Enhanced Vortex Pinning in Annealed $TlBa_2CaCu_2O_x$ Thin Films

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***Abstract*—Furnace anneals of $TlBa_2CaCu_2O_x$ thin films at temperatures above 500°C cause partial TlO_x loss. High-resolution transmission electron microscopy images reveal nanometer-scale discontinuities (pinched stacking faults) in the microstructure of annealed films. Significant increases in the vortex pinning potential and critical current density at elevated temperatures in strong magnetic fields are observed and are attributed to the presence of these localized defects.**

I. Introduction

Many applications of high-temperature superconducting (HTS) thin films require large current densities J in high magnetic fields B at elevated temperatures. Under these conditions, the field penetrates the material via discrete, quantized magnetic vortices and the vortices experience a strong Lorentz force J×B. Early experiments on HTS cuprates showed that the vortices are weakly pinned [1,2]. Hence, the substantial thermal energy causes "giant flux creep" and the resulting large dissipation. Maintaining high J values under these conditions requires the incorporation of lattice defects or secondary phases to pin the vortices, thus suppressing their motion.

Modest improvements in vortex pinning were achieved by creating *localized defects* through irradiation with fast neutrons [3,4] or high-energy light ions [5]. Strong vortex pinning in HTS materials was demonstrated for *extended defects* introduced in $YBa_2Cu_3O_{7-\delta}$ single crystals by high-energy, heavy-ion irradiation [6,7]. Detailed structural studies confirmed that the pinning sites were amorphous, linear damage tracks produced by these heavy ions [8]. For Tl-based superconductors, both bulk ceramics [9] and thin films [10] showed strongly enhanced vortex pinning when extended defects were incorporated.

We have recently reported that the superconducting properties of $TlBa_2CaCu_2O_x$ (Tl-1212) thin films can be enhanced by annealing in nitrogen at temperatures from 250 to 600°C [11]. These reducing anneals raise the superconducting transition temperature T_c from ~70 K for films as-grown in one atm oxygen to ~95 K. In addition, the low-field critical current density J_{cm} measured by magnetic hysteresis increases significantly after annealing in nitrogen above 500°C. The maximum J_{cm} at 5 K in self-field was $1(\pm0.2)\times10^7$ A/cm^2 following a one-hour nitrogen anneal at 600°C, ~50% higher than the J_{cm} for as-grown films [11].

These enhanced properties are attributed to partial TlO_x loss suggested by energy dispersive x-ray compositional analyses comparing the as-grown and high-temperature-annealed films [12]. Cross-sectional, phase-contrast, high-resolution transmission electron microscope (HRTEM) images show two types of disorder in annealed films, circular regions of contrast modulation on a 100 nm scale and pinched stacking faults on a 1 nm scale surrounded by lattice disorder extending for 2-10 nm. The latter microstructural defects are ideal in size for vortex pinning. Hence, simple furnace annealing offers a promising technique for creating controlled, nanometer-scale microstructural damage that enhances the superconducting properties of these films.

In this paper we report new annealing studies and magnetization measurements on Tl-1212 films. The annealing produces significant increases in both J_{cm} for large magnetic fields and the vortex pinning potential $U_{eff}(J,T)$ for large current densities J at elevated temperatures T.

II. Experimental Details

Thin films (~600 nm) of Tl-1212 are grown in one atm oxygen in a two-zone furnace using an amorphous BaCaCuO precursor on a single crystal (100) $LaAlO_3$ substrate [13]. The resulting films are nearly phase pure and highly oriented with the crystallographic c-axis normal to the substrate. Post-growth anneals at 600°C in flowing nitrogen using the same two-zone furnace produce a significant enhancement in both T_c and J_{cm} [11].

However, new annealing studies in a separate tube furnace in flowing nitrogen showed that 600°C produces excessive TlO_x loss and destroys the superconductivity in these films. The discrepancy arose from the presence of Tl_2O_3 condensed on the walls of the two-zone furnace from prior film growth. This condensed material provided an internal, unrecognized source of both oxygen and TlO_x during our initial high-temperature anneals in flowing nitrogen. Recent measurements using an oxygen sensor show that the oxygen partial pressure at the film is ~0.01 atm during the 600°C "nitrogen" anneal in the two-zone furnace when condensed Tl_2O_3 is present.

This paper compares the superconducting properties of films before and after one-hour, high-temperature anneals

Manuscript received August 26, 1996.
This work was performed at Sandia National Laboratories and supported by the U. S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC04-94AL85000.

in a tube furnace using two distinct flowing gases: 100% oxygen and 10% oxygen in nitrogen. These experiments produced improvements in T_c and J_{cm} comparable to those observed for the two-zone annealed films, but with optimum annealing temperatures near 685°C in 100% oxygen and 630°C in 10% oxygen. Anneals in lower oxygen partial pressures are in progress and will be reported elsewhere.

Magnetic measurements were performed with a commercial SQUID magnetometer (Quantum Design MPMS). The superconducting transition temperature T_c was determined from the Meissner signal (field cooling) in a 0.2 mT field applied normal to the film (i.e., along the crystallographic c-axis). J_{cm} was calculated from isothermal hysteresis loops and the vortex pinning potential was extracted from isothermal flux creep data.

III. Enhanced superconducting properties

Several films were annealed in 100% flowing oxygen between 600 and 750°C to determine the optimum temperature (685°C) for enhanced J_{cm} and vortex pinning. These anneals lowered T_c to between 70 and 80 K, similar to the T_c's for the films as-grown in oxygen. Hence, a subsequent reducing anneal at 250°C in flowing nitrogen was added to raise T_c to its maximum value before additional J_{cm} studies. Anneals below 700°C in 100% oxygen plus 250°C in nitrogen did not change J_{cm} in self-field at 5 K by more than the 5% experimental error; T_c ranged from 88 to 90 K for these films. Anneals at 700°C or higher in 100% oxygen plus 250°C nitrogen caused a systematic decrease in both T_c and J_{cm} at 5 K in self-field. The highest temperature anneal (750°C) lowered T_c to 80 K, broadened the Meissner transition, and decreased J_{cm} by 75%. Though anneals below 700°C in 100% oxygen did not change J_{cm} in self-field, they did increase vortex pinning and J_{cm} in large magnetic fields at temperatures to 60 K with the optimal annealing temperature being 685(±10)°C.

Similarly, several films where annealed in 10% oxygen in flowing nitrogen between 600 and 650°C to determine the optimum temperature (630°C) for enhanced J_{cm} and vortex pinning. A subsequent reducing anneal at 250°C was not beneficial since T_c was maximized between 88 and 90 K after the 10% oxygen anneal. Anneals at 600 and 650°C in 10% oxygen changed J_{cm} in self-field at 5 K by less than 5% while anneals between 625 and 635°C increased J_{cm} between 10 and 30%. More importantly, the greatest enhancement in hysteresis and vortex pinning at temperatures to 60 K was observed for these latter anneals, suggesting that 630(±10)°C is optimum for 10% oxygen anneals.

Fig. 1 compares the Meissner transition in three annealed films: (1) after a low-temperature reducing anneal (one hour at 250°C in flowing nitrogen, open triangles), (2) after a high-temperature anneal (one hour at 630°C in 10% oxygen, solid triangles) and (3) after a double anneal (one hour at 685°C in 100% oxygen followed by one hour at 250°C in nitrogen, open squares).

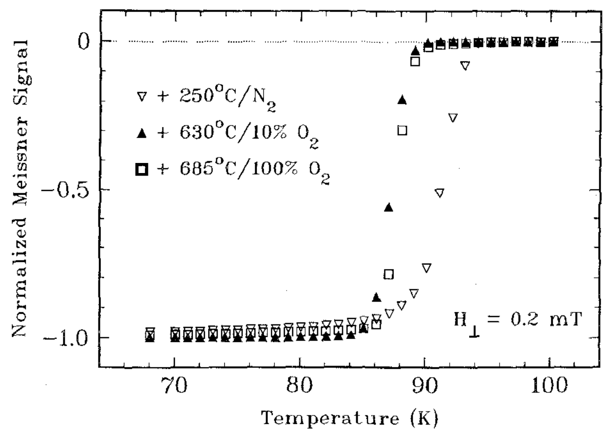

Fig. 1. Meissner transition (field cooling) for three Tl-1212 films. The high-temperature anneal suppresses T_c by ~5%.

The low-temperature nitrogen anneal increases T_c to ~94 K (typical for our Tl-1212 films grown at 800°C in a two-zone furnace) [13]. Both of the high-temperature oxygen anneals (100% and 10%) reduce T_c by 4 K to ~90 K, but yield a slightly sharper transition in 0.2 mT. Note that the 100% oxygen anneal was followed by a 250°C anneal in nitrogen. The sharp Meissner transitions suggest that the high-temperature anneals and accompanying TlO_x loss do not result in a macroscopically nonuniform carrier concentration with a distribution of T_c values or a preferential degradation at grain boundaries. However, there is evidence in the HRTEM cross-sectional images that between 20 and 30% of the upper (free surface) part of the film is structurally disordered following the oxygen anneal. The current density values in the annealed films were calculated using its original thickness, ignoring any structural changes that affect supercurrents near the surface.

The remainder of this section compares J_{cm} and the vortex pinning potential of a Tl-1212 film annealed first at 250°C in nitrogen and subsequently at 630°C for one hour in 10% oxygen. (Comparable enhancements in the superconducting properties were measured for another film annealed at 685°C in 100% oxygen followed by 250°C in nitrogen.) At 5 K *in self-field* J_{cm}, determined from magnetic hysteresis using the Bean critical state model and the dimensions of the entire sample with appropriate geometric corrections [14], increased from 6×10^6 A/cm^2 after the 250°C nitrogen anneal to 8×10^6 A/cm^2 after the 630°C anneal. Further, J_{cm} was higher at all field strengths to 5 tesla at 5 K following the 630°C anneal. Fig. 2 compares J_{cm} versus field at 40 K before and after the 630°C anneal. The marked increase in J_{cm} at higher fields indicates that the structural changes accompanying high-temperature anneals provide strong pinning sites for vortices. Hysteresis loops at 20 and 60 K also show higher J_{cm} after the 630°C anneal.

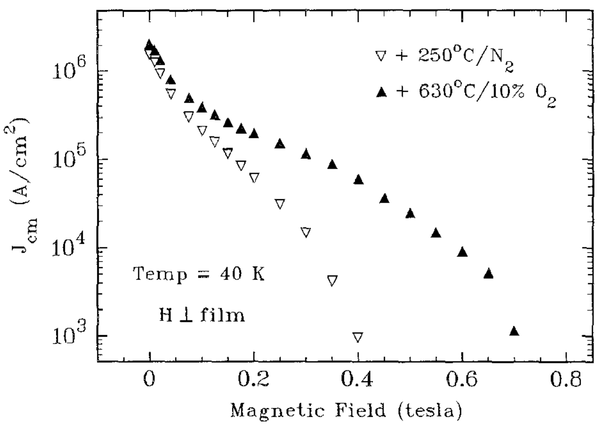

Fig. 2. Critical current density J_{cm} at 40 K versus applied magnetic field from hysteresis loops measured before and after a 630°C anneal in a 10% oxygen atmosphere.

The increased vortex pinning that supports the higher J_{cm} can be shown directly by calculating the pinning force density F_p versus applied field from the data in Fig 2. The critical current density J_{cm} for a given induction field B is reached when the Lorentz force density on the vortices, $J_{cm} \times B$, balances the pinning force density F_p. The log-log plot in Fig. 3 emphasizes the additional pinning attributed to the microstructural defects in the annealed film. Both the magnitude and position of the peak in F_p and the rapid decrease approaching the irreversibility line are shifted to considerably higher field strengths after annealing.

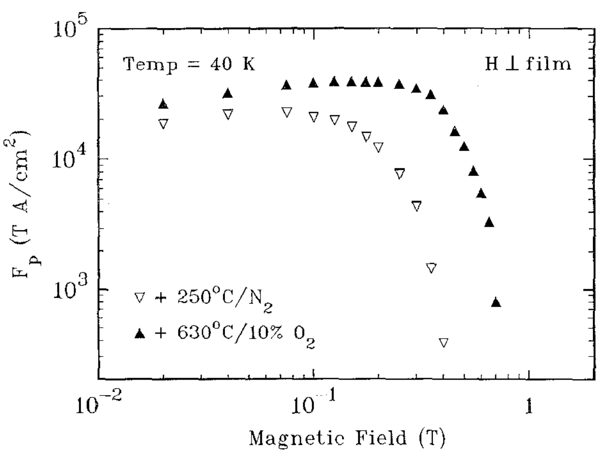

Fig. 3. Vortex pinning force density F_p versus applied magnetic field at 40 K before and after 630°C anneal.

Additional confirmation of the enhanced pinning after high-temperature annealing is the comparison of effective vortex pinning potentials $U_{eff}(J,T)$ versus current density J shown in Fig. 4. These data are calculated from a series of isothermal magnetic relaxation measurements in a fixed field (one tesla applied normal to the film for Fig. 4). The creep experiment involves cooling from above T_c to the measurement temperature in zero field, applying the desired field and monitoring sample moment versus time (up to two hours at each temperature). The current density J is determined from the measured moment and sample dimensions, while $U_{eff}(J,T)$ is calculated from the moment versus time using the procedure of Maley et al. [15]. Selected temperatures are indicated in the figure.

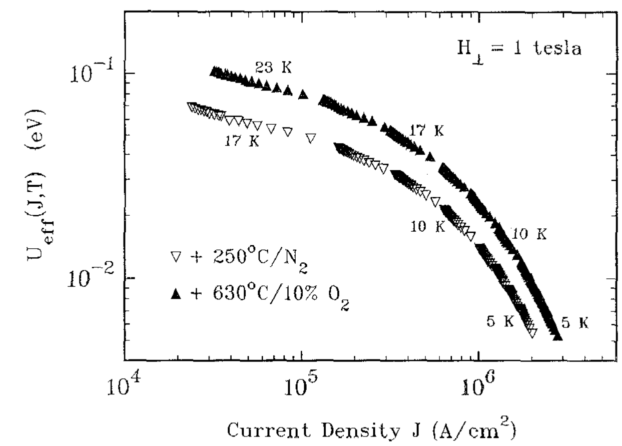

Fig. 4. Effective vortex pinning potential in one tesla versus current density before and after 630°C anneal. Data were calculated from isothermal flux creep measurements.

The data in Fig. 4 illustrate two significant changes following the high-temperature oxygen anneal. First, the current density in one tesla at 5 K is increased by ~50%. Second, the film annealed at 630°C supports a measurable current density (irreversibility) up to 23 K in one tesla in contrast to 17 K after the 250°C anneal. More importantly, $U_{eff}(J,T)$ is increased by ~50% for current densities J in the 10^5 A/cm^2 range. Since the dissipation at a given field and temperature varies exponentially with U_{eff}, this increase means substantially lower losses in practical applications at elevated temperature in large fields.

IV. Concluding Remarks

We have shown that simple, low-cost furnace anneals of Tl-1212 thin films in 100% oxygen or 10% oxygen in nitrogen can be used to significantly enhance both J_{cm} and vortex pinning at elevated temperatures in large magnetic fields. The microstructural changes produced by these anneals, identified by HRTEM as ~1 nm pinched stacking faults surrounded by 2-10 nm of lattice disorder, are thought to be the source of the enhanced superconducting properties. These structural changes are driven by partial TlO_x loss during the high-temperature anneals. Although the anneals cause a small decrease in T_c (~5%) compared to films annealed at 250°C in nitrogen, enhanced J_{cm} is observed at all temperatures up to 60 K.

The incorporation of small secondary phase impurities has been shown to enhance the vortex pinning and J_{cm} of *bulk* cuprate superconductors. This was first noted for melt-textured $YBa_2Cu_3O_7$ where the thermal gradient processing generated Y_2BaCuO_5 inclusions that provided pinning sites [16]. Subsequently, partial melting of single TlO_x layer $Tl_{0.5}Pb_{0.5}Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_y$ produced micron-sized inclusions of $(Ca,Sr)_2CuO_3$ and $BaPbO_3$ and much larger J_{cm} values in ceramic samples. The present work differs in several respects. First, the furnace anneals involve temperatures well below any melting or decomposition events and any trace impurities are actually lowered after annealing [11]. Second, the present samples are highly oriented thin films that carry substantial macroscopic supercurrents both before and after the high-temperature anneals. And, third, the microstructural defects occur on a much smaller length scale, a few nanometers as opposed to microns, and involve stacking fault dislocations rather than secondary phases [13]. Hence, these strong pinning sites are matched closely to the in-plane coherence length for a vortex the in cuprate superconductors.

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