Synthesis and Properties of Superconducting (Tl,Pb)-(Sr,Ba)-Ca-Cu-O Thick Films on Ag

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Abstract—We report successful texturing of screen-printed (Tl,Pb)-(Sr,Ba)-Ca-Cu-O thick (20 μm) films on both LaAlO$_3$ and Ag foil using rapid thermal processing (RTP) followed by furnace annealing. An RTP cycle to +915°C for 20 seconds in Ar produces massive melting of the superconducting powder but not the Ag substrate. Subsequent annealing under O$_2$ in sealed Au foil with a Tl source yields a brick-wall microstructure consisting of c-axis aligned, plate-like grains. X-ray diffraction and Melssner data show a mixture of the Tl-1223 and Tl-1212 phases while energy-dispersive spectroscopy identifies the plate-like grains as the desired Tl-1223. Magnetization data suggest intergranular supercurrents flowing across the entire film. Critical current densities inferred from hysteresis are $9 \times 10^4$ A/cm$^2$ at 5 K in low fields, decreasing by a factor of 5 in 5 tesla.

I. INTRODUCTION

Several proposed applications of high-temperature superconductors at liquid nitrogen temperatures require bulk materials (thick films, wires or tapes) with large critical current densities $J_c$ in moderate magnetic fields. These requirements can only be met through the combination of an aligned microstructure and strong vortex pinning. Due to the extreme anisotropy of these materials, misalignment between adjacent grains produces a dramatic decrease in intergranular critical current $J_c$. This problem can be partially alleviated through melt-textured growth to generate an aligned microstructure of the ceramic grains. Orientation of the crystallographic c-axes of plate-like grains leading to a brick-wall structure has led to useful critical current densities in Bi-based superconducting tapes [4] and moderately thick (1-3 μm) Tl-1223 films [5],[6].

The single Ti-layer 1223 structure superconductor has been shown to exhibit useful vortex pinning at liquid nitrogen temperatures [7]-[9]. This phase appears to be stabilized by the partial substitution of Pb for Tl [10] and Ba for Sr [11]. Here we summarize the properties of thick (20 μm) films of (TlPb)$_2$(Sr$_x$Ba$_{2-x}$)$_2$Ca$_2$Cu$_3$O$_y$ screen-printed on LaAlO$_3$ and Ag substrates and sintered by rapid thermal processing (RTP) followed by furnace annealing. The RTP cycle is chosen to produce significant melting, allowing the subsequent growth of a c-axis oriented microstructure of plate-like Tl-1223 grains. This brick-wall thick film has substantial critical current densities at low temperatures.

II. EXPERIMENTAL DETAILS

Two Tl-free precursor powders, Pb$_x$(Sr$_y$Ba$_{2-y}$)$_2$Ca$_2$Cu$_3$O$_y$ and Pb$_x$(Sr$_y$Ba$_{2-y}$)$_2$Ca$_2$Cu$_3$Ag$_{x}$O$_y$, were coprecipitated in a continuous aqueous process described elsewhere [12]. These Pb and Sr concentrations promote the growth of the Tl-1223 phase with strong vortex pinning at elevated temperatures [7]. The addition of 5 wt. % Ag has been shown to enhance the growth kinetics, lower the growth temperature, and improve morphology of Pb- and Sr-free Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_y$ thick (3 μm) films on yttria-stabilized zirconia substrates [13]. The slurry for screen printing was prepared by suspending reagent grade Tl$_2$O, powder plus calcined precursor in a commercial HTSC vehicle (ZYP Coating, Inc.). The 20 μm thick precursor films were formed by printing the slurry through a 200 mesh screen onto single crystal (100) LaAlO$_3$ (using Ag-free precursor) or polished Ag foil (Ag-containing precursor) substrates about 3×3 mm in size. After air drying, films were heated to 500°C for 15 min in flowing O$_2$ to burn out the vehicle binder.

All films were wrapped in Au foil together with additional Tl$_2$O$_3$ to minimize thallium loss and melt processed in a rapid thermal processing (RTP) system (AET Addax, model R 1000 4°). The Ag-free films on LaAlO$_3$ were sintered under pure O$_2$ while the Ag-containing films on Ag foil were sintered under Ar (see below). Following RTP, the films on Ag foil were rewrapped in Au foil with a Tl source (Tl-1223 pellet) and annealed under O$_2$ in a conventional furnace at 900°C for one hour, cooled to 850°C and held for 3 hours, and then furnace cooled.

Morphology and composition of the films were determined using an Amray model 1645 scanning electron microscope equipped with a Tracor Northern energy-dispersive (EDS) detector. X-ray powder diffraction data were obtained with a Siemens model D500 automated diffractometer using Cu K$_a$ radiation. Magnetization measurements were made using a Quantum Design model MPMS SQUID magnetometer.

III. RESULTS

A. Ag-Free Films on LaAlO$_3$

Ag-free thick films on LaAlO$_3$ were processed in pure O$_2$ to explore the effects of peak RTP temperature, hold time and cooling cycle on phase development, microstructural evolution and superconducting properties. The amount of Tl-1223 phase increased with increasing peak temperature. Processing above 940°C produced substantial amounts of Tl-1223 with a plate-like grain morphology, but the grains were randomly oriented.
Using higher peak temperatures for short times followed by a controlled cool resulted in substantial melting and texturing (c-axis normal) of the platy Tl-1223 grains.

Fig. 1 compares the Meissner transitions (cooling in a field of 1 mT) for a bulk ceramic pellet and a 20 μm thick film on LaAlO₃ prepared from the same Ag-free precursor powder. For both samples the Tl₂O₃ content was adjusted to achieve a starting T/Pb ratio of 1.4; the excess Tl (above an expected T/Pb ratio near unity in the final product) was introduced to compensate for Tl loss during processing at high temperatures. The pellet was wrapped in Au foil and reacted in a furnace at 920°C for 2 hours in Ar. Its Meissner data show a single transition with an onset of superconductivity near 117 K. X-ray powder diffraction shows complete conversion to the Tl-1223 phase, consistent with the large Meissner fraction of 0.60 and shielding fraction (below) of 0.95 at low temperature.

The film on LaAlO₃ was rapidly heated (30°C/sec) under O₂ in the RTP held above 960°C for a few seconds, rapidly cooled to 920°C, then cooled to 860°C at 0.1°C/sec with intermediate 5 minute holds at 890°C and 870°C. The Meissner data indicate two superconducting phases: ≈70% Tl-1223 with a superconducting onset above 100 K and ≈30% Tl-1212 with an onset near 50 K. This is consistent with X-ray diffraction results which confirm the presence of both phases. The Tl-1223 phase is dominant and has preferred c-axis normal orientation. This preferred orientation leads to a demagnetizing enhancement of the Meissner signal at low temperature.

Fig. 2 compares the low-field diamagnetic shielding at 5 K for furnace-annealed bulk pellet and RTP thick film synthesized from Ag-free powder. The shielding slope for the bulk ceramic corresponds to a volume magnetic susceptibility of -0.95/4π using the sample weight and the estimated density for (Tl₂Pb₁ₓ)(SrₓBa₂₋ₓ)₂Ca₂Cu₃O₇₋₇ based on X-ray lattice parameters (5.94 g/cm³) [14]. In contrast, the shielding slope for a field applied normal to the thick film is strongly enhanced by demagnetizing effects at low field; the volume susceptibility is -85/4π. This suggests that shielding supercurrents are flowing throughout this partially textured film. The measured shielding enhancement of 85 is close to the theoretical demagnetizing factor of 96 calculated for a spheroid with semi-axes equal to the film dimensions: 0.020×2.8×3.2 mm³ [15]. Magnetic hysteresis loops for this 20 μm film yield low-field J's of 5×10⁴ A/cm² at 5 K and 1×10⁴ A/cm² at 40 K using the Bean model and the film dimensions. J decreases rapidly above 40 K due to the Tl-1212 phase present in this film.

B. Ag-Containing Films on Ag Foil

Producing a similar textured Tl-1223 film on a Ag substrate presents a new challenge, the existence of a Ag/Ag₂O eutectic which lowers the Ag melting to 931°C in O₂. Using pure Ar in the RTP has two advantages: the Ag melting point is raised to 962°C and the melting reactions in the cuprate superconductor system are enhanced by the low O₂ partial pressure. In fact, the Ag-containing precursor films on Ag foil begin to show melting in pure Ar at RTP temperatures above 890°C. Unfortunately, films processed in the RTP under Ar show minimal superconductivity. Hence, our approach for processing films on Ag has been a brief RTP treatment in Ar above 900°C to produce significant melting followed by wrapping the film in Au foil with a Tl₂O₃ source for a 2 hour, post-RTP furnace anneal in O₂ at 900°C.

Fig. 3 is a back-scattered electron photomicrograph of a textured 20 μm film on Ag produced by melting in the RTP under Ar (30°C/sec to 920°C, hold for 20 sec, rapid quench) followed by the 2 hour furnace anneal. (The image in Fig. 3 is approximately 59×62 μm².) The film showed no superconductivity after RTP melting and X-ray diffraction indicated no superconducting phases. Furnace annealing promoted growth of the relatively large (≥ 15 μm), c-axis oriented Tl-1223 (from EDS) plates seen in Fig. 3.

Low-field diamagnetic shielding data for this film show a demagnetization enhancement consistent with the film dimensions, suggesting supercurrent flow throughout the brickwall structure. Fig. 4 shows a magnetic hysteresis loop taken at 5 K with the field applied normal to the film. The substantial
hysteresis which persists for fields beyond 5 tesla indicates that the microstructure in Fig. 3 supports large intergranular supercurrents.

Fig. 5 shows magnetic $J_c$ versus field at 5 and 20 K inferred from hysteresis using the Bean model and the film dimensions. The $J_c$ at 5 K is $9 \times 10^4$ A/cm$^2$ in low fields, decreasing by a factor of 5 in 5 tesla. Similar modest field dependence is shown at 20 K. Due to the dense brick-wall microstructure achieved in this film, substantial $J_c$ values with strong vortex pinning are observed. However, there is still a large fraction of the Tl-1212 phase present, and $J_c$ decreases rapidly for temperatures above 20 K. Present efforts include post-RTP annealing in a two-zone furnace to enhance the fraction of the Tl-1223 phase while preserving the textured microstructure.

IV. DISCUSSION

RTP processing conditions were determined which yielded substantial melting and the desired brick-wall microstructure of platy Tl-1223 grains for 20 μm thick films on both LaAlO$_3$ and Ag foil substrates. These films support useful critical current densities at low temperatures in large magnetic fields. For films on both substrates, however, significant amounts of the Tl-1212 phase were present. This phase has a relatively low superconducting transition, typically 50 K, leading to a drastic decrease in $J_c$ at temperatures above 40 K and have no measurable $J_c$ at liquid nitrogen temperatures.

In an attempt to reduce the Tl-1212 phase fraction, we have replaced the conventional furnace anneal used to produce the film shown in Fig. 3 by a two-zone furnace anneal in a pure O$_2$ atmosphere. In this series of experiments, we first melted the Ag-containing precursor film on Ag foil in the RTP under Ar. This sample was then processed in an exposed (no Au foil wrap) configuration in a two-zone furnace using sample temperatures below the Ag/Ag$_2$O melting eutectic at 931°C. The TiO$_4$ source temperature was held at 750°C since this favors the Tl-1223 phase in powders with the same Pb and Sr-doped composition used here [14]. Although the two-zone annealing produced the Tl-1223 phase with little Tl-1212 as indicated by both x-ray diffraction and Meissner data, electron microscopy showed no preferred orientation for the platy Tl-1223 grains. Consistent with this microstructure, diamagnetic shielding data showed the "weak-link" grain decoupling at low fields observed in all samples (thick films and tapes) lacking the brick-wall stacking.

An alternate approach is to skip the RTP step and process the screen-printed films exclusively in a two-zone furnace. If the desired superconducting phase and microstructure could be achieved, this process would be scalable to produce continuous, open-faced tapes. Two-zone processing has been successful for pure Tl-Ba-Ca-Cu-O films between 1 and 3 μm thick on both yttria-stabilized zirconia [9] and Ag foil [6] substrates. We are attempting to develop a similar process for 20 μm (or thicker) films on Ag.

Partial melting appears to be essential in forming the brick-wall microstructure with the Tl-1223 phase. It is impractical to operate a two-zone furnace in very low O$_2$ partial pressures where melting the Ag substrate is not a problem, thus limiting the sample processing temperatures to 930°C or lower. Hence, we have systematically varied the composition of the calcined precursor powder and used differential thermal analysis to identify thermal events (melting) in the constituent oxides, both with and without Ag.

Increasing the TVPb ratio from 1.0 to 3.0 resulted in a substantially lower temperature for the first melt reaction; the presence of 5 wt. % Ag in the Tl-containing precursor powder resulted in an additional decrease. An initial two-zone experiment in pure O$_2$ employed a Tl-rich precursor film on Ag and a sample temperature below the lowest melt onset temperature without Ag but above that melt temperature in the presence of Ag. It was hoped that this would confine partial melting to the Ag substrate/thick film interface, allowing platy grain growth upward through the film. The Tl source temperature was chosen to favor the Tl-1223 phase.
X-ray diffraction and Meissner data confirmed the predominant phase, resulting in the formation of platy Tl-1223 grains with random orientation near the film/substrate interface, but this was not Deusen for their technical assistance in this work.

Electron microscopy showed that melting had occurred, resulting in the formation of platy Tl-1223 grains with random orientation near the film/substrate interface, but this was not Deusen for their technical assistance in this work. X-ray diffraction and Meissner data confirmed the predominant TI-1223 phase, and diamagnetic shielding showed the weak-linked response characteristic of tapes or thick films with an unoriented grain structure. We are currently exploring alternate methods of inducing melting that would produce the brick-wall microstructure during two-zone processing.

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**REFERENCES**


