Control of Flux Pinning in MOD YBCO Coated Conductor

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***Abstract*—Two different types of defect structures have been identified to be responsible for the enhanced pinning in Metal Organic Deposited YBCO films. Rare earth additions result in the formation of nanodots in the YBCO matrix, which form uncorrelated pinning centers, increasing pinning in all magnetic field orientations. 124-type intergrowths, which form as laminar structures parallel to the ab-plane, are responsible for the large current enhancement when the magnetic field is oriented in the ab-plane. TEM studies showed that the intergrowths emanate from cuprous containing secondary phase particles, whose density is partially controlled by the rare earth doping level. Critical process parameters have been identified to control this phase formation, and therefore, control the 124 intergrowth formation. This work has shown that through process control and proper conductor design, either by adjusting the composition or by multiple coatings of different functional layers, the desired angular dependence can be achieved.**

***Index Terms*—Angular dependence, coated conductor, hybrid, intergrowth, nanodots, pinning, RABiTS, RE addition, YBCO.**

I. Introduction

THE development of Second Generation (2G) YBCO high temperature superconducting wire has transitioned from a demonstration of the technical feasibility and evaluation of potential manufacturing processes to the scale-up of a commercially viable 2G HTS wire manufacturing technology. For many applications, such as cables and fault current limiters (FCL), the self field critical current is the important parameter. However, for other applications, such as motors and generators, the wire performance in applied magnetic fields is very important. In addition, the dependence of the critical current on the field orientation is critical for maximizing the wire performance in coil applications.

The incorporation of pinning centers into YBCO films has been widely studied using Pulsed Laser Deposition (PLD). MacManus-Driscoll [1] studied the relationship between pinning and the variance of RE ion size in the $Y_x(RE_{1-x})Ba_2Cu_3O_y$ system. The addition of $BaZrO_3$ particles has been shown to result in strong pinning behavior in the H//c direction [2], [3]. Matsumoto showed that by decorating the substrate surface with nanodots YBCO films grown by PLD inherit the defect structure resulting in tremendous pinning forces along the H//c direction [4]. All these studies focused on the introduction of random point pinning or correlated pinning along the H//c direction.

In this work, we report on different types of pinning centers that can be incorporated in Metal Organic Deposited (MOD) YBCO films and their effects on the pinning force as a function of the field orientation. We also report the results of increased pinning both in H//c and H//ab directions through RE additions to YBCO films and through the process control of $Y(RE_x)BCO$ superconductors.

II. Experimental

American Superconductor's 2G manufacturing approach is based on the YBCO(MOD)/RABiTS (Metal Organic Deposition/Rolling Assisted Biaxially Textured Substrates) technology. The coated conductor architecture discussed here is based on textured Ni(5at%W) substrates where heteroepitaxial buffer layers Y_2O_3, YSZ, and CeO_2 are deposited by high-rate reactive sputtering. On top of the buffer layers, a metal trifluoroacetate-based precursor is deposited by metal organic deposition (MOD) [5]. The precursor film is then dried and decomposed to form a mixture of metal oxy-fluorides. A subsequent high-temperature heat treatment is used to convert the precursor into a crack-free, nominally 0.8 μm YBCO superconducting film. The composition of the films was varied from $Y_{1-x}(RE_x)BCO$ (RE = Yb, Eu, Gd, Ho, Sm and x = 0–0.33) to $Y(RE_x)BCO$ (RE = Er, Dy, Ho, and x = 0–0.5). The critical current was measured by the standard four probe method. In-field performance was tested at 65 K and 77 K up to 7 T.

III. Results and Discussion

A. Origin and Control of 124-Type Intergrowths

MOD-derived YBCO films grow with a laminar structure. This microstructure contrasts sharply with the columnar structure typically seen in physical vapor deposition processes, such as PLD [5]–[7], and is responsible for the unique properties of the films. The MOD-derived YBCO films have a significant current enhancement with the magnetic field oriented in the ab-plane, as shown in Fig. 1, due to the existence of a high density of planar defects [6]. Understanding the formation of

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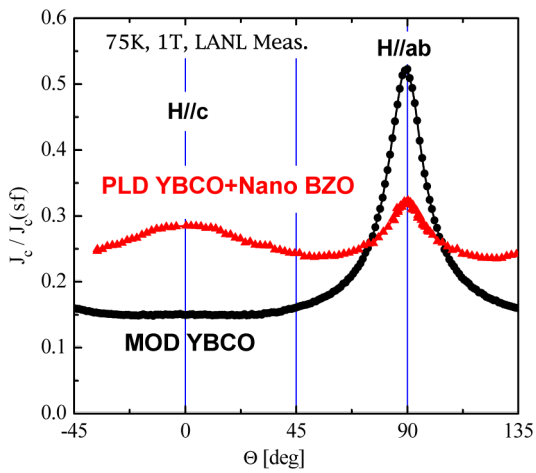

Fig. 1. Angular dependence of MOD YBCO/RABiTS and PLD films $\mathrm{YBCO} + \mathrm{BaZrO_3}$ addition.

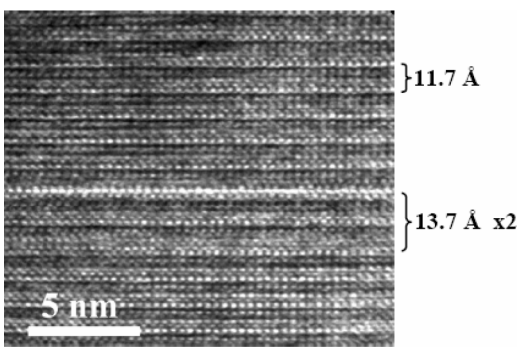

Fig. 2. HRTEM shows the lattice of 123 and the intergrowth.

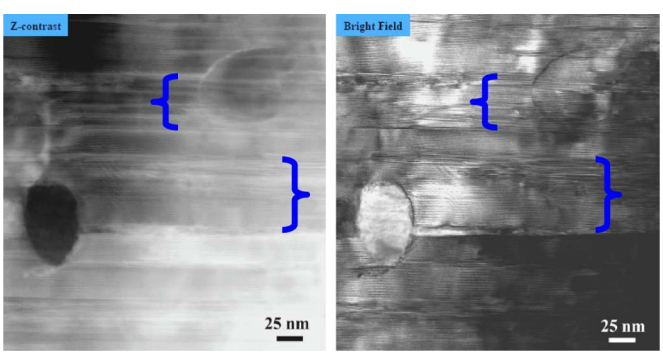

Fig. 3. TEM images of YBCO sample with Z-contrast and bright field images. 124 type intergrowths emanate from Ba-Cu-O particles.

the planar defects is important since it controls the H//ab plane performance.

HRTEM studies of the oxygenated films showed that the planar defects have a lattice parameter of 13.7 Å, corresponding to a $\mathrm{YBa_2Cu_4O_x}$ type lattice as shown in Fig. 2. Z-contrast image (Fig. 3) showed the planar defects have lower average Z, consistent with $\mathrm{YBa_2Cu_4O_x}$ layers. X-ray (2-theta) analysis of YBCO films at various stages of processing show a broadening of (002) and (003) peaks (Fig. 4) during the oxygenation step (400–500°C). This peak broadening has been shown to correspond to the density of 124-type intergrowths in the YBCO films [8].

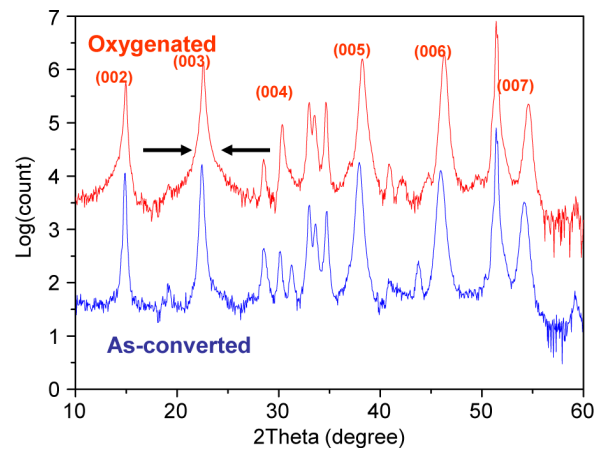

Fig. 4. XRD of as converted and oxygenated films.

TEM analysis of the intergrowths shows that they frequently form in groups, emanating from a common particle as shown in Fig. 3. Raman, HRTEM and EELS analysis of as reacted YBCO film, in which the intergrowths are just forming, show the particles associated with the intergrowths are a barium cuprite $(\mathrm{Cu^{1+}})$ phase [9]. Other particles, such as CuO and $\mathrm{Y_2Cu_2O_5}$ are generally not associated with the intergrowths. Raman microscopy measurements [9] also indicate the involvement of a cuprous entity in the as-reacted MOD film. However, the detailed structure and composition of this cuprite phase has not been identified in this study.

B. Control of Random Pinning

Although the performance of the MOD-based YBCO films is suitable for cable and FCL applications requiring high self-field critical current, it is desirable to improve the performance in perpendicular fields present in coil-based applications. One approach to enhancing the pinning of the MOD-based YBCO films is to introduce random pinning to increase the overall pinning force. Fig. 5(a) shows the microstructure of the pure YBCO composition. The microstructure shows the presence of porosity and secondary phases. The primary and largest secondary phase, identified by EDS analysis, is predominately a barium cuprate phase. Other secondary phases, with sizes of 10 to 50 nm, include $\mathrm{Y_2Cu_2O_5}$ and $\mathrm{Y_2O_3}$.

From the pinning view point, small particles have better pinning effects than large particles and therefore are preferred. In order to increase the density of the small secondary phases, we added additional RE to the film by adjusting our overall composition of $\mathrm{Y(RE_x)BCO}$. Fig. 5(b) shows the microstructure of a film with the composition $\mathrm{Y(Dy_{0.5})BCO}$. EDS analysis of the Dy doped film indicated the secondary phase particles were primarily $\mathrm{RE_2O_3}$ and $\mathrm{RE_2Cu_2O_5}$ ($\mathrm{RE} = \mathrm{Y}$ and Dy) with a significantly reduced amount of barium cuprite. TEM analysis shows the 20 $\sim$ 50 nm $\mathrm{RE_2O_3}$ and $\mathrm{RE_2Cu_2O_5}$ nanoparticles were uniformly distributed in the YBCO matrix as shown in Fig. 6.

The introduction of these nanoparticles results in a significant increase in the random pinning compared to that of an undoped YBCO film as shown in Fig. 7. Although the Dy-doped sample shows a significant increase in Ic for H//c, the ratio of $\mathrm{I_c[H//ab]/I_c[H//c]}$ falls to $\sim$1.3 from $\sim$4.5 in the undoped YBCO film. These changes in the pinning properties are independent of the RE identity as seen in Fig. 7 which also shows

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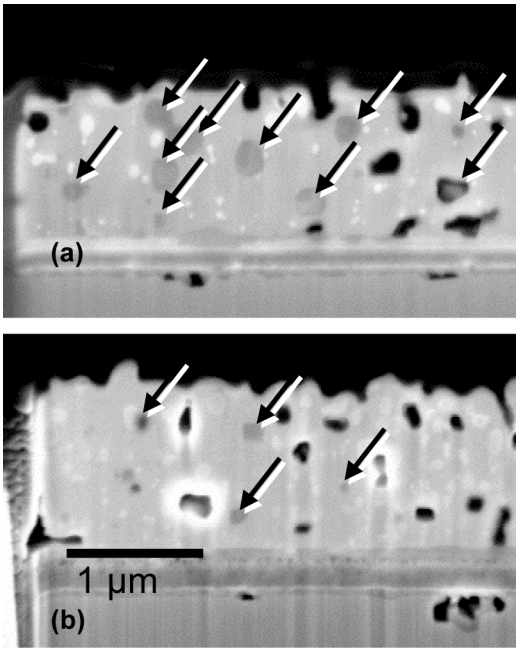

Fig. 5. SEM micrographs of (a) YBCO and (b) $Y(Dy_{0.5})BCO$ films showing differences in second phase particles. Arrows point to Ba-Cu-O phase in both micrographs.

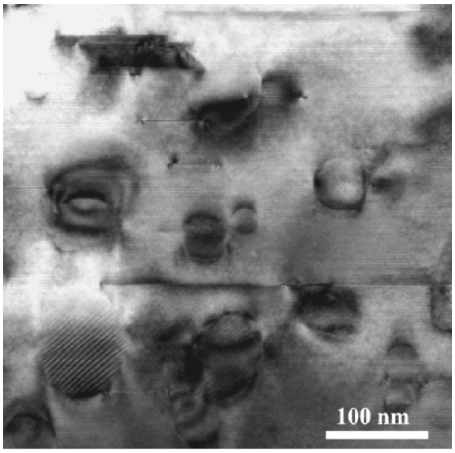

Fig. 6. TEM image of nano-particles in $Y(Dy_{0.5})BCO$.

the angular dependence of $Y(Er_{0.5})BCO$ and $Y(Ho_{0.5})BCO$ films.

Fig. 8 shows that both the enhancement in the random pinning and decrease in ab-plane pinning vary with the level of RE doping, with the effect saturating around $Y(RE_{0.5})BCO$. This decrease in the *ab*-plane pinning correlates to the decrease in the 124-type stacking fault density as shown in Fig. 9, which can be monitored and modeled by the broadening of the 002 and 003 peak-broadening in the 2-theta scans of the YBCO. This decrease in 124-type intergrowths is believed to be associated with reduction in the amount of the cuprite phase formed in the presence of the increased RE concentration.

The compositional analysis of the RE-doped films indicated that the Y site in the 123 phase is partially substituted with the RE. To evaluate whether the substitution of Y by RE element contributes to the increased random pinning, we tested films

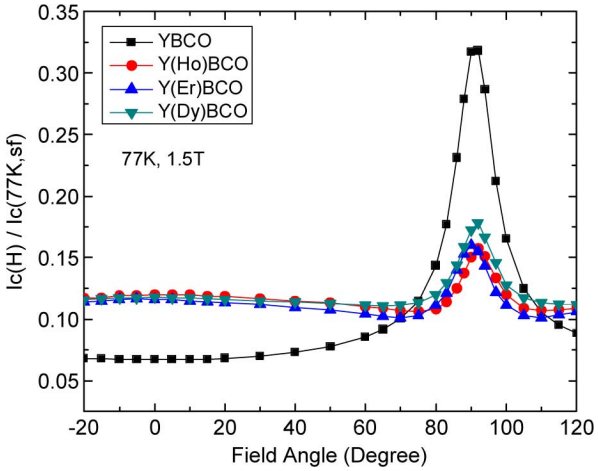

Fig. 7. Angular dependence of YBCO and Y(RE0.5)BCO ($RE = Dy$, Ho, Er) at 77 K, 1.5 T.

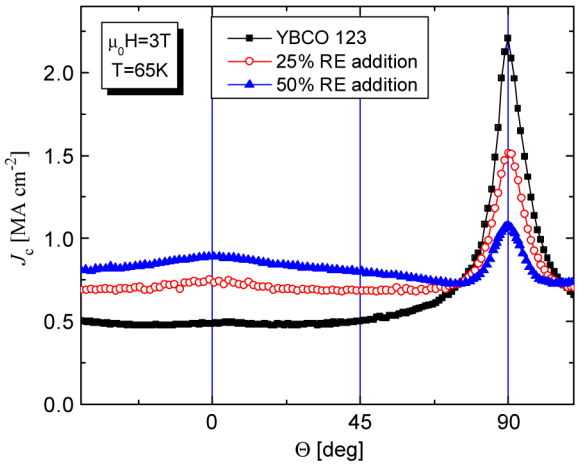

Fig. 8. Angular dependence YBCO and $Y(Er_x)BCO$ ($x = 0.25$ and 0.5) films.

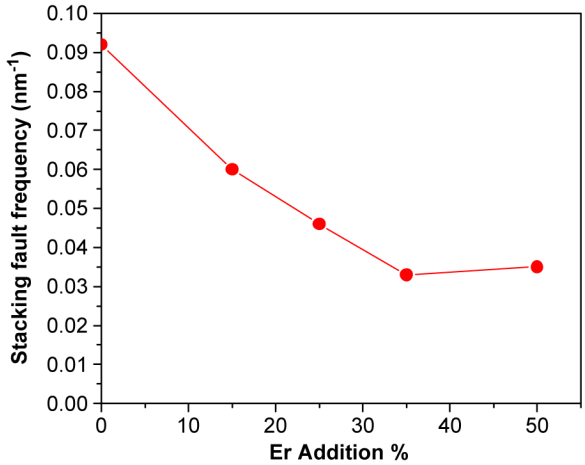

Fig. 9. Stacking fault density as a function of Er additions.

prepared with substitution of Y by RE with the composition of $Y_{1-x}(RE_x)BCO$. The in-field measurements showed that with up to 33% substitution of Y by Yb, Eu, Gd and Sm, no substantial pinning enhancement is observed compared with pure YBCO samples. Therefore, it is clear that the pinning increase

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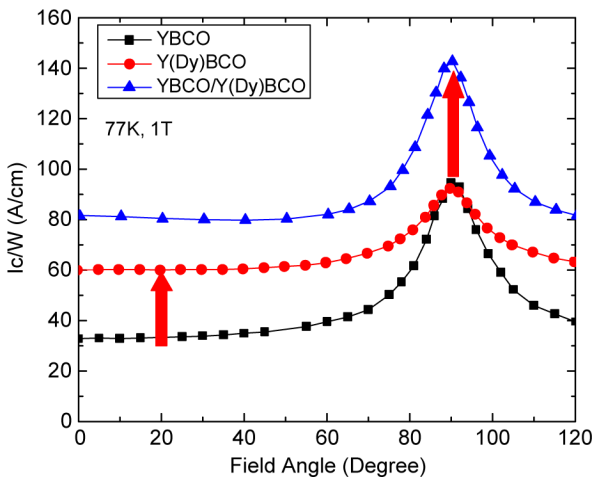

Fig. 10. Angular dependence of YBCO (0.8 μm) and $Y(Dy_{0.5})BCO$ (0.8μm) and a hybrid superconductor $Y(Dy_{0.5})BCO/YBCO$ (0.8 μm/0.6 μm).

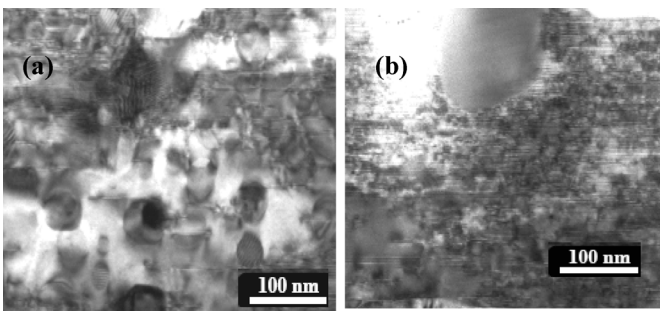

Fig. 11. TEM images of hybrid film. (a) Bottom $Y(Dy_{0.5})BCO$ layer. (b) Top YBCO layer.

with RE addition is due to the introduction of the RE-based nanodots observed by TEM.

C. Engineering the Pinning Through Design of a Hybrid Superconductor

Although the RE-doped YBCO films show a significant enhancement in the random pinning, most coil applications require $I_c[H//ab]/I_c[H//c]$ ratios of $\sim$2 to accommodate differences in the relative strengths of the magnetic field as a function of position in the coil. One approach to controlling this ratio is to adjust the RE doping level as shown earlier. Alternately, we can engineer a hybrid film constructed of an undoped YBCO layer with strong *ab*-plane pinning and a RE-doped layer with enhanced random pinning. The hybrid films in this study were made with a bottom layer of $Y(Dy_{0.5})BCO$ and a top layer of YBCO with nominal thicknesses of 0.8 and 0.6 μm, respectively. The hybrid film was prepared by depositing and decomposing the layers individually and reacting the 1.4 μm film in a single step. Through process optimization, a well tuned high I_c hybrid superconducting wire was produced with a 77 K, self field I_c of 508 A/cm-width. Fig. 10 shows the angular dependence of this hybrid conductor along with that of undoped YBCO and $Y(Dy_{0.5})BCO$ films. The ratio of $I_c[H//ab]/I_c[H//c]$ is $\sim$1.8 for the hybrid film. Microstructural analysis of the hybrid film shows a high density of $RE_2Cu_2O_5$ and RE_2O_3 nanoparticles in the bottom layer [Fig. 11(a)] and a high density of 124-type intergrowths in the top layer [Fig. 11(b)]. These results show that by varying the RE-doping levels and relative thickness of the individual layers, it is possible to selectively tune the anisotropy of the 2G wire to meet the field and temperature requirements of the targeted applications.

IV. Conclusion

Two different types of defect structures have been identified and characterized in MOD-based YBCO films. RE addition to the YBCO films resulted in the formation of nanodots in the YBCO matrix, which can serve as uncorrelated pinning centers, enabling a significant increase in pinning in all field angles. On the other hand, the 124-type intergrowths, which are present in a high density in undoped YBCO films, are responsible for the large peak in the H//ab direction. A high I_c hybrid film, containing individual $Y(Dy_{0.5})BCO$ and YBCO layers was demonstrated. This novel hybrid 2G conductor provides a path for selective tuning of the anisotropy of the 2G wire for targeted application requirements.

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