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Effect of holmium additions on microstructure in $YBa_2Cu_3O_{7-\delta}$

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Abstract

The microstructure of Y–Ho–Ba–Cu–O samples with two different levels of Ho, Ho/Y = 0.5 and 1.0, processed by the trifluoroacetate metalorganic deposition process, have been studied by transmission electron microscopy (TEM) techniques, including high-resolution TEM, conventional TEM and fine-probe energy-dispersive spectroscopy. Oxide nanoparticles with varying levels of Ho have been characterized in detail, and related to other microstructural features. At a lower level of Ho, the (1 1 0) coarse twins with the boundary spacing of 30–60 nm form. Further increase in Ho content considerably produces fine microtwins, and increases the density of nanoparticles and microtwins. Ho additions increase the critical current for the magnetic field parallel to the *c*-axis, and decrease it for the field parallel to the *a*–*b* plane, resulting in a decreased anisotropy of critical current with field angle compared with undoped Y–Ba–Cu–O samples processed under similar conditions. These trends are discussed in terms of the detailed microstructural observations.

Keywords: Nanoparticles; Rare earth additions; Superconductors; Microstructure; Electron microscopy

1. Introduction

The need for improving the current density of second-generation superconducting wire consisting of $YBa_2Cu_3O_{7-x}$ (YBCO) films, on templates manufactured using ion-beam assisted deposition (IBAD) or rolling-assisted biaxially textured substrates (RABITS), has attracted considerable attention worldwide [1,2]. The metalorganic deposition (MOD) process based on trifluoroacetate (TFA) precursors [3–5] is a high-rate and cost-effective technique for manufacturing YBCO coatings [6,7]. Although the manufacturing cost per kiloampere-meter [8] of TFA-MOD-processed YBCO is very encouraging for future applications, significant performance improvements are still desired. In particular, there is a need for a higher critical current at high temperatures and high magnetic fields, for both military and commercial applications. The targeted critical current (I_c) for military applications such as motors, inductors and generators is 80–105 A cm^{-1} (width) in a magnetic field of 2–3 T parallel to the *c*-axis at 65 K; for commercial applications the required I_c is about 400–600 A cm^{-1} (width) in a magnetic field of 2–5 T parallel to the *c*-axis at 27 K [9]. One of the most effective ways to enhance I_c is to introduce strong flux pinning centers in the YBCO matrix. Recent work shows that the introduction of nanoparticles of Y_2BaCuO_5 [10], $BaIrO_3$ [11], $BaZrO_3$ [12,13] and $BaHfO_3$ [14], and chemical substitution by rare earth (RE) atoms [15–17], are very effective at increasing the critical current at considerably high magnetic fields. It has been shown that a high number density (10^{11} cm^{-2}) of YBa_2CuO_5 nanoparticles, 8 nm in size, can increase the critical current at higher magnetic fields by a factor of two or three [18]. Significant improvement of J_c in TFA-based YBCO films containing nanoparticles of $BaZrO_3$ [19] and $BaHfO_3$ [20] have also been reported very recently. In fact, the increase in the critical current at higher magnetic fields by using $BaZrO_3$ nanoparticles is greater than 400%, as compared with YBCO films without any nanoparticles [19].

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Since the addition of RE elements (with the exception of Ce, La and Pr) to YBCO does not cause any suppression of the superconducting transition temperature (T_c) [21], a large number of RE elements has been tried as dopants to YBCO to enhance the flux pinning force. A significant enhancement of this pinning force has been obtained in the case of lighter RE atoms, such as Nd, Sm and Eu [15,16], mostly with sintered powders of $Re_{0.2}Y_{0.8}$-$Ba_2Cu_3O_{7-y}$. The partial substitution of Sm for Y, for example, has strongly enhanced the critical current density, J_c, for the composition of $Y_{2/3}Sm_{1/3}Ba_2Cu_3O_{7-y}$, resulting in a critical current density of 4.7×10^6 A cm^{-2} (75.5 K, 0 T) [17]. A factor of two improvement in J_c has also been reported for $Dy_{0.33}Ho_{0.66}Ba_2Cu_3O_{7-x}$ compared with $YBa_2Cu_3O_{7-x}$ at 0.2 T applied parallel to c-axis [22]. J_c and flux pinning have been observed to be significantly improved by Ho substitution for Y in YBCO [23]. It was reported that in $Y_{1-x}Ho_xBa_2Cu_3O_y$ ($x = 0$, 0.2, 0.4 and 0.6) samples prepared by a powder melting process, the J_c in-field can be enhanced because of the reduction of size of YBa_2CuO_5 particles and the increase in stress-field pinning centers, but detailed electron microscopy studies to elucidate details of the effects of Ho on the fine scale microstructure were not presented [23].

Although considerable attention has been paid to understanding the microstructure and critical current density in YBCO films produced by the TFA-MOD methods e.g. [2,4,5,7,19,20,24,25], fewer investigations have been undertaken to study the effect of RE additions on microstructural evolution in TFA-MOD-produced YBCO. In this regard, it has been reported very recently that the addition of dysprosium (Dy) to YBCO films processed using TFA-MOD methods lowers the density of Y-214 type stacking faults significantly compared with undoped YBCO films produced using the same approach [26]. In order to optimize the design and processing of these materials, it is thus important to investigate how the microstructure changes with different levels of RE additions, including the size distribution and chemistry of nanoparticles, twins and stacking faults, and the stability of tweed structures. In the present work, detailed studies have been made of the effect of Ho additions on the microstructure of $YBa_2Cu_3O_{7-\delta}$. High-resolution transmission electron microscopy (HRTEM) and fine-probe energy-dispersive spectroscopy (EDS) were employed here to characterize the microstructure of these materials as a function of Ho content, and where possible to relate these observations to the critical current. This type of information provides the microstructural basis needed to help optimize the properties, including critical current, of such materials.

2. Experimental

The MOD precursors were deposited onto a continuous length of rolling assisted biaxially textured substrate of Ni–5 W coated with 75-nm-thick epitaxial films of Y_2O_3, YSZ and CeO_2. The YBCO precursor films were thermally decomposed to a film with a nominal composition of Y_2O_3–Ho_2O_3–BaF_2–CuO at temperature below 600° C in a humidified atmosphere. This films were subsequently converted to the tetragonal YBCO phase at around 750–790 °C in a controlled H_2O and O_2 atmosphere. The films were then annealed in O_2 at about 500 °C, in order to convert the tetragonal to the orthorhombic structure. Further details of the TFA-MOD process are discussed elsewhere [3,7]. Ho–Y–Ba–Cu–O samples corresponding to two different levels of Y to Ho ratios, Y:Ho = 1:0.5 and Y:Ho = 1:1, were prepared in this way. Samples for TEM were prepared by using in a Fischione™ ion mill with a gun voltage of 5 kV, a current of 5 mA and a sputtering angle of 12°. Philips CM-30 and JEOL 2200-FX analytical transmission electron microscopes were then employed to examine the microstructure. A standard four-point probe technique was used to measure the critical current in YBCO films, with a voltage criterion of 1 μV cm^{-1}. The measurements were carried out in the temperature range of 65–77 K and in the magnetic field range of 0–3 T, on YBCO films with bridges ~1 cm in length and 2 mm in width.

3. Results and discussion

Detailed microscopy was performed on samples with two different levels of Ho addition. A large number of very fine oxide particles were observed in the superconducting matrix in the sample with the 1:0.5 ratio of Y to Ho. Fig. 1a is a typical TEM image showing the particles to be in the size range of 20–300 nm diameter. Around 80% of the particles were observed to be below 40 nm in size and about 15% were in the range of 100–300 nm, suggesting that the majority of particles are in a size range that is greater than the superconducting coherence length (~2–4 nm, a–b plane). Although the particle sizes are mostly greater than the coherence length, the fine particles have often been observed (under proper tilted conditions) to have an associated strain field, possibly resulting from small differences in coefficients of thermal expansion between YBCO and the oxide particles. Note that the specimen was heated to 750–790 °C for conversion of the mixture of oxide particles to tetragonal phase, and subsequently annealed in O_2 atmosphere at 500 °C for conversion of tetragonal to orthorhombic. The strain contrast associated with one of these fine particles is indicated by the dark lobes in the inset of Fig. 1a. The fine particles thus likely act as pinning centers. Also, the density of the particles appears to be relatively high in this material (Fig. 1a). A large number of (1 1 0) transformation twins were observed in images taken with the beam direction close to the [0 0 1] orientation (see e.g. Fig. 1a). The spot splitting along the ⟨110⟩ directions, which is a characteristic of (1 1 0) twins, was observed in the selected area diffraction patterns (Fig. 1b and c). An HRTEM image near the [0 0 1] zone shows the (1 1 0) twins (Fig. 2) in the vicinity of the particle–matrix interface; in some cases the twins appear to bend near the particle–matrix interface.