Self-assembling nano-diameter needlelike pinning centers in YBCO, utilizing a foreign element dopant

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Abstract. Although pinning centers created by irradiation presently produce the highest $J_c$, it is probable that ultimately these will be emulated by chemical pinning centers. The best pinning centers produced by irradiation nevertheless provide guidelines for desirable morphology of chemical pinning structures. The highest $J_c$ produced earlier in textured HTS was obtained using isotropic high-energy ions produced by fission of $^{235}$U. This so-called U/n process produces pinning centers of diameter $\leq$ 4.5 nm, with an effective length of $\sim$ 2.7 $\mu$m. Maximum $J_c$ occurs for pinning center density of $\sim$ 10$^{10}$ cm$^{-3}$. We use this as a model for desired chemical pinning centers. Our approach to introducing chemical pinning centers has been to produce precipitates within the HTS containing elements not native to the HTS, and to seek needlelike (columnar) deposits of small diameter. We report here on the formation of needlelike or columnar deposits in textured Y123 containing a dopant foreign to Y123. It serves as a demonstration that self-assembling nanometer diameter columns utilizing a dopant foreign to the HTS system are a feasible goal. These deposits, however, do not fully meet the ultimate requirements of pinning centers because the desired deposits should be smaller. The self-assembling columns formed contain titanium, are $\sim$ 500 nm in diameter, and up to 10 $\mu$m long. The size and morphology of the deposits vary with the mass of admixed Ti dopant. $J_c$ is decreased for small dopant mass. At larger dopant masses needlelike precipitates form, and $J_c$ increases again. A small range of mass of admixed Ti exists in which $J_c$ is enhanced by pinning. In the range of admixed Ti mass studied in these experiments there is a negligible effect on $T_c$. Magnetization studies of $J_c$ are also reported.

1. Introduction

Critical current density ($J_c$) is one of the most important properties of high temperature superconductors (HTS). The achievement of high $J_c$ or trapped magnetic field ($B_{trap}$) makes it practical for HTS to be used in devices such as motors and generators, and power transmission. In textured HTS, $J_c$ or $B_{trap}$ can be greatly enhanced by the introduction of pinning centers. Pinning centers are regions in the HTS that can trap magnetic fluxoids. In HTS, pinning centers can be created by as-grown and artificial methods. Presently the highest $J_c$ in textured HTS is produced by irradiation techniques. One such method is the U/n process [1].

In this process $^{235}$U is admixed into the HTS powders, textured, and then irradiated with thermal neutrons. Ions from the fission process then move within, and damage, the HTS. Fission fragment defects are composed of short columns, broken aligned columns and “string of beads”. These defects
are \( \leq 4.5 \) nm in diameter with an effective length for pinning of \( \approx 2.7 \mu \) m, and are isotropically distributed within the HTS. The fission fragment defects act as pinning centers and greatly improve \( J_c \) or \( B_{\text{trap}} \) [1]. Maximum \( J_c \) or \( B_{\text{trap}} \) occurs for a pinning center density of \( \approx 10^{10} \) cm\(^{-3}\). There are, however, negative aspects to U/n processing.

In the U/n process, samples must be irradiated with neutrons; consequently, this extra step in processing incurs additional costs. Also, U/n processed samples have a residual radioactivity, which may make the process unattractive to implement by industry. Nevertheless, irradiation pinning centers provide guidelines for desirable morphologies of chemical pinning structures. It is probable then that pinning centers with residual radioactivity will ultimately be emulated by purely chemical methods.

Our approach to producing chemical pinning centers has been to admix elements not found in the HTS, which may then form precipitates and act as pinning centers [2]. We report here our first successful attempt to emulate columnar irradiation pinning centers by a chemical method. It demonstrates that self-assembled nanometer-diameter columnar deposits can be formed, and that these deposits act as pinning centers to increase \( J_c \) or \( B_{\text{trap}} \) in textured YBa\(_2\)Cu\(_3\)O\(_7\)-\(\delta\) (Y123).

### 2. Sample Processing and Testing

In this experiment we used titanium (IV) oxide (TiO\(_2\)) as the dopant. The TiO\(_2\) was quoted by the manufacturer to be spherical in shape with a diameter of 34 nm. Several batches of textured Y123 samples were produced. Each batch contained Y123 + 30 mol% \( Y_2 \text{BaCuO}_5 \) (Y211) + 0.5 wt% platinum + a fixed wt% of TiO\(_2\). TiO\(_2\) was admixed in doping levels from 0.0 wt% (undoped control samples) to ~ 0.6 wt%. The samples were Y123 cylinders of diameter 1.5 cm and 6.5 mm thick.

\( B_{\text{trap}} \) was measured after samples were cooled in liquid nitrogen while in the field of a 1 T electromagnet. Microstructure studies were done with a JEOL JXA-8600 electron microprobe with wavelength dispersive (WDS) and energy dispersive (EDS) x-ray spectrometers attachments. \( J_c \), as a function of applied field \( (B_{\text{app}}) \), was measured at 77 K with a 1.5 T vibrating sample magnetometer (VSM). The VSM was also used to measure critical temperature \( (T_c) \). \( J_c \) and \( T_c \) measurements were done using rectangular tiles, 3 mm x 3 mm x 1 mm, cut from the larger cylinders.

### 3. Results and Discussion

The leading discovery of this experiment is the formation of deposits with a columnar or needlelike morphology. Analysis of microstructure data indicates that they are \( \approx 500 \) nm in diameter and typically \( 5-10 \mu \) m long. The needles grow shorter for increasing wt% of Ti. As the needles grow shorter, the formation of spherical deposits is also observed. Predominantly spherical shaped deposits are seen in the higher wt% Ti-doped samples. Figure 1 shows a sampling of the morphology of samples from this experiment. All needles and spherical deposits contain Ti as confirmed by the analysis of EDS and WDS data. For samples containing < 0.15 wt% TiO\(_2\), there are no observed Ti-rich deposits. At 0.15 wt% TiO\(_2\), needles were formed. As the TiO\(_2\) concentration is increased beyond 0.15 wt%, the needles grow shorter; spheroids are also formed. Most of the Ti-rich deposits were spherical for > 0.4 wt% doping.

Ti deposits do not appear to be uniformly distributed within the Y123 grain. For all samples doped with Ti, there is substitution of Ti into the Y123 crystal matrix [3-4]. The amount of admixed TiO\(_2\) appears to affect the morphology and composition of Ti-rich deposits. By comparing Ti-doped samples to undoped samples, it appears that Ti did not interfere with the ability of Pt to refine Y211 particles. In all samples containing Ti, there were areas in the Y123 that were free of Y211. These Y211 segregated areas were not seen in control samples. Also, the growth of single grains along the c-axis decreases as the wt% of admixed TiO\(_2\) is increased. Reproduction of exact morphology and pinning center density is difficult. This indicates that we are operating some parameter close to a critical value. This could be a processing parameter such as melt temperature, or a chemical parameter such as wt% of admixed Pt.
Figure 1. Micrographs of TiO₂ doped Y123 showing Ti-rich deposits (small white spots) of varying morphologies for increasing Ti wt%. Notice the formation of needles at 0.15 wt%.

Figure 2. The effect of Ti doping on samples (1.5 cm diameter x 6.5 mm thick) as measured by trapped field. The line is meant to guide the eye. Error bars are ± 6%.

B Trap was measured on cylindrical samples of 1.5 cm diameter to characterize the pinning properties of Ti deposits, and also the Ti doping effect on grain growth. B Trap of Ti-doped samples were compared to B Trap of the undoped samples. The results are shown in figure 2. In general, B Trap decreases for samples containing ≤ 0.2 wt% TiO₂, increases again in the region 0.20 wt% < TiO₂ ≤ 0.4 wt%, and decreases for wt% > 0.4. The multiple effects of Ti doping can be used to explain the behavior of B Trap. Recall that for all samples containing Ti, there is substitution into the Y123, and the growth of single grains diminishes with increasing wt% TiO₂; these effects generally deteriorate Jc and B Trap. Ti-rich deposits of a columnar or needlelike morphology are observed at 0.15-0.2 wt%. The needles act as pinning centers and tend to increase Jc, thereby partially negating the effects of Ti substitution and deceasing grain growth. As the Ti-rich deposits become a mixture of shorter needles and spheroids (TiO₂ > 0.2 wt%), the number of pinning centers also increases and hence Jc increases. At 0.4 wt%, where most of the Ti-rich deposits are spherical, B Trap recovers to the value of undoped samples, which were typically 2700 Gauss (Jc ~ 10 kAcm⁻²) for 1.5 cm diameter x 6.5 mm thick cylinders. B Trap decreases again for > 0.4 wt% doping. This is probably because the high wt% Ti inhibits the growth of single grains [4]. The appearance of a peak in B Trap (and therefore Jc) at 0.4 wt% suggests that an optimum level of Ti doping for pinning is 0.15 wt% < TiO₂ < 0.4 wt%.

To separate the behavior of Jc from the problem of grain growth along the c-axis caused by Ti doping, smaller samples (3 mm x 3 mm x 1 mm) were cut from the larger cylindrical samples, and analyzed by VSM. By comparing similar grain sizes, a more accurate pinning effect of Ti doping on Jc can be obtained from B Trap. Jc was measured at 77 K with B applied parallel to the c-axis of the sample. Figure 3 shows the results. For B applied ~ 0.1 T, Jc of undoped samples is ~ 40 kAcm⁻². Jc decreased to ~ 30 kAcm⁻² in Ti-doped samples that did not contain distinguishable Ti deposits, i.e., at 0.1 wt%. For samples containing mostly Ti-rich needles, i.e., 0.15-0.2 wt%, Jc no longer decreased. Instead, Jc increased to ~ 35 kAcm⁻², indicating that the needles act as pinning centers. Jc continued to increase as more deposits were formed, with an assortment of morphologies from a mixture of short needles and spheroids to mostly spheroids. At B applied ~ 0.6 T, for 0.2 wt%, where only needles are formed, Jc is ~ 1.1 times the Jc of undoped samples. For a mixture of shorter needles and spheroids at 0.3 wt% there is also an increase in Jc of ~ 10%. This indicates that, although there are a greater number of deposits with different morphologies (a mixture of needles and spheroids) at 0.3 wt%, the columns or needles at 0.2 wt% not only act as pinning centers but also appear to be more effective pinning centers than are the spherical deposits.
Figure 3. Critical current density as a function of applied field (parallel to the c-axis) at 77 K.

Figure 4. Critical temperature measurements of Ti-doped samples.

Tc measurements are shown in figure 4. For all samples, including the undoped ones, the midpoint of the temperature transition was 91–92 K. A decrease in Tc of ~ 0.5 K was measured in samples doped with ≥ 0.3 wt%. A broadening of the Tc transition was observed for samples doped with > 0.2 wt% TiO2. Tc for undoped samples was ~ 91.8 K.

4. Summary
Our exploratory experiments on nanometer-sized TiO2 doping of Y123 showed that self-assembled, nano-sized columnar chemical pinning centers are achievable. Processing conditions still need to be optimized to reduce grain growth problems and better control morphology. The formation of chemical columns appears to be very sensitive to the doping level of TiO2, and also to the processing conditions. We speculate that the formation of needles depends critically on the dopant’s particle size. It was previously shown that softer and smaller sized dopants produce smaller deposits [5]. Needlelike pinning centers are typically ~ 5-10 μm long and ~ 500 nm in diameter, and are formed with 0.15-0.2 wt% TiO2 doping. This range also appears to be optimum for Ti doping as it has a minimal effect on Tc. Although the effect on Tc is measured to be small, it is desirable to use a dopant that does not substitute into the crystal matrix. Such a dopant may not inhibit grain growth as much as Ti doping. Additionally, the diameter of the needles is still too large to emulate the best irradiation pinning centers. If the diameter of these Ti needles can be decreased, e.g., by a factor of 2, then the number of needlelike chemical pinning centers should increase Jc in textured Y123 to > 100 kAcm⁻².

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5. References
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