Thermal stability and annealing of columnar defects in $Bi_2Sr_2Ca_1Cu_2O_8$/Ag superconductor

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This work establishes the stability at elevated temperatures of columnar defects, artificially formed in the Bi-based cupric oxide superconductor $Bi_2Sr_2Ca_1Cu_2O_8$ for enhanced vortex pinning. Isochronal anneals, conducted in air, led to losses of critical current density in two stages. The defects were relatively stable up to ~550 °C, where second stage annealing began; above this, the pinning diminished rapidly. The recrystallization and loss of columnar defects were corroborated by transmission electron microscopy.

Understanding and improving the current-carrying capability of high-temperature superconductors (HTS) is a formidable intellectual and technical problem.[1] A general method for increasing the density and effectiveness of vortex pinning sites, which determines the critical current density J_c, is to create artificial defects by particle irradiation.[2] Irradiation with low-energy light ions, such as 3 MeV protons, creates mostly random pointlike defects that pin vortices collectively. However, the pinning energy for a single defect is small, meaning that thermal effects easily depin a vortex at elevated temperature $T<T_c$.

Columnar defects, which were first produced and imaged[3] in $Y_1Ba_2Cu_3O_{7-\delta}$ single crystals by irradiation with heavy ions such as 0.6 GeV Sn, are much more effective pins than point defects. In passing through an HTS material, each ion amorphizes the crystal in a columnar track of diameter ~60 Å and length of 10–40 μm. These experiments and subsequent work on the more highly layered Bi–Sr–Ca–Cu–O system[4–6] showed that columnar defects effectively support supercurrent flow at high temperatures and fields, where the HTS contains magnetic flux in the form of vortex lines or stacks of "pancake" vortices.[7] Consequently, defects with linear geometry pin flux particularly well and lead to persistent supercurrent densities J_p near 10^7 A/cm^2 in YBaCuO and Bi-2212 single crystalline materials at low temperatures. In addition, the region of potential operation in the magnetic field-temperature plane, where the current density remains usefully large, is expanded. The expansion is particularly extensive in the case of the highly anisotropic Bi-based cuprate.

Bi-based superconductors, either deposited on Ag substrates or clad in Ag, are particularly interesting. In these materials, the problem of "weak links" is closer to solution, through the formation of basal plane-aligned structures. This interest is heightened by the discovery[8] that highly effective columnar defects can also be created using *deeply penetrating light ions* of medium energy, such as protons with 0.8 GeV that have a range of ~1/2 m in the superconductor. These energetic particles cause massive nuclei such as Bi to fission and the energetic fission fragments (like heavy ions) create linear defects.

Along with the promising features just cited, some important questions remain: since the columnar tracks are just microscopic rods (~5–10 nm in diameter) of amorphized or highly disordered material, how stable are these structures? How easy is it to recrystallize them and destroy their effectiveness? To assess the stability of columnar defects at potential processing temperatures, we performed isochronal annealing studies of textured Bi-2212 open-faced tapes that had been irradiated with 580 MeV Ag ions. As discussed below, the magnetically measured current density diminished with increasing annealing temperature T_A in two stages. The first stage occurs between room temperature and 300 °C. The second stage commences near 550 °C, setting an upper bound on processing temperature. Following higher temperature anneals, the columnar defects that were previously visible by transmission electron microscopy (TEM) disappeared, and the current density returned to its pre-irradiation levels.

Small particles of $Bi_2Sr_2Ca_1Cu_2O_8$ were formed from nitrate solutions using aerosol pyrolysis, then drying and vacuum annealing at 650 °C to remove the nitrates. A liquid suspension was formed and painted on Ag substrates. The open faced assembly was subjected to a heat schedule that evaporated the carrier, then partially melted the material in the temperature range 890–870 °C, and finally cooled it slowly to room temperature. The resulting BSCCO layers were c-axis oriented, as evidenced by x-ray diffraction, with thicknesses of ~25 μm. Disks of 3 mm diameter were cut from larger area samples.

The materials were characterized with a commercial moving sample magnetometer.[9] All magnetic studies were conducted with the applied magnetic field $H\perp$ (tape surface), i.e., parallel to the nominal crystallographic c axis. Thus the induced currents flowed in the copper–oxygen planes. According to the critical state model,[10] the circulating current density $J=15\Delta M/r$ is proportional to the magnetic hysteresis ΔM. Here, ΔM is defined as the difference in M (magnetic moment per volume of superconductor) for in-

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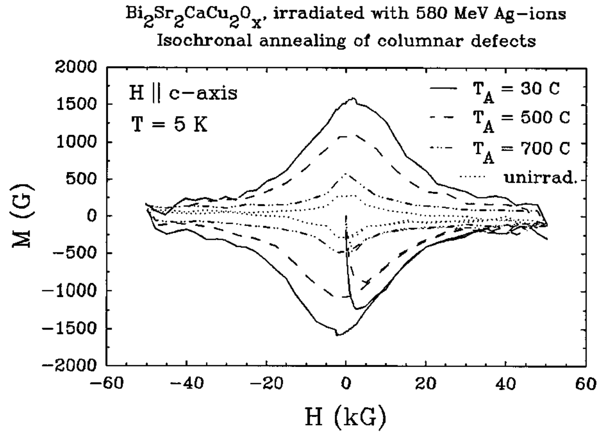

FIG. 1. Magnetization M vs applied field H for $Bi_2Sr_2Ca_1Cu_2O_8$/Ag tape at 5 K, with $H \| c$ axis. When unirradiated, the hysteresis loop was relatively narrow; after irradiation to form columnar defects, the hysteresis increased substantially ($T_A = 30$ °C), and then decreased when annealed at elevated temperatures T_A.

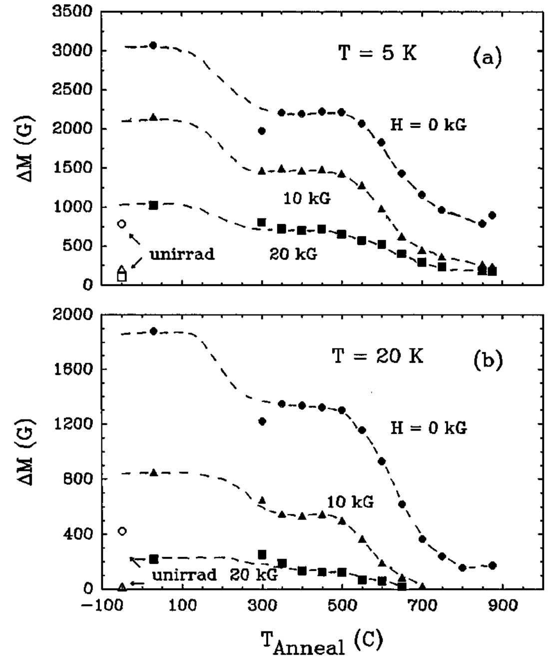

FIG. 2. The magnetic hysteresis ΔM vs annealing temperature T_A, for Bi-2212/Ag tape at (a) 5 K and (b) at 20 K. Measurements with columnar defects (solid symbols) were conducted in the fields shown. After anneals near 850 °C, ΔM decreased to its small pre-irradiation levels denoted by the corresponding open symbols (offset horizontally for clarity). Lines are guides to the eye.

creasing versus decreasing magnetic field history; and r is the average radius of the circulating current. Once precharacterized, open-faced disks of the composite were irradiated with 580 MeV Ag ions using the Holified Accelerator Facility at the Oak Ridge National Laboratory. The ion fluence was 2.3×10^{11} ions/cm^2, which produced the same areal density of columns as the density of vortices in an equivalent matching field $B_\phi = 4.7$ T. The radiation damage depressed T_c slightly, from 86 to 82 K. We then performed 15 min isochronal anneals in air at progressively higher temperatures T_A up to 875 °C. Complementary transmission electron microscopy was conducted on thin chips taken from nearly identical samples, irradiated and annealed simultaneously.

The objective of this study is to determine the robustness of the columnar defects and especially their ability to withstand elevated temperatures. This capability is important, for example, in some processing routes and in procedures for joining tapes. At the outset, irradiation greatly enhanced the persistent current density J_p, as evidenced by large increases in magnetic hysteresis that are illustrated in Fig. 1. The figure shows magnetization loops $M(H)$ versus H at 5 K for one disk: unirradiated; as-irradiated ($T_A = 30$ °C); and isochronally annealed at $T_A = 500$ ° and 700 °C. It is evident that annealing decreases the large hysteresis ΔM originating from strong columnar pinning of vortices. In Fig. 2,, we trace this decrease by plotting ΔM versus annealing temperature T_A.

Figure 2 shows that the defects anneal in two primary states. The first stage occurs between room temperature and 300 °C. There follows a plateau extending up to 500 °C, after which a second stage of annealing develops. The second stage is fairly broad, with $\Delta M \propto J_p$ progressively collapsing with higher temperature T_A. Finally, anneals above 800 °C reduce ΔM to levels near its pre-irradiation values. For comparison, the corresponding, preirradiation values are included in the figure as open symbols.

Qualitatively, we attribute the two stages of annealing to diffusion of low mass anions and higher mass metal cations, respectively. The initial loss of current density at low annealing temperatures likely arises from diffusion and redistribution of the more mobile oxygen anions.[11] This hypothesis is corroborated by a comparison with tracer measurements[12] of the diffusion constant D of oxygen in the basal planes in Bi-2212. In particular, we locate the first stage by finding the temperature T at which an oxygen ion diffuses a distance $x = [2D(T)t]^{1/2}$ = columnar radius ~3 nm in the annealing time $t = 900$ s. The procedure gives the estimate 150 °C for first stage annealing. (This result depends only weakly on the distance criterion, as the exponentially activated diffusion dominates other dependencies.) In the second stage, the amorphous columns recrystallize, which requires diffusion of heavier cations. Unfortunately, diffusion data for cations are scarce. Luckily, however, Nan Chen, Rothman and Routbort[13] measured D for Sr ions in Bi-2212 and similar family members. Applying the same criterion ($x = 3$ nm) for the mean distance shows that diffusion of Sr becomes significant near 650 °C. In fact, this temperature lies in the midst of the second annealing stage. In the absence of reliable data for the other species, we make the plausible conjecture that the lighter ions Ca and Cu diffuse somewhat faster and at lower temperatures than Sr, while Bi becomes mobile only at comparatively high temperature. Hence, one expects second stage annealing to begin somewhat below 650 °C, as observed. Overall, the existence of two annealing stages and their onset temperatures are consistent with independent diffusion measurements to a semiquantitative level. Also, the need for some diffusion by multiple cation species (with onsets at different temperatures) helps to explain the relatively large breadth of the second stage.

We reinforce this interpretation with complementary

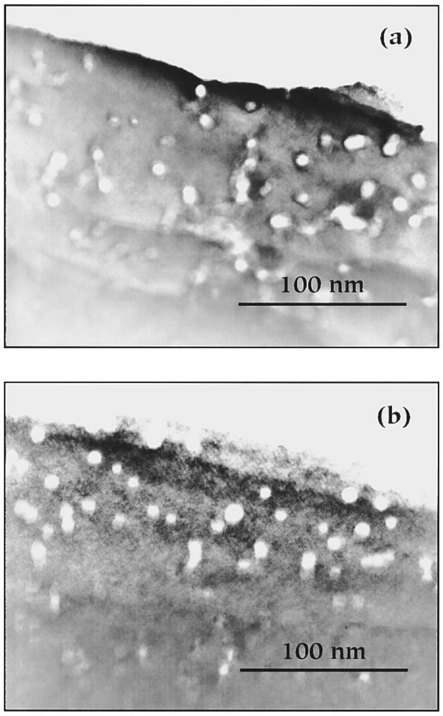

FIG. 3. Plan-view TEM micrographs of Ag-ion-irradiated Bi-2212 layers, after annealing (a) at room temperature and (b) at $T_A = 300$ °C for 15 min. The view is along the crystallographic *c* axis and along the ion path. In (a), a (dark) strain field surrounds each defect; this mostly disappears in (b) after annealing at 300 °C. After annealing at 700 °C, the columnar defects themselves were no longer visible.

high-resolution TEM studies. This work confirms that the columns are still present on the annealing plateau, but they disappear during the second stage. The presence of columnar defects is illustrated in Figs. 3(a) and 3(b), which show images of small areas after annealing at 30° and 300 °C, respectively. In further TEM studies with $T_A = 700$ °C (not shown), we were unable to locate any columns, indicating that their number and/or size were reduced below our limits of detection. The disappearance of columnar defects is consistent, of course, with the eventual collapse of ΔM to its pre-irradiation level.

To understand qualitatively the decrease in current density in the first annealing stage, we determined the mean radius R for ~100 columnar defects, using images like those in Figs. 3(a) and 3(b). This gave values $R_{30\,°\mathrm{C}} \approx (29 \pm 3)$ Å for the as-irradiated material, and after annealing at $T_A = 300$ °C, $R_{300\,°\mathrm{C}} \approx (25 \pm 2)$ Å, a decrease of ~14%. To interpret this, we assume pinning of vortex cores, for which the pinning energy per unit length[1] is $u_0 = \eta(H_c^2/8\pi)\pi\langle R\rangle^2$. Here, $\eta \leqslant 1$ is a pinning efficiency factor; $H_c^2/8\pi$ is the condensation energy; and the last factor is the area of a columnar defect. Then the critical current density is $J_c \approx u_0 c/\phi_0 \xi_{ab}$, where ϕ_0 is the flux quantum. This uses the fact that ξ_{ab} (the coherence length in the ab plane) is the shortest length scale over which the order parameter can change. Since J_c sets the scale of the observed J_p, we have $\Delta M \propto J_p \propto J_c \propto R^2$. Hence, we obtain $\Delta M(T_A = 300\,°\mathrm{C})/\Delta M(T_A = 30\,°\mathrm{C}) = (R_{300\,°\mathrm{C}}/R_{30\,°\mathrm{C}})^2 = (25\ \text{Å}/29\ \text{Å})^2 = 0.74$. This reduction agrees surprisingly well with the falloff in the first annealing stage, where ΔM decreases to 62%–72% of its as-irradiated value. Finally, we briefly note that the circulating currents in polycrystalline Bi- and Tl-based materials flow partly within individual grains and partly through a percolative network[14,15] of strongly coupled grain boundaries,[16] with typical efficiencies of 1%–5%. With strongly coupled networks, the vortex pinning provided by columnar defects enhances both the transport and ''magnetic'' current density.[17,18] To set the scale of J, we take the radius of the disk (0.15 cm) for the transverse distance ''r'' and obtain the value $J_p = 2.3 \times 10^5$ A/cm^2 for $\Delta M = 3000$ G.

Overall, the thermal stability of these very effective pinning sites is encouraging.

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