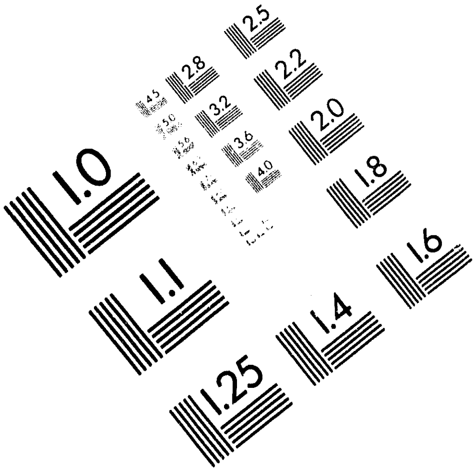

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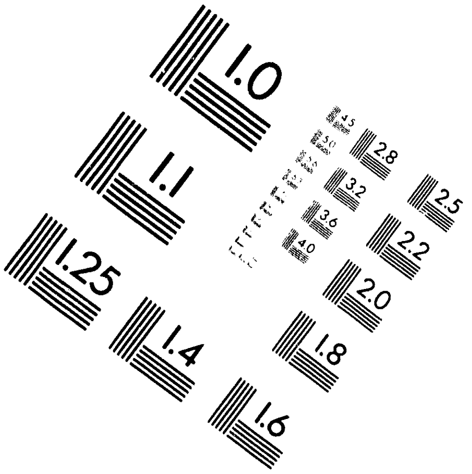

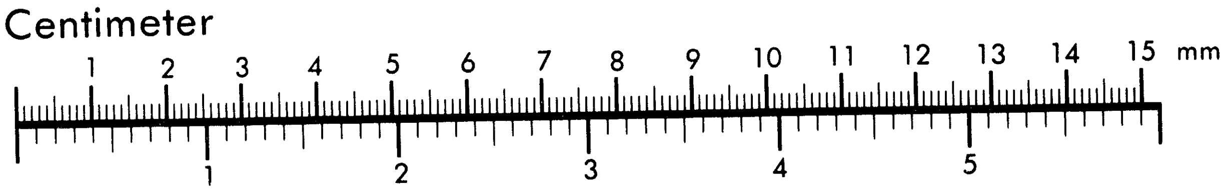

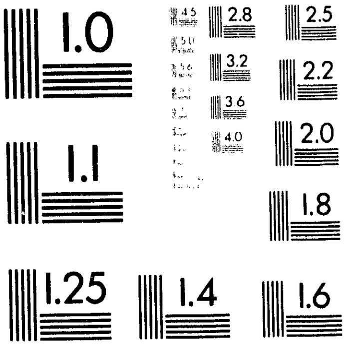

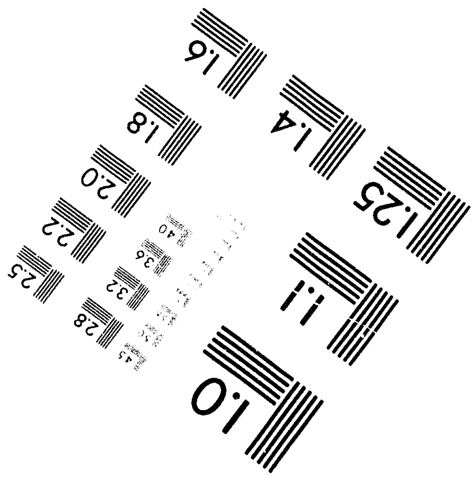

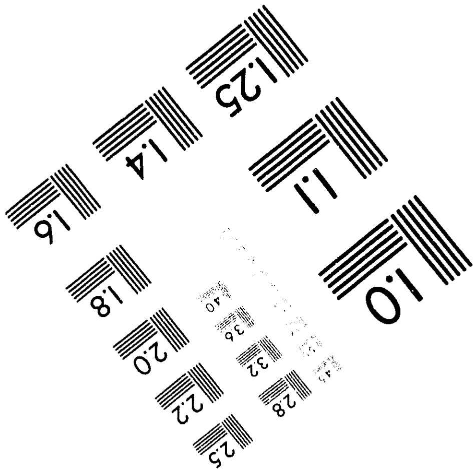

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PROGRESS IN THE DEVELOPMENT OF THE SILVER-ADDITION PROCESS FOR PREPARING TEXTURED "1223" TL-CA-BA-CU-OXIDE THICK FILMS

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Abstract

Progress in key areas is reported for the continued development of the silver-addition process for preparing textured "1223" Tl-Ca-Ba-Cu-oxide thick films; film homogeneity, film growth mechanism, scale-up, and flexible substrates. As a consequence of refinements in the precursor oxide film preparation and the development of a "flow" reactor, superconducting films on polycrystalline YSZ have been prepared that exhibit zero-field J_c values (77K) as high as 366,000 A/cm^2. Advantage has been taken of these process improvements to prepare a textured "1223" thick film with T_c=109K on a zirconia coated metal substrate. When placed in a magnetic field there is an initial drop in J_c, attributed to the presence of weak links. However, after this initial drop, the film exhibits the characteristic behavior expected of strongly linked "1223". The film growth mechanism underlying the silver-addition process is discussed in light of the results of microstructural studies of samples quenched at different times into the thallination process.

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1. Introduction

Interest in the development of the "1223" Tl-Ca-Ba-Cu-oxide superconductor and other "single Tl-O layer" materials for electrical power applications has been stimulated by reports emphasizing not only their high superconducting transition temperatures but also their good "in-field" behavior at temperatures above 40 K [1-7]. Good performance of superconductors above 40 K in magnetic fields of 1-5 Tesla is especially attractive, because it raises the possibility of significant improvements in the efficiency, size, and weight of a wide variety of electrical equipment in which the superconducting elements are cooled by efficient and reliable cryogenic refrigerators. A significant challenge to achieving these goals is the fabrication of the long lengths of wires or tapes required for such applications; wires or tapes that it is generally agreed would contain an oxide superconductor in polycrystalline form. Toward this end we have pursued the development of a process suitable for the fabrication of "1223" Tl-Ca-Ba-Cu-oxide superconducting tape by the reaction of thallium oxide vapor with a silver-containing Ca-Ba-Cu-oxide precursor film [8-10]. In this paper we report on progress in several key areas of our process development efforts; film homogeneity, film growth mechanism, scale-up, and flexible substrates.

2. Experimental

Precursor oxide films having the cation stoichiometry, $Ca_2Ba_2Cu_3Ag_{0.37}$, were prepared by spraying an aqueous solution of the metal nitrates on to appropriate substrates which were held on a heating block maintained at 275C [8]. After the deposition process the samples were subjected to additional heat treatments both in air and oxygen as detailed below. The amount of material deposited was selected to yield a superconducting oxide film of ~3μm thickness. The precursor oxides were converted to superconducting "1223" films using our "two-step" thallination process [8]. In this process the precursor oxide film is placed (oxygen ambient) in one zone of a two-zone reactor and a boat filled with thallic oxide is placed in the second zone. The sample is heated to 860C. The source is heated first to 690C (step #1) and then to 745C (step #2). The reaction is allowed to proceed for 30 minutes with the source at 745C and then the furnace power is turned off and the system allowed to cool. The temperature/time schedules for both the sample and source can be found in Figure 2 of our earlier report [8]. Process or reactor modifications required for the studies reported in this work are described below.

2a. Film Homogeneity

In an earlier study [9] we found evidence that the manner in which the spray deposited precursor oxide film is prepared affects the current transport characteristics of the final superconducting film. To aid us in understanding this effect we first prepared coatings which were heated to 400C on the deposition heater block. The coatings were removed from the substrates and used as samples for thermogravimetric analysis. We found that ~90% of the weight change upon heating occurred before the sample temperature reached 600C, and we observed inflections in the TGA plot between 500C and 600C that are associated with melting of the calcium and barium nitrate in the deposit. We performed a additional TGA analysis in which the sample temperature was programmed to rise to 500C, remain at 500C for one hour, and then continue to rise to 1000C. In this experiment we found that ~90% of the total weight change occurred during the heating at 500C, thus showing that film decomposition can be achieved without substantial melting of the nitrates.

In light of the TGA data, we prepared precursor oxide films on polycrystalline yttria-stabilized zirconia (poly-YSZ) using three deposition/decomposition schedules. **Schedule #1** - (a) the total amount of material required for an ~3μm superconducting film was spray deposited at 275C, (b) the film was heated in air at 650C (5 minutes) while it was still on the deposition heating block, and (c) the film was placed directly into a combustion tube furnace at 500C (oxygen ambient), and the temperature was programmed to rise to 850C in 30 minutes at which point the furnace power was turned off and the sample allowed to cool under a flow of oxygen. **Schedule #2** - (a) 1/4 of the amount of material required for an ~3μm superconducting film was spray deposited at 275C and the sample subjected to treatment-1b. After four such depositions/treatments the sample was subjected to treatment-1c. **Schedule #3** - (a) the total amount of material required for an ~3μm superconducting film was spray deposited at 275C, (b) the sample was heated in air at 500C (10 minutes) while still on the spray heater block, (c) the sample was placed directly into a combustion tube furnace at 500C (oxygen ambient); the temperature was programmed to remain at 500C for an hour and then rise to 850C in 50C steps with a one hour dwell at temperature after each increment; the sample was allowed to cool under a flow of oxygen.

The precursor oxide films were converted to "1223" superconducting films using the apparatus and process schedule described above [8-11]. Also, as described previously, the "1223" samples were patterned with a four-segment 4mmx0.2mm test bridge. They were then annealed in oxygen at 600C [8,9] prior to a determination of the R vs T characteristics of the full bridges and the zero-field J_c values at 77 K, J_c(zf-77K), of the segments. The average superconducting transition temperatures (and standard deviation), T_c(SDEV), for the three groups were; **Schedule #1** - 106K(1), **Schedule #2** - 107K(2), **Schedule #3** - 107K(1). Following are listed the average segment J_c(zf-77K), the ratio of the standard deviation to the average, and the number of segments measured. **Schedule #1**: 16,000 A/cm^2-1.21-44. **Schedule #2**: 38,000 A/cm^2-0.54-56. **Schedule #3**: 40,000 A/cm^2-0.32-20. We examined a precursor oxide film prepared by each of the three schedules using a scanning electron microscope (Cambridge Stereoscan 240) equipped for energy dispersive spectroscopy (EDS-Tracor Northern spectrometer). SEM micrographs of these films are shown in Figure 1.

2b. Film Growth Mechanism

To observe the evolution of the microstructure of our thick films we analyzed a series of samples each one of which had been brought to a different point in the process and then quenched by moving the reactor tube assembly to a position outside of the furnace. Samples were examined by X-ray diffraction, scanning electron microscopy equipped with energy dispersive spectroscopy, and transmission electron microscopy. For this report we will only summarize the results of these investigations. A more detailed description will be published at a later date.

The evolution of the microstructure is evident in the SEM micrographs shown in Figure 2. In our two-step process significant thallium oxide incorporation into the film and growth of the highly oriented "1223" phase occurs only after the thallium oxide boat temperature is raised to 745C. We have found that the thallium oxide is not incorporated in a uniform manner. Rather, it enters the film at isolated sites such as that indicated with an arrow in Figure 2a, which is an SEM micrograph of a sample quenched 5 minutes after the thallium oxide boat temperature reached 745C. Our analysis indicates that at these sites a liquid phase forms from which the "1223" phase grows. As more thallium oxide is incorporated, these sites grow in size until the entire sample is converted to the "1223" phase. This is evident in Figures 2b and 2c which are micrographs of samples quenched 6 and 42 minutes, respectively, after the thallium oxide boat temperature reached 745C. The data indicate that, although the thallium incorporation occurs at sites in areas that are predominately calcium oxide, barium and copper oxides and silver must also be present. We have found no evidence of a significant incorporation of silver into the "1223" phase. Rather, the silver is found only as isolated nodules in the final films.

2c. Scale-Up

We refer to the two-zone reactor used in all of our studies to date [11] as a "static" reactor because of its closed alumina-tube geometry. In this reactor transport of the thallium oxide vapor from the thallic oxide boat to the sample, over a distance of ~20 cm, takes place via gaseous diffusion. One consequence of this design from the point of view of process scale-up is that the thallium oxide incorporation rate into the film may be diffusion-transport limited. Another is that there will be a gradient in the thallium oxide partial pressure in the reactor tube which presents significant problems for obtaining samples with homogeneous properties over large areas. For example, in our "static" reactor we have evaluated the processing of three 12.5 cm long coated poly-YSZ substrates placed end to end in the sample zone (less than 3 degrees temperature difference across zone). Representing the cation stoichiometry of the film by X:2:2:3:0.37 (Tl:Ca:Ba:Cu:Ag), we have found in a typical experiment "X" values of 0.84, 0.70, and 0.43 for samples 1, 2, and 3 respectively (sample 1 was closest to the thallium oxide boat. For comparison we note that our optimum samples have compositions in which $0.75 \leq X \leq 0.90$

Because we believe that controlled transport of the thallium oxide vapor will be important in any scaled-up version of our process, we initiated an evaluation of the preparation of films in the "flow" reactor shown schematically in Figure 3. We have used the same two-step process/process times described above with only minor modifications, namely; 1.) an oxygen flow is maintained both through the outer quartz tube (300 SCCM) and the alumina reactor tube (1.7 SCCM), and 2.) the thallium oxide boat temperature has been reduced to 730C in order to to obtain the desired thallium content in the films ($0.75 \leq X \leq 0.90$). Using these modifications, we can now obtain textured "1223" thick films (poly-YSZ/Schedule #2) with "X" values in the optimum range for each of three samples placed end to end in the sample zone. In Table 1 are listed the "segmented bridge" J_c(zf-77K) values obtained on four samples prepared in our flow reactor. The T_c values of the samples ranged from 104K to 107K.

Table 1

J_c(zf-77K) in A/cm^2

Sample	Segment 1	Segment 2	Segment 3	Segment 4
1	46,000	67,200	336,000	148,000
2	166,000	26,800	16,300	80,500
3	51,700	10,300	16,800	41,900
4	31,900	124,000	97,300	80,500

2d. Flexible Substrates

A superconducting element for power applications must satisfy stringent electrical and mechanical performance requirements [12,13]. An important first step in meeting these requirements is the demonstration of good superconducting properties on a flexible substrate [14-16]. In our process the substrate material must resist chemical reaction at 860C with oxygen and thallium oxide vapor, as well as chemical and interdiffusion interactions with the precursor and superconducting layers. To minimize cracking of the films, the substrate should match closely the thermal expansion coefficient of the superconducting layer. Our demonstration that highly textured thick films can be obtained on a polycrystalline surface removes the requirement for a substrate that will support epitaxial growth. However, it is likely that optimum texturing of the films will require that a flat substrate surface be maintained throughout the growth process. This presents additional challenges for metallic substrates [16].

For our first "flow reactor" experiments on forming "1223" thick films on metallic substrates we elected to use Fecralloy^R [17], a high-temperature, oxidation-resistant iron-chromium-aluminum alloy. Earlier work in our laboratory [9] had shown that, although this alloy can withstand exposure to both oxygen and thallium oxide vapor at 860C, it reacts readily with the deposited film. In light of this, we have initiated work to evaluate the effectiveness of various barrier layers for minimizing this deleterious reaction. In the present case a sample of Fecralloy^R (3.2x0.64x0.005cm) was coated by sputter deposition with an ~0.2μm thick layer of undoped zirconia. A amount of precursor oxide sufficient to form an ~3μm thick superconducting film was prepared using Schedule #3 described above. The sample was processed in the two-zone reactor and subsequently annealed in oxygen at 600C using the schedules previously reported [8,9]. Similar to the case of our samples on poly-YSZ substrates, x-ray diffraction analysis showed the film to consist primarily of strongly c-axis textured "1223" with only traces of an unidentified secondary phase. The sample exhibited a T_c=109K and J_c(zf-77K)=10,000 A/cm^2. The J_c vs field behavior at various temperatures is shown in Figure 4.

Discussion

Although the three sample groups in our homogeneity study have similar T_c values, the precursor oxides prepared by Schedules #2 and #3 yielded superconducting films with significantly higher average J_c(zf-77K) values and less scatter in the segment values than those prepared from Schedule #1 precursor films. We believe that this behavior is related to the melting/decomposition characteristics of the calcium and barium nitrates. In the Schedule #1 precursors the rapid evolution of gas may cause some disruption of the film while the flow of the liquid nitrates before they decompose completely results in compositional inhomogeneities. The same processes occur during Schedule #2. However, the disruption by evolving gas is likely to be less severe and the effects of seggregation "averaged out" as the thinner layers are processed in sequence. In Schedule #3 the nitrates are decomposed slowly without melting, a situation expected to result in minimal disruption of the film and no post deposition seggregation. This interpretation is supported by the results of the microstructural characterization of precursor films. The SEM micrographs of the Schedule #3 and #2 precursors, shown in Figures 1a and 1b, respectively, reveal a fine-grained, uniform-appearing microstructure. The micrograph in Figure 1c of a Schedule #1 precursor has a coarser-grained, less uniform appearance. The EDS analysis of the Schedule #3 and #2 precursors revealed a relatively uniform chemical composition. On the other hand, the EDS analysis of the Schedule #1 precursor revealed a less homogeneous chemical composition and areas could be identified that were clearly either calcium or barium rich.

The results of our film growth mechanism studies are of particular interest. In our earlier work [8,9] we found that the silver addition is necessary to achieve the formation of a well interconnected and textured "1223" film via a process believed to involve a liquid phase assisted growth. Because silver exists as nodules in the final films and is found only in trace amounts in the "1223" phase, we believe that it plays an role only in the formation of the liquid phase. It is also important to note that, although all five metals must be present for the liquid to form, the liquid phase formation appears to initiate in regions that are calcium oxide rich. This suggests that, in addition to the chemical composition, the phase composition of the precursor is critical to the success of the process. That is, a "well calcined" precursor, in which the constituent oxides have fully reacted to form well defined compounds, may not give the desired results. This possibility should be taken into consideration in any attempt to adapt the silver-addition approach to other polycrystalline conductor fabrication processes.

Consistent with this picture of film growth are the results of a characterization of texture in our "1223" thick films from XRD azimuthal scans [18]. In that study it was determined that, on a macroscopic scale, the films exhibit excellent c-axis orientation but are essentially untextured with respect to basal plane orientation. However, on a microscopic scale, it was found that the films consist of an intergrowth of crystallite colonies within each of which there is a high degree of basal plane alignment. We believe that such colonies nucleate at sites, such as that indicated by the arrow in Figure 2a, where the liquid phase first forms as the thallium oxide vapor reacts with the precursor oxide films. Because the manner in which these colonies intergrow may determine the transport characteristics of the film [18], better control of this process may lead to significant improvements in the critical current densities obtainable.

The results of our first "flow-reactor" experiments with films on poly-YSZ substrates are very encouraging, especially when one considers the fact that in this initial set of samples are found three segments with J_c(zf-77K) values close to, and four segments with J_c(zf-77K) values well in excess of, the highest value (105,000 A/cm^2) ever measured by us in well over a hundred samples (four hundred segments) prepared in the "static" reactor. Additional work is required to understand why the J_c(zf-77K) values of the "flow" reactor samples are noticably higher than those prepared in the "static" reactor. However, we consider it likely that this is related, at least in part, to the presence of a more uniform thallium oxide partial pressure throughout the reactor which permits the "1223" phase to form under optimum equilibrium conditions at all positions on the film. It is apparent from the data in Table 1 that there is still a considerable segment to segment variation in J_c. Variations on the 200μm scale of the test bridge may be an unavoidable consequence of the film growth mechanism in the present process. Actually, we believe that the results obtained using this relatively narrow test bridge may present a misleading picture of the average properties over film dimensions of significance for practical conductors. To that end, we are presently assessing the suitablity of a wider test bridge.

In our first experiment with barrier-layer coated metallic substrates we have demonstrated the growth of a highly textured "1223" film. The T_c value of 109K, which is comparable to the highest values measured for us for films on poly-YSZ, indicates that the zirconia layer is effective in limiting film/substrate interactions. The J_c(zf-77K) value of 10,000 A/cm^2 measured for our film on Fecralloy^R:ZrO_2 is relatively low compared to our poly-YSZ samples, and the drop in J_c to ~1,000 A/cm^2 in weak fields indicates the presence of weak links. However, we find it most encouraging that the J_c vs field behavior after this initial low field drop indicates the presence of strongly linked current paths throughout our film.

Conclusion

The silver-addition process continues to show considerable potential for the production of superconducting tapes for use above 40K. Through refinements in the precursor deposition process and the development of a well controlled "flow-reactor", we have demonstrated significant improvements in the superconducting properties of "1223" thick films. The refinements reported here have permitted us to achieve an important milestone in the evolution of this technology, namely the preparation of a superconducting thick film, exhibiting characteristic "1223" strong linked behavior, on a flexible metal substrate.

Acknowledgments

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Figure Captions

Figure 1

SEM micrographs are shown for precursor oxide films prepared using (a) Schedule #3, (b) Schedule #2, and (c) Schedule #1 described in the text.

Figure 2

SEM micrographs illustrating the evolution of the textured microstructure obtained in the silver-addition process. Shown are micrographs for samples quenched (a) 5 minutes, (b) 6 minutes, and (c) 42 minutes after the thallium oxide boat temperature attained 745C. The platelike "1223" growths are readily evident in (b) and (c). The arrow in (a) points to a growth front in its early stages of development.

Figure 3

This diagram illustrates the essential features of the two-zone "flow" reactor.

Figure 4

Critical current density vs. field at various temperatures for a textured "1223" film on zirconia coated Fecralloy^{R} having J_c(zf-77K)=10,000 A/cm^2. The field was applied perpendicular to the substrate surface (parallel to c-axis).

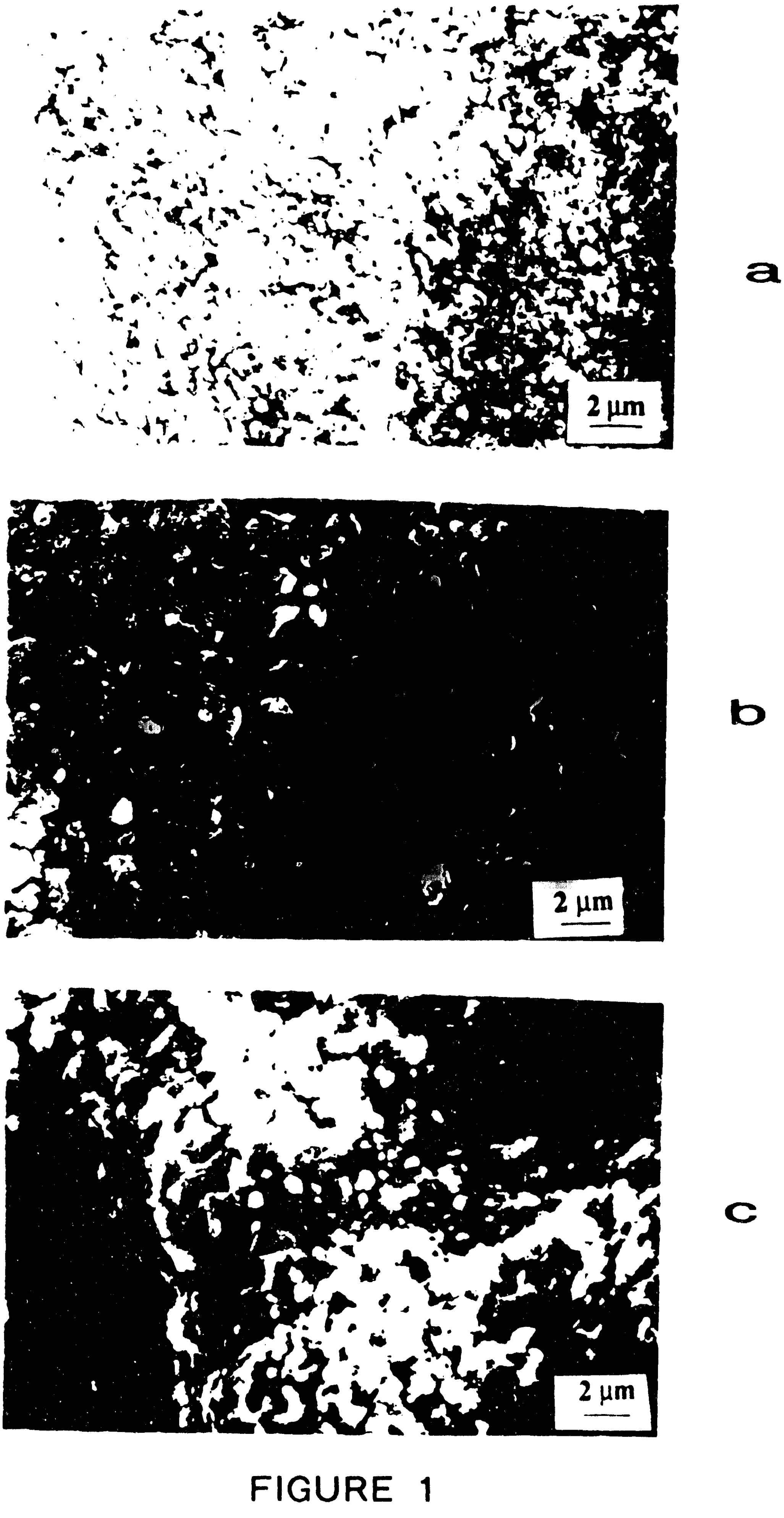


FIGURE 1

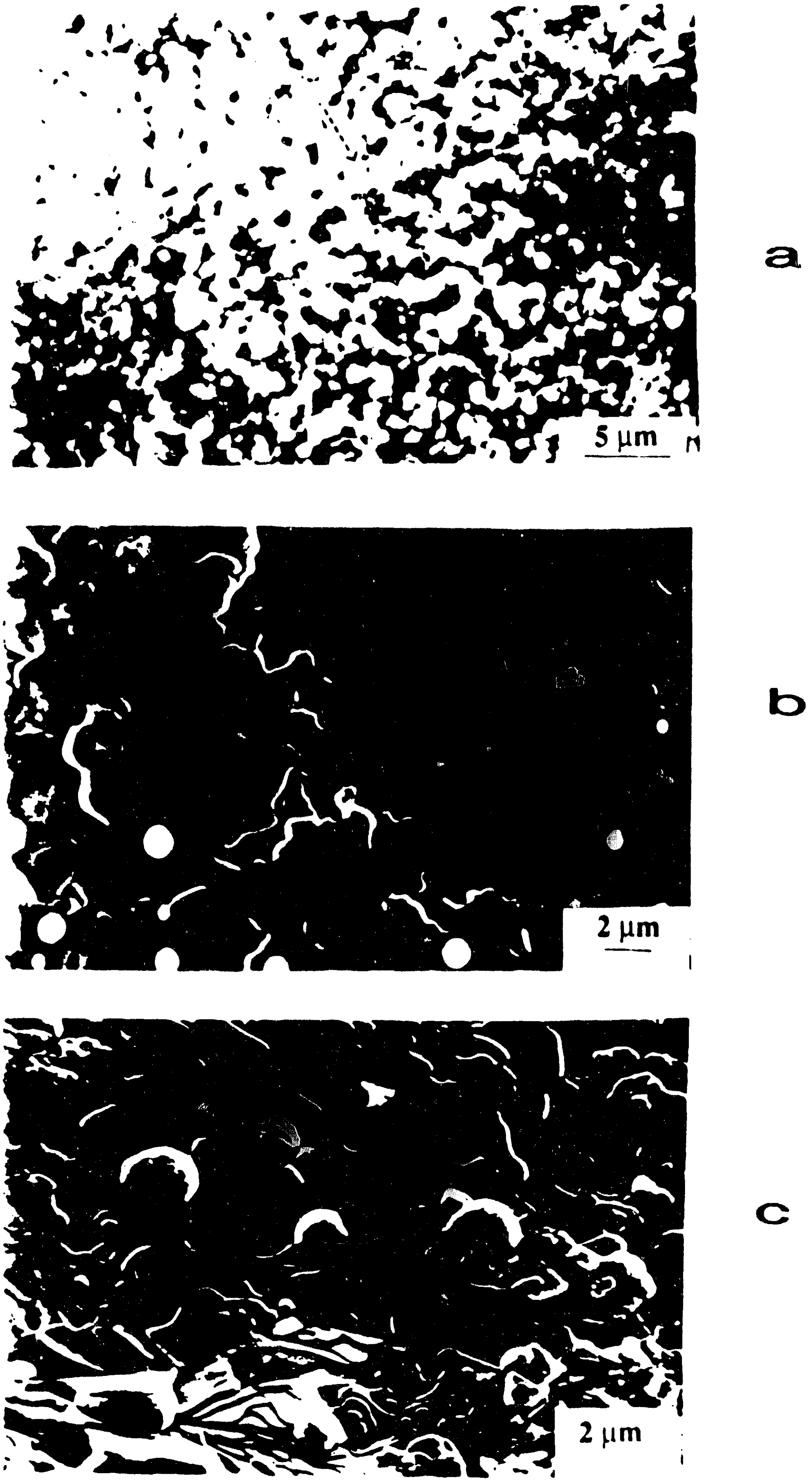


FIGURE 2

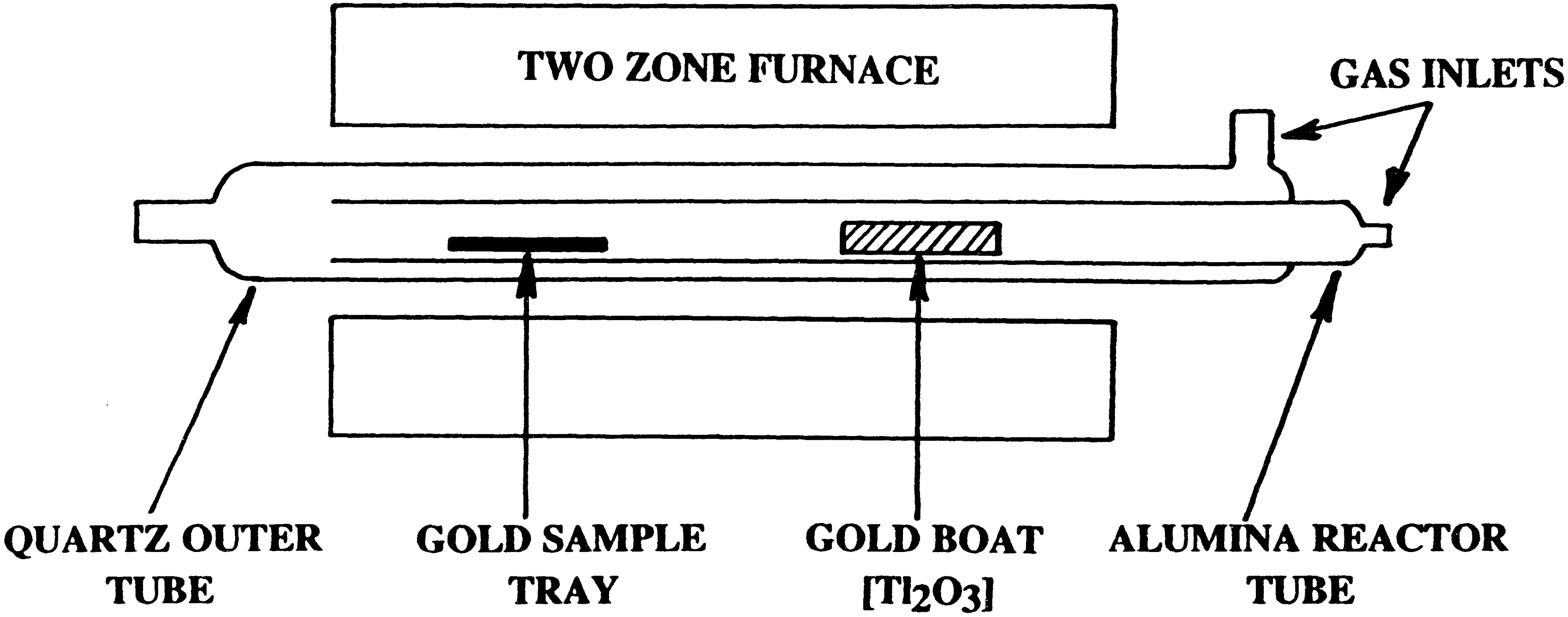
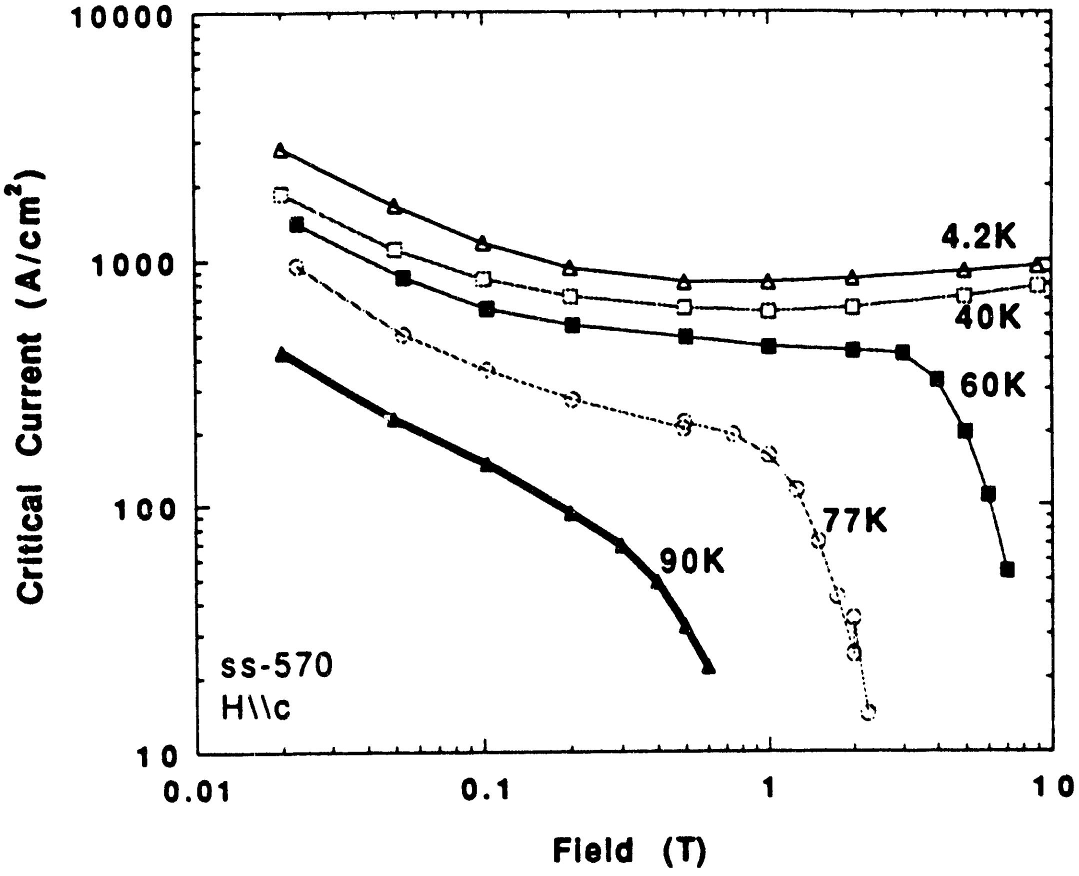

TWO ZONE FURNACE
GAS INLETS
QUARTZ OUTER TUBE
GOLD SAMPLE TRAY
GOLD BOAT [Tl_2O_3]
ALUMINA REACTOR TUBE

FIGURE 3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1000
100
10
0.01
0.1
1
10
Critical Current (A/cm^2)
Field (T)
4.2K
40K
60K
77K
90K
ss-570
H\\c

FIGURE 4

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