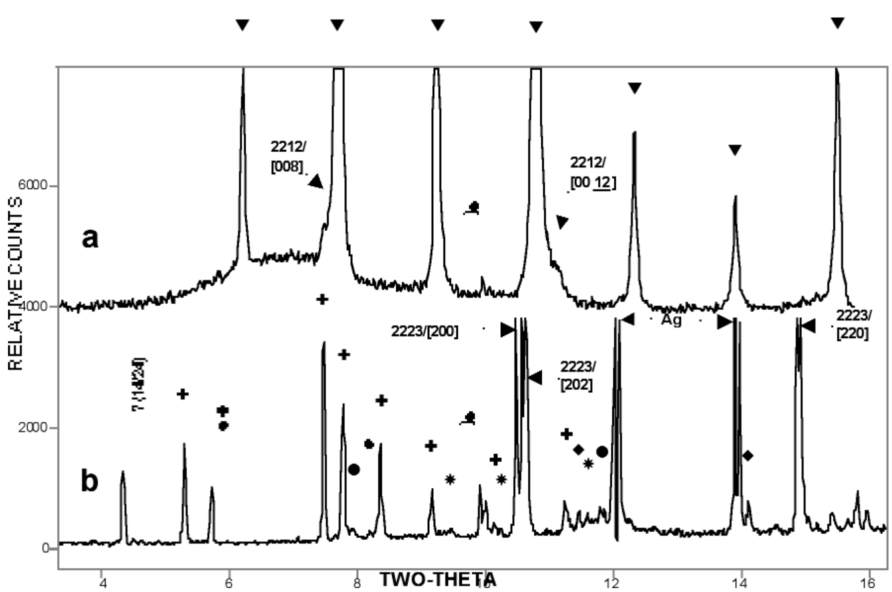

*FIG. 1. Pattern (**a**) is a theta/two-theta diffraction pattern of an abraded Ag/Bi-2223 composite wire taken with a Cu-kα laboratory source and recomputed to a wavelength of 0.49594 Å. Pattern (**b**) is a transmission-type 2θ diffraction pattern of the same composite wire recorded using 0.49594 Å x-rays at the APS/MR-CAT insertion device beamline. ▼ = [00L] of Bi-2223, ✚ = [10L] and [11L] of Bi-2223, ● = [11L)] of Bi-2212, ✷ = [11L)] of Bi-2201, and ◆ = [HKL] of the 3221 phase. Beyond 2θ = 15o, the pattern consists of a near continuum of Bi-2223, Bi-2212, and Bi-2201 diffraction lines.*

Results and Discussion

The results in Fig. 1 show a comparison of XRD scans for a typical Ag/Bi-2223 specimen obtained using the conventional/ laboratory-source-based method (Cu-kα) and the synchrotron-based transmission method. For purposes of the comparison, the Cu-kα data were recomputed to the 0.49594 Å wavelength used in the transmission experiment. Pattern (**a**) in Fig. 1, obtained with the laboratory source/configuration, is dominated by the [00L] reflections of Bi-2223, with only trace evidence of the 3221 phase (near $2\theta = 10°$). Pattern (**b**) in Fig. 1, obtained using the transmission technique at APS/MR-CAT, contains diffraction lines for at least four other phases in addition to the Bi-2223 phase. It is noteworthy that in pattern (**b**), the [00L] reflections of Bi-2223 are not observed. This is a consequence of the fact that the x-ray beam is imposed on the Ag/Bi-2223 wire at a right angle to the rolling direction and is, therefore, parallel to the crystallographic c-axis of the Bi-2223 grain colonies. Instead of the [00L] reflections of Bi-2223, the pattern contains mainly [10L] and [11L] reflections of the Bi-2223, Bi-2212, and Bi-2201 phases, plus four or five diffraction lines of the 3221 phase, and a low-angle reflection (ca. 4.3°) that may be due to either the $(Ca,Sr)_{14}Cu_{24}O_{41}$ alkaline earth cuprate or layered phase intergrowth boundaries. Also, the [200], [202], and [220] reflections of Bi-2223 appear with considerable intensity, and like the two silver diffraction lines, they are actually off scale in pattern (b) because of detector saturation. Beam attenuation is necessary to bring these two lines back on scale.

Clearly, the 25 keV transmission XRD technique provides much more information about impurity phases in Ag/Bi-2223 composites than does the conventional laboratory-source-based method. This is due, in large part, to the full transverse penetration of the Bi-2223 filaments achieved with the transmission method. Also, the absence of the Bi-2223 [00L] reflections in the transmission 2θ configuration is a testimony to the quality of the reaction/deformation-induced Bi-2223 grain colony texture achieved by the powder-in-tube process.

Acknowledgments

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References

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