Superconducting $\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_9$ Thick Films
Final Report

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General Electric
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GE Corporate Research and Development's (GE-CRD) program to develop the two-zone silver addition (TZSA) process [1-4] for fabricating superconducting films of $\text{TlCa}_2\text{Ba}_2\text{Cu}_3\text{O}_9$ has activities in the areas of 1.) precursor preparation, 2.) the thallium oxide vapor process, 3.) the effects of post-synthesis annealing ambient and temperature on superconducting properties, 4.) the influence of film stoichiometry and composition on superconducting properties, 5.) microstructure and film growth mechanism, 6.) the preparation of thicker films, 7.) the fabrication of films on flexible substrates, and 8.) process scale-up. As part of its effort under the ANL Pilot Center Agreement, GE-CRD has supplied to ANL a complete two-zone furnace, has provided consultation on its use and on the planning of experiments, has processed ANL samples in GE's furnaces to help define optimum process conditions, and has provided precursor and finished films as requested. These contributions are described more fully in the descriptions of the work performed at ANL presented elsewhere in this report. Under the Pilot Center Agreement work at GE-CRD has been directed toward the optimization of the TZSA process with emphasis on A.) process improvement, B.) effects of silver content on film properties, C.) the relationship between microstructure and J_c , and D.) toward the assessment of the compatibility of silver substrates with the process chemistry.

Unless otherwise noted, 3-4 μm thick highly textured superconducting films of "1223" Tl-Ca-Ba-Cu-oxide were prepared on polycrystalline-YSZ substrates by the reaction of thallium oxide vapor (thallination) with precursor oxide films heated at 860 C in an oxygen ambient. The precursor films were prepared by first spray depositing a Ca-Ba-Cu-Ag nitrate solution on to a heated substrate followed by decomposition of the deposited nitrates in an oxygen ambient. A post growth anneal of the "1223" films in oxygen has been shown to improve J_c by factors of 2 to 5. Films have been prepared with $T_c \approx 105\text{K}$ and zero-field critical current densities at 77 K (zf-77K) in the 10,000 to 200,000 A/cm^2 range. These films also exhibit the excellent pinning characteristics of the "1223" phase [5].

A. Process Improvement

Precursors: Significant improvements in J_c have been obtained in our films through modification of the spray deposition process. Precursor films were prepared by three methods; our originally used Deposition-#1: (a) the amount of material required for a 3-4 μm film was first spray deposited, (b) the film was heated rapidly in air to 650°C, (c) the film was then heated in oxygen going from 500°C to 850°C in 30 minutes; Deposition-#2: the film was prepared using four depositions, each of which was subjected to heat treatment 1b, and finally the fully deposited film was subjected to heat treatment 1c; Deposition-#3: the amount of material required was spray deposited; the sample was heated in air to 500°C, and then it was heated in oxygen using a very slow temperature ramp from 500°C to 850°C. All precursor films were thallinated under the same conditions and were then patterned with a 4 mm x 0.2 mm test bridge consisting of four 1 mm test segments. Following are listed for each deposition test the mean value of the J_c (at 77°K) values of the segments, the ratio of the standard deviation to the mean value, and the number of segments. Deposition-#1: 16,000 A/cm²:1.21:44, Deposition-#2: 38,000 A/cm²:0.54:56, Deposition-#3: 40,000 A/cm²:0.32:20. Clearly, deposition processes #2 and #3 are superior to process #1. Microstructural analysis of the precursor films revealed that Deposition #1 produces precursor films with significantly greater inhomogeneity in chemical composition than films prepared by Deposition #2 or #3 which showed comparable chemical homogeneity.

Flow Reactor: The low mass transport rates and thallium oxide pressure gradients inherent in our original "static-reactor" design were judged to be a limitation not only for scaling-up the TZSA process, but also for the process studies pursued at GE-CRD and ANL. Consequently, we redesigned our two-zone system to accommodate a "flow-reactor" in which oxygen gas flows over the thallium oxide source boat and establishes a forced mass transport of the vapor to the sample. As expected, some modification of the process conditions was required. Specifically, a lower thallium oxide boat temperature is needed to achieve the same thallium content in the superconducting films. For example, films with optimum properties (J_c) are obtained in the "static reactor" from $\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{7-0.37\text{Ag}}$ precursors at a sample temperature of 860°C and a thallium oxide boat temperature of 745°C. High quality films are prepared in the "flow reactor" at 860°C and 730°C, respectively.

The presence of a significant gradient in the thallium oxide partial pressure in the "static reactor" is evident in experiments in which 12.5 cm long samples are placed end to end. In a typical experiment the "x"-value of the film closest to the thallium oxide source was 0.85 while the other sample was found to have $x=0.70$ ($\text{Tl}_x\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_y$). On the other hand, samples prepared end to end in the "flow reactor" show very similar "x" values (eg. $x=0.85$ and

x=0.82). Clearly, the "flow reactor" has advantages for the preparation of longer samples with better compositional homogeneity than obtainable in the static design.

B. Silver Content

We have initiated a series of experiments to determine the effects of silver content on the properties of our superconducting films. For this study $\sim 3 \mu\text{m}$ thick "1223" films are prepared on poly-YSZ substrates in a "flow reactor" using our "two-step" process schedule [1]. We used Decomposition #2 to prepare the precursor films for this study, because we had determined previously that Decomposition #3 requires additional development effort. For convenience we express the silver content in terms of a mole per cent based on the metals Ca, Ba, Cu, and Ag. Thus, a 5% Ag sample is one prepared to have the stoichiometry $\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{Ag}_{0.37}$. Samples containing 0.5% Ag are found to be poorly reacted mixed phase material. To date we have prepared and characterized six to eight samples each containing 2 mole %, 8 mole %, and 11 mole % silver. In each case the X-ray diffraction pattern indicates the presence of essentially single phase highly textured "1223". For determination of the superconducting properties a segmented test bridge (1 mm segments) is used which is 4 mm long and 2 mm wide, a factor of ten wider than the test bridge previously used. The mean T_c value, the mean $J_c(\text{zf-77}^\circ\text{K})$ value of the 1 mm bridge segments, and the ratio of the standard deviation to the mean $J_c(\text{zf-77}^\circ\text{K})$ for the various compositions are; 2% Ag - $105^\circ\text{K}:113,000 \text{ A/cm}^2:0.32$; 8% Ag - $104^\circ\text{K}:89,400 \text{ A/cm}^2:0.46$; 11% Ag - $104^\circ\text{K}:103,000 \text{ A/cm}^2:0.33$. To complete this study we are in the process of preparing six to eight samples each of the compositions 1%, 5%, 14%, 17%, and 20% Ag.

C. Microstructure/Film Growth Mechanism

Microstructural examinations (aspects of this work are being done in collaboration with Oak Ridge National Laboratory) have been made of a series of samples which include both precursor films and films "quenched" at different points in the thallination process. The data indicate that the accelerated film growth characteristic of GE's TZSA process is the result of the formation of a liquid phase which first forms in regions of the precursor film that are CaO rich but which also contain small amounts of Ba, Cu, Tl, and Ag (see Figure 1). Liquid formation occurs at different sites in the film as the thallium oxide vapor reacts with it. The "1223" phase grows out of this liquid which advances throughout the film as additional thallium oxide is incorporated. Additional microstructural studies show that the samples consist of regions or "colonies" of crystallites with excellent orientation in the ab direction as well as the c direction [6,7]. This leads to the suggestion that the

transport J_c 's are likely to be very high within a colonie, but that the average J_c of a film is determined by the degree of ab alignment at the grain boundaries of intergrowing "colonies". Consistent with this picture are the results of measurements made on a segmented 4mm x 0.2mm test bridge which show that segments of high J_c correlate with the presence of a colonie structure that spans the entire segment.

D. Silver Substrates

GE-CRD's program includes studies of "1223" films prepared on flexible ceramic substrates, metal substrates, and barrier layer protected metal substrates. As part of our work with ANL, we prepared "1223" films on silver substrates using the "static reactor" in operation at the time. Excessive film cracking occurred on 10 mil thick silver substrates, a problem minimized by using 1 mil substrates which were able to deform in response to the stresses induced by the cooling film. We also found evidence for interaction between the film and substrate. This revealed itself in many samples as the formation of an excess of liquid phase during thallination. Subsequent chemical analysis revealed that the silver content of the films increased from the initial 5% to 10%. Of ten samples prepared on the 1 mil substrates only a few were suitable for measurement. The best of these exhibited a $T_c = 105^\circ\text{K}$, a $J_c(\text{zf-}77^\circ\text{K})$ of 22,000 A/cm², and the good pinning characteristics associated with our "1223" films on YSZ. In Figure 2 we show the plots of J_c vs field at 77°K for 3 μm thick "1223" films prepared by the TZSA process on poly-YSZ, silver foil, and a ZrO₂ coated Fe-Cr-Al high temperature alloy. The zero-field J_c values are 105,000 A/cm², 22,000 A/cm², and 8,900 A/cm², respectively. It should be noted that we consider these results very encouraging. Work on this aspect of the problem was temporarily suspended only because we felt that further progress would benefit greatly by the improvements being developed in precursor preparation and "flow reactor" processing.

Proposed Follow-on Tasks

Direct Support of ANL Tasks:

- As specified under the tasks proposed for ANL, GE-CRD will provide spray deposited precursor samples as well as "1223" films on flexible substrates for evaluation of their superconducting properties.
- GE-CRD will provide precursor powders derived from Ca-Ba-Cu-Ag nitrates and processed in a manner similar to used for the precursor films. These will be used both in ANL's work on thick film inks and two-powder processing.

GE-CRD Activities:

- **Bulk Powder Processing:** Work will be directed toward evaluating the potential of the silver addition chemistry for achieving high transport J_c 's and good pinning behavior in conductors formed from bulk powders. These studies will focus on the use of $\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{7:2\% \text{ Ag}}$ precursor powders prepared from the mixed nitrates which are decomposed using a schedule similar to that used for the precursor films. The emphasis will be on the processing of these materials (eg. silver tubes), so that thallium oxide will be mixed with the precursor powders before reaction. For these studies the mixed powders will be pressed into small disks which will then be wrapped in silver foil. The influence of reaction temperature, silver content, and process schedule on the reaction will be investigated. The information gained in this work will be of direct benefit to ANL's proposed work on inks and the two-powder process (and vice versa).
- **Thicker Films by the TZSA Process:** Improving the current carrying capacity of conductors prepared using the TZSA process will require either improvements in the critical current density of the films or the preparation of thicker films without degradation in the presently achievable superconducting properties. Consequently, a goal of the GE-CRD program is the fabrication of high quality "1223" films significantly thicker than $3 \mu\text{m}$. This work will involve an evaluation of Deposition #3 for preparing precursor films, as that technique has a considerable advantage with respect to process time over that of our presently employed Deposition #2. We will also investigate the effects of silver concentration and thallium oxide vapor reaction times on the processing of thicker films.

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Figure Cations

Figure 1

Visible in this SEM micrograph, taken of a sample "quenched" early in the thallination process, are two particles that have started to incorporate thallium oxide. The high calcium content of the particles is evident in the high Ca/Ba ratio. For the "1223" phase this ratio would be ~ 1.2 . The thallium up-take can be monitored by the normalized thallium peak height, $Tl/(Ba+Ca+Cu)$. For comparison, we note that a ratio of 0.09 was typical for the matrix surrounding the particles. Note the close association of the two particles with silver particles which image white in the micrograph.

Figure 2

Shown are the plots of J_c vs field for $\sim 3\mu m$ thick "1223" films prepared by GE-CRD's TZSA process on polycrystalline YSZ, 1 mil thick silver foil, and a 5 mil thick sample of an Fe-Cr-Al-alloy that was coated with a ZrO_2 buffer layer. The zero-field J_c values for the samples were $105,000 A/cm^2$, $22,000 A/cm^2$, and $8,900 A/cm^2$ respectively.

<u>Spot</u>	<u>Ba/Cu</u>	<u>Ca/Ba</u>	<u>Tl/(Ba+Ca+Cu)</u>	<u>Ag/Ca</u>
1	0.45	4.15	0.20	0.61
2	0.40	4.70	0.21	0.40

Fig. 1

Fig. 2