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Characterization of coated conductors by magneto-optical imaging, Raman spectroscopy, and electron microscopy

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Abstract

Argonne National Laboratory has established and implemented a coordinated set of characterization methods for coated-conductor specimens that can be applied in a manner compatible with further processing or utilization of the respective specimen. These characterization methods include measurements of superconductor transport properties, phase composition, microstructure, and epitaxy quality for YBCO-coated conductors that range in size up to multi-meters. Recent progress will be reported on the integrated application of Raman microscopy, magneto-optical imaging, and focused-ion-beam-assisted electron microscopy to a meter-length tape produced by SuperPower, Inc. This non-destructive, multifaceted characterization approach has allowed us to develop a seamless methodology for the interrogation of coated-conductor tapes during the course of sequential high-temperature treatments. The aim of this research effort is to identify performance-limiting defects, clarify their origin/cause, and prescribe methods to eliminate them during coated conductor manufacturing.

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1. Introduction

Thin films of $MBa_2Cu_3O_{7-x}$ (MBCO, M = yttrium or a rare-earth metal) on textured metal substrates (commonly referred to as "coated conductors") are the object of intensive research and development aimed at deploying them in a wide variety of electric power applications [1,2]. A key challenge to the commercialization of the MBCO-coated conductor is the acute sensitivity of its performance properties to imperfections in film chemistry and microstructure. For maximum current-carrying capacity, an MBCO film must (1) possess a high degree of contiguous biaxial texture with the *a*, *b* planes aligned and connected along the substrate surface, (2) be relatively free of impurity species, and (3) be properly oxygen doped to maximize the critical-current-carrying and flux-pinning properties of the MBCO phase.

At Argonne National Laboratory, we are pursuing the development, validation, and implementation of a coordinated set of characterization methods for evaluating superconductivity in coated conductors to pinpoint the causes of degraded performance. These characterization methods include measurements of local supercurrent transport, phase composition, microstructure, and epitaxy quality for MBCO-coated conductors ranging in size up to multi-meter-length tapes. The features of this "coordinated characterization of coated conductor" (hereafter referred as C^4) consist of (1) the integration of magneto-optical imaging and Raman microscopy with transmission electron microscopy assisted by focused-ion-beam sample sectioning and (2) the extension of this integrated characterization protocol to long-length coated conductors supplied by collaborating industries and institutions. In this paper, we describe the results of C^4 application to a long-length YBCO tape produced by SuperPower, Inc., using their metal-organic chemical vapor deposition (MOCVD) process [3].

2. Experimental

In the C^4 protocol, high-resolution magneto-optical imaging (MOI) is used to directly visualize the normal component, B_z, of the magnetic induction at the surface of a coated-conductor tape segment. The methodology for these measurements has been described elsewhere [4]. For thin superconducting samples the resulting B_z profile is converted into a quantitative map of critical current (I_c) magnitude that permits imaging of inhomogeneities in the superconducting properties of YBCO films with a spatial resolution of about 2 μm.

Raman microscopy measurements are made using a Renishaw System RM2000 equipped with a He–Ne laser (633 nm) that delivers ≈1 mW power to the sample surface. Typically, spectra are recorded with the laser defocused to a spot ≈6–8 μm in diameter (see [5,6] for additional details).

C^4 microstructural characterization is carried out in the Electron Microscopy Center at Argonne National Laboratory using focused ion beam (FIB) milling, high-resolution scanning electron microscopy (SEM), electron energy loss spectroscopy (EELS), and transmission electron microscopy coupled with energy filtering (EFTEM). The FIB and SEM measurements are carried out with a Zeiss 1540XB that provides ion beam imaging and patterning capabilities together with high-resolution electron beam imaging. EFTEM is done on an FEI Tecnai F20 field-emission instrument equipped with a Gatan Image Filter. Specimens are FIB-extracted from specific locations identified by MOI and further studied by SEM, TEM, EELS, and EFTEM.

3. Results and discussion

The results presented in this paper provide an illustration of the studies being performed in the C^4 program at Argonne. These results were obtained for a fully processed MOCVD-type YBCO film (≈1 μm thick) on a CeO_2 buffered, ion-beam-assisted-deposition (IBAD) template supported on a nickel alloy substrate (fabricated by SuperPower, Inc. [3]). The characterization of this 50-m-long, tape proceeded in the following way. After fabrication, SuperPower measured I_c along selected segments of the tape in 1-cm increments. A particular meter-long section that showed a threefold variation in I_c was forwarded to Argonne for C^4 analysis to interrogate the various I_c segments with the aim of determining the causes for the low I_c performance. The I_c profile for the section of tape submitted for C^4 analysis has been reported elsewhere [7]. Two 1-cm increments of this tape section, one from the region of highest I_c (150 A) and one from the region of lowest I_c (75 A), were subjected to C^4 analysis.

The magneto-optic images for each of these segments revealed domains of relatively high and relatively low I_c that were 10–100 μm in dimension. The 150 A segment exhibited a greater presence of high I_c domains, but the MOI images indicated that even high-I_c segments contain domains where the I_c is relatively low. The magneto-optic image for the 75 A segment is presented in Fig. 1. (The lighter shading in Fig. 1 generally indicates a region of high I_c, and the darker shading indicates a region of low I_c.) Selected domains for both the 150 A and the 75 A segment were "indexed" and submitted for further examination by SEM and Raman microscopy.

Raman spectra recorded at a half-dozen locations within each of the 10 mm-by-10 mm segments selected for study were averaged to produce a representative spectrum for each segment. These averaged spectra, shown in Fig. 2, exhibit several revealing features. The peak positions and relative

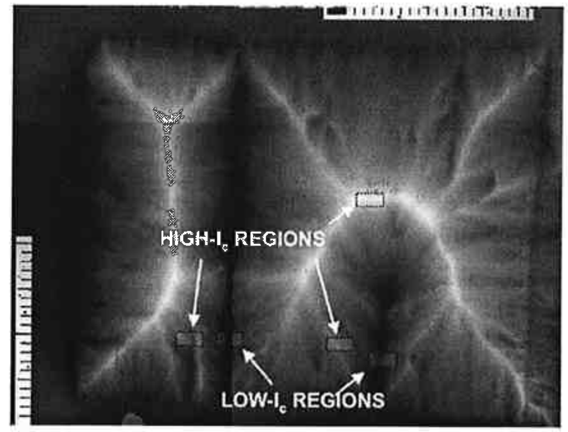

Fig. 1. Magneto-optic image of a portion of the 75 A segment showing domains of high-I_c (light shading) and low-I_c (dark shading). The tick marks along the left edge and top indicate 0.1-mm spacings. The entire image is approximately 4 mm × 4 mm.

intensities of the YBCO phonons indicate the presence of a mix of orthorhombic (O) and tetragonal (T) YBCO in both segments. Specifically, the spectra give the appearance of a mix of O-II and T′ YBCO as described by Iliev [8]. We know from prior experience [6] that the observed Raman scattering arises mainly from the top portion of the YBCO film (the first 0.2–0.3 μm). We see evidence of cation disorder in the YBCO phase, as well as

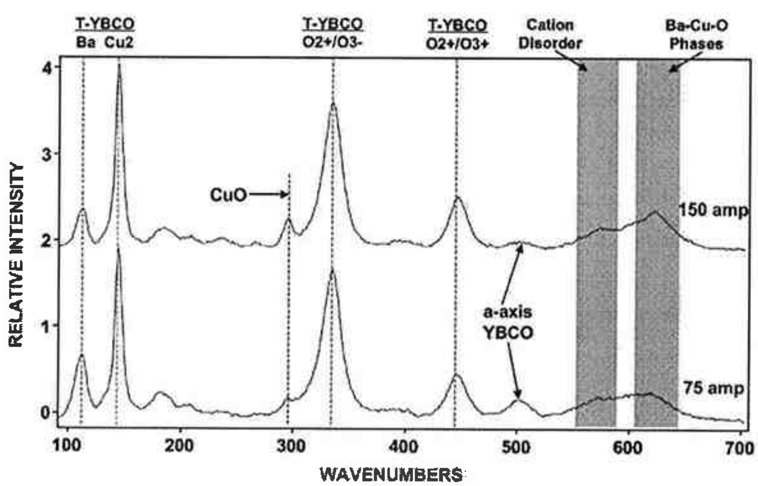

Fig. 2. Averaged Raman spectra from six locations in the 150 A and the 75 A segments of the MOCVD-YBCO coated conductor from SuperPower, Inc.

the presence of CuO and Ba–Cu–O second phases. The most telling observation is the appearance of the YBCO O4 mode at ≈500 cm^{-1}. This mode is considerably more prominent in the spectrum of the 75 A segment; in fact, its relative intensity with respect to the O2+/O3− mode at ≈330 cm^{-1} is 3–4 times greater for the 75 A segment than for the 150 A segment. Observation of this mode in the instrumental orientation we use with the Raman microprobe indicates *c*-axis tilted and/or straight-up *a*-axis YBCO grains [5,6,8]. So, the most significant finding from the Raman data is the more tilted YBCO grain structure in the 75 A segment than the 150 A segment.

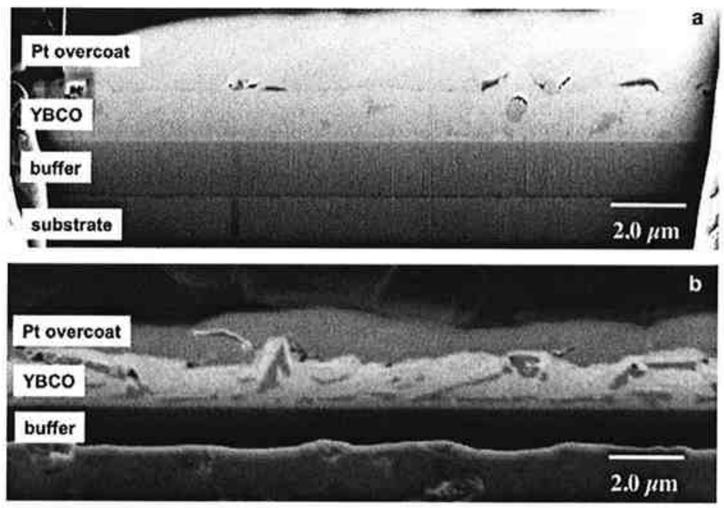

Fig. 3. SEM images of FIB-cut specimens from (a) the 150 A segment and (b) 75 A segment of the MOCVD-YBCO coated conductor from SuperPower, Inc. Within the YBCO layer (as indicated in the images), the light shaded areas are YBCO grains, the darker gray areas are second phases, and the black spots are pores.

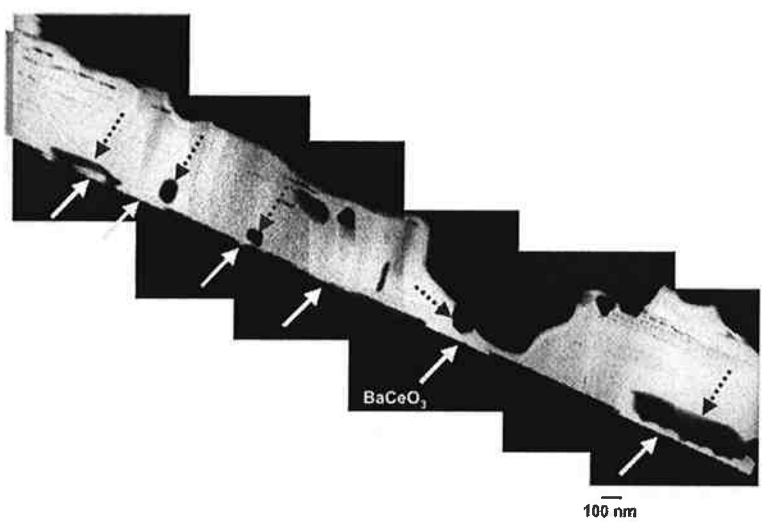

Fig. 4. Barium EFTEM map for a portion of a FIB-cut specimen from a typical low-I_c region of the MOCVD-YBCO coated conductor from SuperPower, Inc.

After completion of the Raman measurements, FIB cuts were made in the vicinity of the MOI indexed regions of both the 150 A and the 75 A segments. Fig. 3 shows SEM images of FIB-cut specimens from the two samples. The image for the cut from the 150 A segment (Fig. 3a) reveals mostly dense, well-textured YBCO grains (the light gray areas) with some second-phase crystallites dispersed throughout the film (the darker spots in the YBCO layer). In the image of the cut from the 75 A segment (Fig. 3b), we see mostly severely tilted YBCO grains interspersed with second phases and pores. Movies made during the FIB milling reveal the extensive nature of these types of defected structures in three dimensions. These same defects are also present in the 150 A segment, but to a considerably lesser extent than in the 75 A segment.

To explore second-phase development in greater detail, EFTEM analyses were performed on specimens from selected segments of the SuperPower tape exhibiting a range of I_c values. Fig. 4 shows a barium EFTEM map for a FIB specimen extracted from a typical low-I_c domain as determined by MOI. This map depicts regions where barium has intruded into portions of the CeO_2 buffer layer (solid arrows in Fig. 4). Above these intrusion regions (presumed to be partially composed of $BaCeO_3$), we often observe second-phase crystallites (dashed arrows in Fig. 4), whereas, the

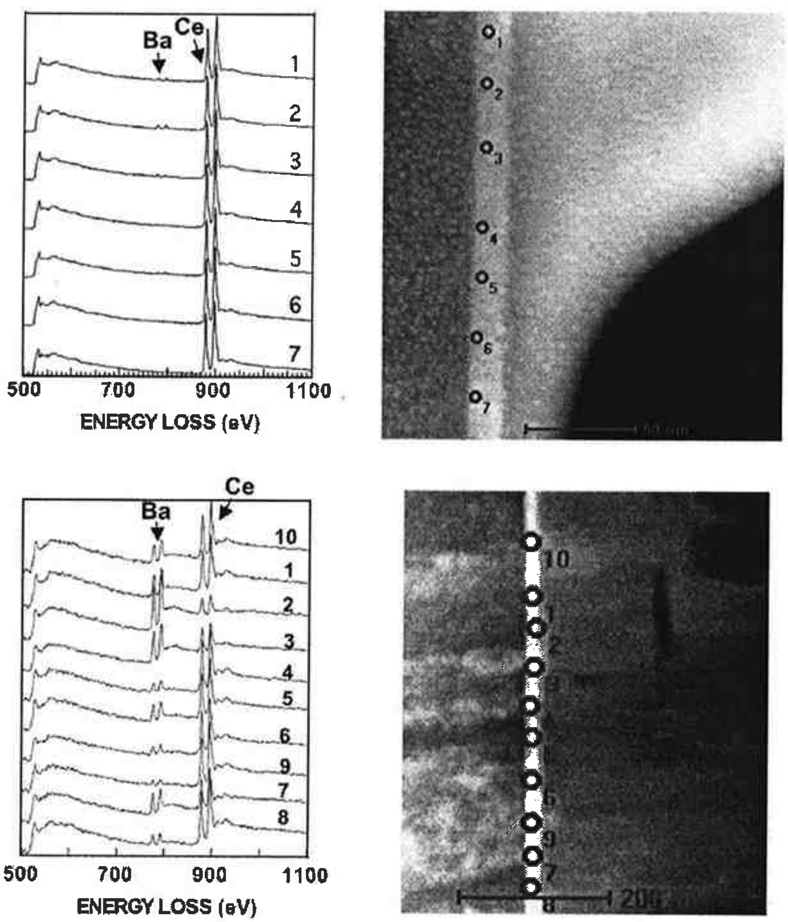

Fig. 5. STEM images and EEL spectra obtained from representative high-I_c and low-I_c regions of the MOCVD-YBCO coated conductor from SuperPower, Inc.

region of the buffer layer where barium-free CeO_2 is apparent typically has an overlayer of YBCO. This connection of $BaCeO_3$ formation with second phase development has been a recurring observation in our studies of this particular conductor specimen [7] and may be symptomatic of YBCO/CeO_2 interfaces. The important issue we are working to resolve about this apparent relationship concerns why the reaction is localized and not prevalent to the entire CeO_2 layer. Do preexisting second phases trigger $BaCeO_3$ formation or do the second phases get nucleated by the $BaCeO_3$, which in turn forms due to other as yet undetermined defects?

Fig. 5 shows scanning transmission electron microscopy (STEM) images and electron energy loss (EEL) spectra for representative high- and low-I_c domains (as identified by MOI) extracted from the SuperPower tape. Noteworthy in the EEL spectra is the substantially greater barium intrusion into the CeO_2 layer in the low-I_c domain as compared to the high-I_c domain. Also note that, in the STEM image for the low-I_c domain, the microstructure of the CeO_2 layer retains its uniformity in spite of the barium intrusion.

Comparing the combined results of Raman, SEM, EFTEM, and STEM/EEL measurements on segments from the SuperPower tape, there is clear evidence of increased porosity, tilted YBCO grains, second phase development, and attack at the YBCO/CeO_2 interface in the transition from high- to low-I_c domains of performance.

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