Optimal, Nanodefect Configurations via Strain-Mediated Assembly for Optimized Vortex-Pinning in Superconducting Wires from 5K-77K

A. Goyal1,2 and S. H. Wee1,3
1Oak Ridge National Laboratory, Oak Ridge, TN 37831
2Now at University at Buffalo, Buffalo, NY 14227
3Now at Tribogenics Inc., 5440 McConnell Ave, Los Angeles, CA 90066

Email: agoyal@buffalo.edu

Abstract. Engineered nanoscale defects within REBa$_2$Cu$_3$O$_{7-\delta}$ based coated conductors are of great interest for enhancing vortex-pinng, especially in high-applied magnetic fields. We have conducted extensive research to optimize vortex-pinning and enhance $J_c$ via controlled introduction of various types of nanoscale defects. This paper provides a summary on how density, morphology, and composition of these engineered nanoscale defects affects vortex-pinning in different field and angular regimes in the temperature regime of 5K-77K. It is shown that certain nanodefect configurations that provide the best performance at high-operating temperatures also result in the optimal properties with record values of the critical current density and the pinning force at low operating temperatures and high-applied magnetic fields.

1. Introduction

High Temperature Superconductors (HTS) wires or coated conductors based on REBa$_2$Cu$_3$O$_{7-\delta}$ (REBCO) hold promise to revolutionize the electric grid of the 21st century. The superconducting wire is processed in the form of an epitaxial film deposited by different methods on a near single-crystal flexible template comprising a metal substrate and epitaxial oxide buffer layers. The template is manufactured using two major technologies: the rolling assisted biaxially textured substrate (RABiTS) technology [1-3], and the ion beam assisted deposition (IBAD) technology [4-6]. Although such superconducting wires can carry several orders of magnitude more power than copper wires of the same cross section, further performance improvements are necessary for the superconducting technology to become cost-competitive, especially in the presence of high-applied magnetic fields. This objective can be achieved by introducing and controlling nano-sized defects and non-superconducting phases within the superconducting film’s matrix to pin the flux-lattice. The first demonstration of significantly enhanced flux-pinning was via incorporation of a YBCO non-superconducting phase Y$_2$BaCuO$_3$ by intermittently depositing YBCO layers and discontinuous 211 layers by PLD using two deposition targets [7]. This approach resulted in pancake-like 211 particles with an average size of 15 nm distributed in the YBCO film, which produced some enhancement in pinning for H//c-axis and much higher improvements for H//ab-planes. The second demonstration of significantly enhanced flux-pinning was by Driscoll et al. via incorporation of randomly oriented, disk shaped BaZrO$_3$ (BZO) nanoparticles with a modal size of 10 nm [8]. It is well known that nanoscale
columnar defects generated by irradiating high-temperature superconducting materials with heavy ions significantly enhance the in-field critical current density. Hence, scientists world-wide had sought means to produce such nanoscale columnar defects in HTS materials without the expense and complexity of ionizing radiation to realize even better vortex-pinning and superior properties in high-applied magnetic fields. Goyal et al. were the first to demonstrate incorporation of irradiation-free, nanoscale, columnar defects comprised of self-assembled BZO nanodots and nanorods resulting in strongly enhanced flux-pinning in REBCO films [9-11]. These results were subsequently reproduced world-wide [12-14]. Kang et al. were the first to demonstrate that such self-assembled, nanoscale columnar defects can be sustained through the thickness in 3-micrometer-thick YBCO films epitaxially grown via pulsed laser ablation on rolling assisted biaxially textured substrates [15]. Enhancements of the critical current, $I_c$, in self-field as well as excellent $I_c$ retention in high-applied magnetic fields in the operating temperature range 65-77K were achieved in the thick films via incorporation of a periodic array of BZO columnar defects, extending through the entire thickness of the film. These columnar defects are highly effective in pinning the superconducting vortices or flux lines, thereby resulting in the substantially enhanced performance of this wire. This technology was transferred to industry and the same self-assembly
process was also demonstrated for MOCVD deposited HTS wires on IBAD templates [16]. In this paper, we show that the strain-driven, self-assembly process invented by Goyal et al. results in stellar vortex-pinning at high operating temperatures (65-77 K) as well as at low operating temperatures (4.2-30 K) in high-applied magnetic fields. At 65-77 K, incorporation of nanoscale BZO columns provides strong correlated pinning as expected. BZO nanocolumn incorporation also significantly enhances critical current density, \( J_c \), and mitigates the \( J_c \) anisotropy at lower temperatures (4.2-30 K) and magnetic fields at up to 16 T (with no sign of decreasing at higher fields), via weak uncorrelated pinning created by oxygen point defects around the nanoscale columnar defects. This weak uncorrelated pinning, shows at 5 K, a record high flux pinning force density, \( F_p > 1.5 \, \text{TN/m}^3 \) in 1.4 μm thick films and a \( J_c \sim 20\% \) of depairing current density \( J_j \) was achieved. This \( J_c \) value is more than 100 times higher than the optimized NbTi superconductors. In addition, \( J_c \) keeps rising with BZO concentration up to 4 vol %.

2. Experimental
All YBCO films with and without different vol% of BZO were prepared by pulsed laser deposition (PLD) using a KrF (\( \lambda = 248 \, \text{nm} \)) excimer laser at a repetition rate of 10 Hz. Laser energy density and

![Figure 2. Pinning force, \( F_p \), as a function of applied magnetic field at various measurement temperatures for a film with 2vol\% BZO additions. The pinning force approaches 1TN/m\(^3\) at 10K; 16T and crosses 1TN/m\(^3\) at 5K, 7T.](image-url)
Figure 3. Pinning force, $F_p$, as a function of applied magnetic field at various measurement temperatures for films with different vol% BZO additions. The pinning force approaches 1TN/m$^3$ at 5K, 16T for the 1 vol% BZO film; crosses 1TN/m$^3$ at 5K, 7T for the 2vol% BZO film and exceeds 1.5TN/m$^3$ at 9T for the 4vol% BZO film. All films were 1.4 µm thick.
Figure 4. The ratio of transport and depairing current density $J_c/J_d$ as a function of temperature for 1, 2 and 4 vol% BZO additions. $J_c/J_d$ increases with decreasing temperature and vol% BZO additions.

field emission scanning electron microscopy using Hitachi S4800 FEG-SEM. TEM foils were prepared by the focus ion beam (FIB) technique, followed by low voltage ion milling and plasma cleaning. The 4.2 K and high field four-probe $J_c$ measurements were performed in a 52-mm warm bore 31 T Bitter magnet at the National High Magnetic Field Laboratory (NHMFL), fitted with a 38 mm bore liquid He cryostat. The 10–77 K measurements were carried out in a 16 T Physical Property Measurement System (PPMS). Samples were always rotated with respect to the external magnetic field around the axis parallel to the current direction to maintain a maximum Lorentz force configuration. The angle $\theta = 0$ is defined as the applied magnetic field perpendicular to the tape plane whose parallelism to the crystallographic c-axis direction has a typical uncertainty of $1-4^\circ$ produced by an offset caused by the IBAD process [17]. Due to the high $I_c$ values observed at lower measured temperatures, samples with different geometries were prepared in order to avoid harmful Joule heating and overstressing by the large Lorentz forces ($I_c \times B$) possible in different regimes of $H$ and $T$. A narrow link $\sim 10 \mu$m wide and $200 \mu$m long, were patterned by SEM/FIB so as to restrict $I_c$ to $\sim 5$ A when the sample was measured in helium gas between 10 and 77 K. Larger bridges about 1 mm wide and 1 cm long were patterned leaving the silver layers present for the high current measurements. Two different home-made $I_c$ probes equipped with rotating sample platforms were used. One had a maximum current-carrying capability of $\sim 500$ A for high $I_c$ measurement in a liquid-helium bath,
while the second had ~5 Å capability in the gas-cooled PPMS cryostat for studies at temperatures above 10 K.

3. Results and Discussion

We have previously reported results on YBCO films of thickness 0.8 μm deposited on LMO/IBAD-MgO/Hastelloy templates via PLD. Detailed XRD analysis based on BZO peak broadening estimates that the size of BZO nanophase is ~6-7 nm and remains nearly unchanged up to 10 vol% BZO, which is also confirmed by transmission electron microscopy (TEM) analysis [18]. YBCO+BZO films also keep excellent texture quality with small full-width-half-maximum values of omega and phi scans (Δω and Δφ) even up to 10 vol% BZO. Δω and Δφ values of YBCO phase are in the ranges of 1.3°~2° and 3.2°~3.6°, respectively, and those of the BZO nanophase range from 2.1° to 2.8° and from 5.8° to 6.2°, respectively. The self-field Jc at 77 K and 65 K is noticeably improved with BZO additions. The highest Jc of 4.1 MA/cm² at 77 K and 12.2 MA/cm² at 65 K are achieved with 1 vol% BZO-additions [18]. In the presence of applied magnetic fields, strong dependence of the optimum BZO doping level on the applied magnetic field strength is observed. Compared to the YBCO film without BZO additions, the 1-4 vol% BZO-doped samples show a significantly improved in-field Jc performance with higher pinning forces, Fp, particularly for H//c, indicating the efficiency of BZO columnar defects as strong c-axis pinning centers. The in-field Jc data at 77 K show that the 1 vol% BZO-doped film has the highest Jc in the self-field and up to the first cross-over field of ~1.6 T. When the field is higher than ~1.6 T, the 2 and 4 vol% BZO doping levels lead to the highest Jc up to and over the second cross-over field of ~7.3 T, respectively. The Jc data at 65 K also show the same trend, but the cross-over fields are shifted to higher fields [18]. Angular dependent Jc data for the samples at 77 K and 65 K show massive enhancement in Jc in all field orientations compared to the YBCO film with no BZO additions. In summary, the YBCO films with BZO additions in the range of 1-4 vol% BZO, show excellent performance in the range of 65-77K [18].

In superconducting films with BZO additions, the incorporated nanocolumns give rise to local strain modulations, which have important effects not only on pinning but also on oxygen stoichiometry and Tc. Differently from (and in addition to) the macroscopic, unidirectional strain that arises in YBCO films due to epitaxial growth on a substrate with slightly different lattice parameter, the array of vertical interfaces between BZO nanocolumns and YBCO matrix produces a much more localized, non-monotone strain field, which varies on the nanoscale and produces measureable broadening of XRD peaks. XRD analysis shows that such a local strain increases with increasing BZO concentration and thus nanocolumns density. In addition to an increase in local strain, increasing BZO additions also results in a significant drop in Tc with a linear decrease in Tc of ~0.4 K/ vol % [19]. A mechanism for this reduction in Tc via local strain can be due to locally reduced oxygen concentration or presence of oxygen vacancies. The local strain can be quantified directly through the Z-contrast scanning TEM images by measuring the local variation of the YBCO c-axis parameter by measuring unit cell dimensions along the c-axis. Such an analysis shows that the strain is peaked away from the BZO column - YBCO interface in the YBCO phase [19]. We then measured the local oxygen stoichiometry by electron energy loss spectroscopy (EELS) elemental mapping of film regions incorporating a BZO nanocolumn. The oxygen signal shows a minimum in the YBCO region immediately surrounding the rod, which is highly strained [19]. Oxygen deficiency was also confirmed via local probing of the Cu valence using the Cu-L_2,3 edge [19]. A picture then emerges in which the strain surrounding the nanorods hinders proper YBCO oxygenation and this oxygen deficiency explains the reduced Tc in YBCO films with self-assembled BZO nanorods. The diameter of the BZO rods is 6 - 8 nm and the average spacing between BZO rods is ~20 nm for a BZO concentration of 4 vol %. The observed spatial extent of oxygen depletion is 3 - 4 times the BZO rod diameter; therefore an overlap of oxygen-depleted YBCO regions surrounding BZO nanocolumns is expected to occur near or above this concentration, leading to the disruption of current percolation through the high Tc phase and to a lower measured Tc. These oxygen vacancies or point defects if present should provide excellent collective pinning at lower temperatures. If this is the case, then
there exists the possibility of BZO nanocolumns to not only provide excellent vortex-pinning at higher operating temperatures but also at lower operating temperatures.

Fig. 1 shows the $J_c$ as a function of applied magnetic field at various measurement temperatures for 1.4 $\mu$m thick YBCO film with 2 vol% BZO additions. A self-field $J_c$ of $\sim 60$ MA/cm$^2$ is observed at 10 K. The extrapolated value of self-field $J_c$ at 5 K is in the range of 70-80 MA/cm$^2$. The $J_c$ for the film is high throughout the operating temperature range as shown in the figure. These values are the highest reported to date for such thick films at 5 K as opposed to a measurement temperature of 4.2 K (there is a massive increase in $J_c$ from 5 K to 4.2 K). It should be noted that these values cannot be compared to thinner films in the thickness range of 0.2-0.8 $\mu$m, as typically for all in-situ fabricated films, there is a strong exponential decrease of $J_c$ with film thickness.

Pinning force, $F_p$, as a function of applied magnetic field at various measurement temperatures for a film with 2 vol% BZO additions is shown in Fig. 2. The pinning force approaches 1 TN/m$^3$ at 10 K, 16 T and crosses 1 TN/m$^3$ at 5 K, 7 T. These values of pinning force are the highest reported to date for a 1.4 $\mu$m thick film with only 2 vol% BZO additions. The $F_p$ as a function of applied magnetic field at various measurement temperatures for 1.4 $\mu$m thick films with different vol% BZO additions is shown in Fig. 3. The $F_p$ approaches 1 TN/m$^3$ at 5 K, 16 T for the 1 vol% BZO film; crosses 1 TN/m$^3$ at 5 K, 7 T for the 2 vol% BZO film and exceeds 1.5 TN/m$^3$ at 9 T for the 4 vol% BZO film. Once again, these are record performance values and the highest reported to date. These high values of $J_c$ and $F_p$ in YBCO films with BZO additions were first presented at the Electronic Materials and Applications (EMA) meeting in January of 2013 [20].

The temperature dependence of $J_c/J_d$, the ratio of the measured $J_c$ to the calculated depairing current density, $J_d$ at 4.2K, can provide the pinning evolution with temperature [21]. As shown in Fig. 4, at $T > 65$ K, due to strong thermal fluctuation, $J_c/J_d$ is dramatically reduced with increasing temperature. Additionally, this decay of $J_c/J_d$ is worsened by increasing of BZO concentration. This fast decline of $J_c/J_d$ partially caused by the reduced $T_c$, and/or might be related to the high-density of straight BZO nanorods [22]. Between, $\sim 30$ K and $\sim 60$ K, $J_c/J_d$ shows flattening temperature dependence. With further decreasing temperature, weak pinning takes over and $J_c/J_d$ rapidly increases with decreasing temperature. This dramatically enhancement of $J_c/J_d$ at $T < 30$ K becomes more pronounced at higher BZO concentration and lower fields. In optimized Nb-Ti thin films, the maximum reached $J_c$ is of order of 10% $J_d$ [23], much lower than $\pm 20% J_d$ achieved in these thick and practical REBCO conductors.

In summary, we have shown possible optimal, nanodefect configurations via strain-mediated self-assembly for optimized vortex-pinning in superconducting wires in broad magnetic field and temperature regimes. At higher operating temperatures, the BZO columnar defects provide strong correlated vortex-pinning resulting in high-$J_c$ and excellent performance in high-applied magnetic fields. At low operating temperatures, oxygen point defects created by local strain at YBCO/BZO interfaces in the films provide excellent weak collective-pinning resulting in very-high $J_c$ (with $J_c/J_d$ more than 100 times higher than the optimized NbTi superconductors) and record $F_p$ values exceeding 1.5 TN/m$^3$. The transport properties reported in this paper surpass all previously reported values in the temperature regime of 5-77 K for 1.4 $\mu$m thick films with only up to 4 vol% BZO additions [24]. The results reported in this paper provide a route for fabrication of commercial HTS wires with outstanding superconducting transport properties over a broad operating temperature regime.

Acknowledgments
Authors wish to acknowledge Aixia Xu and David Larbalestier for transport measurements performed at NHFML.
References

[1] Goyal A et al. 1996 Appl. Phys. Lett. 69 1795.
[2] Goyal A, Paranthaman M and Schoop U 2004 MRS Bulletin 29 552.
[3] Goyal A 2005 Epitaxial superconductors on rolling-assisted-biaxially-textured-substrates (RABiTS) Second Generation HTS Conductor ed A. Goyal (Kluwer, Norwell, MA, 2005), Chapter 2, pages 29-46.
[4] Iijima Y, Tanabe N, Ikeno Y, and Kohno O 1991 Physica C 185 1959-1960.
[5] Wu X D, Folyn S R, Arendt P N, Townsend J, Adams C, Tiwari P, Coulter J W, Peterson D E 1994 Appl. Phys. Lett. 65 1961.
[6] Arendt P 2005 IBAD Template for HTS Coated Conductors Second Generation HTS Conductor ed A. Goyal (Kluwer, Norwell, MA, 2005), Chapter 1, pages 1-28.
[7] Haugan T, Barnes P N, Wheeler R, Meisenkothen F, and Sumption M 2004 Nature 430 867.
[8] Macmanus-Driscoll J et al. 2004 Nat. Mater. 3 439.
[9] Goyal A et al 2004 Presented at the 2004 Annual Peer Review of the US Superconductivity Program for Electric Systems (July 2004). http://www.energetics.com/meetings/supercon04/pdfs/presentations/f rabis strategic talk ffy04 final.pdf
[10] Goyal A et al. 2004 CCA 2004: Presented at the Int. Workshop on Coated Conductor for Applications (Oiso Prince Hotel, Kanagawa, Japan, Nov. 2004).
[11] Goyal A et al. 2005 Supercond. Sci. Technol. 18 1533.
[12] Yamada Y et al. 2005 Appl. Phys. Lett. 87 132502.
[13] Varanasi C, Burke J, Wang H, Lee J H, and Barnes P 2008 Appl. Phys. Lett. 93 092501.
[14] Mele P, Matsumoto K, Ichinose A, Mukaida M, Yoshida Y, Horii S and Kita R 2008 Supercond. Sci. Technol. 21 125017.
[15] Kang et al. 2006 Science 311 5769.
[16] Chen et al. 2009 Appl. Phys. Lett. 94 062513.
[17] Chen et al. 2009 Supercond. Sci. Technol. 22 0550131.
[18] Wee et. al. 2013 Nature Magazine’s Scientific Reports 3 Article number: 2310.
[19] Cantoni et al. 2011 ACS Nano 5 4783–4789.
[20] Goyal et al. 2013 Electronic Materials & Applications in Symposium S12: Recent Developments in High-Temperature Superconductivity,  http://ceramics.org/wp-content/uploads/2013/01/ema2013_finalprogram.pdf, page 14.
[21] Blater et al. 1994 Rev. Mod. Phys. 66 1125.
[22] Maiorov et al. 2009 Nat. Mat. 8 398.
[23] Stejic et al. 1994 Phys. Rev. B 49 1274.
[24] Obradors et al., 2014 Supercond. Sci. Technol. 27 044003.