2

GA-C19465
(12/89)

AD-A218347

HIGH-TEMPERATURE CERAMIC SUPERCONDUCTORS

For Period
October 1, 1989 - December 31, 1989

January 10, 1990

Prepared for:

OFFICE OF NAVAL RESEARCH
800 North Quincy Street
Arlington, Virginia 22217-5000

DARPA/ONR Contract N00014-88-C-0714

GA Project 3850

Prepared by:

K. S. Mazdiyasni, Program Manager (619) 455-4587
A. Chen
K. C. Chen
D. M. Duggan
E. I. Glatter
F. C. Montgomery
S. S. Pak
M. B. Maple, UCSD
L. Paulius, UCSD
P. K. Tasai, UCSD

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

Approved by: T D Gulden
T. D. Gulden
Director, Defense Materials

The views and conclusions contained in this quarterly report are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Project Agency of the U.S. Government.

GENERAL ATOMICS

90 02 05 0

CONTENTS

FIGURES

TABLES

1. INTRODUCTION

This is the fourth quarterly progress report on the work performed in the period from October 1, 1989 through December 31, 1989 on Office of Naval Research (ONR) Contract N00014-88-C-0714, entitled "High-Temperature Ceramic Superconductors." The principal objectives of this program are (1) to demonstrate fabrication of high-temperature ceramic superconductors that can operate at or above 90 K with appropriate current density (J_c) in forms useful for application in resonant cavities, magnets, motors, sensors, computers, and other devices; and (2) to fabricate and demonstrate selected components made of these materials, including microwave cavities and magnetic shields.

Kelvin

KEYWORDS: HIGH TEMPERATURE, CERAMIC MATERIALS, SUPERCONDUCTORS, ELECTRICAL CONDUCTIVITY, CAVITY RESONATORS, ENGINES, SENSORS, DETECTORS.

1.1. PROJECT OUTLINE

This program consists of six tasks: (1) metal alkoxide synthesis and processing, (2) microstructural evaluation and property measurement, (3) electrical and magnetic property measurement, (4) superconductor ceramic processing, (5) component fabrication and demonstration, and (6) reporting.

DTIC COPY INSPECTED

☑
☐
☐

per call

Codes

d / or
ial

A-1

Task 1 is to synthesize a homogeneous alkoxide solution that contains all the constituent elements that can be easily made into powders, thin film, or drawn into fiber form. Ideally, this solution should possess precise stoichiometry, adequate stability, polymerizability, adherence, and spinnability. Also, the polymeric materials formed from this solution should be thermosetting, be able to be dissolved in organic solvents, and contain as little as possible low-temperature pyrolyzable organics with high char yield.

STATEMENT "A" per Dr. W. Smith
ONR/Code 1131N
TELECON 2/9/90 CG

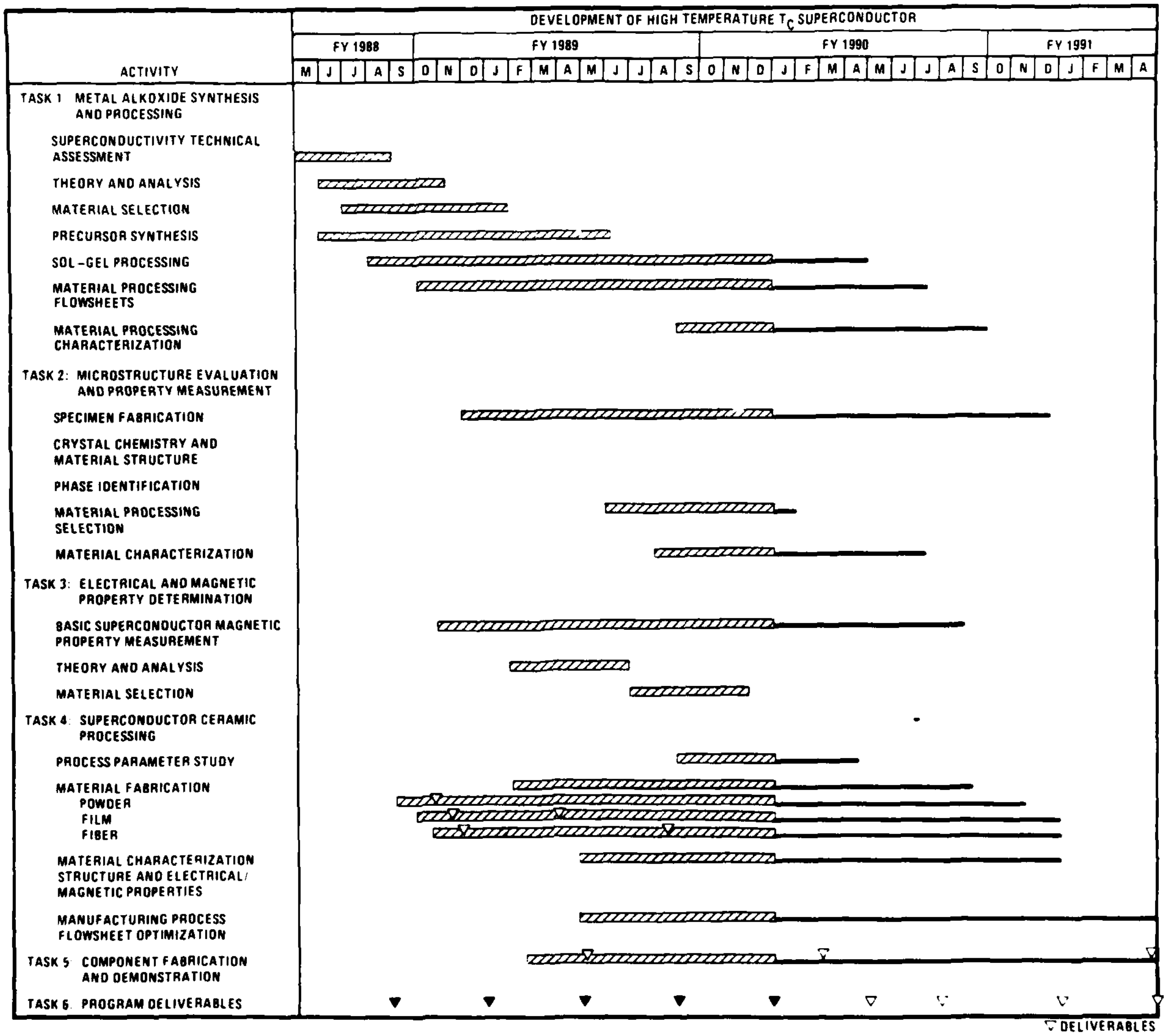
Task 2 is to study the microstructure as a function of processing parameters. The study includes: density, pore size, and pore size distribution, phase identification, chemical composition and purity, environmental stability, effects of heat treatment, residual strain, seeding, annealing in magnetic fields, and epitaxy on grain growth and orientation.

Task 3 is to study the electrical and magnetic properties of the $YBa_2Cu_3O_7$ (123) high T_c ceramic superconductors. It will include both the ac electrical resistance (R_{ax}) and the ac magnetic susceptibility (χ_{ac}).

Task 4 is to investigate superconductor ceramic processing. Most of the important applications of superconductors require material in the form of fiber or films. Magnets, conductors, motors, and generators are examples of applications employing fiber; while detectors, microwave cavities, and microcircuitry require superconducting material in the form of films. The sol-gel process is ideally suited to producing materials in these forms; in fact, it is used commercially to produce antireflection and mirror coatings and to produce continuous ceramic fibers for structural reinforcement in composite materials and for thermal insulation.

Task 5 is to demonstrate component fabrication. General Atomics (GA) will design and build a high Q, high T_c superconducting cavity, using its unique sol-gel coating process capabilities. This task will proceed after some initial coating tests have verified dc superconductivity and after we have answered questions of adhesiveness, surface preparation, and processing procedures. As the fabrication process and the materials quality are improved throughout the three-year program, two additional cavities will be constructed and tested. Coupling will be through a waveguide inductive iris into an end wall, with a logarithmic decrement technique of Q measurement considered most appropriate for the high Q anticipated. An X-band (10 GHz) frequency choice allows for convenient dimensions of 4.3 cm diameter by 2.8 cm height.

This report will focus primarily on Tasks 1, 2, 3, and 4.



J-358(1)
1-22-90

2. PROGRESS

2.1. SOL-GEL PROCESSING

With reference to the work described in the last progress report, the types of sol required for fiber and thin film applications are different than that desired for powder synthesis. As stated in the previous report, for powder synthesis, a suspension containing uniform submicron size precipitate, with all three materials (Y, Ba, and Cu) distributed homogeneously, would be ideal. This depends on the rate of hydrolysis and aggregation of a dispersed powder, which strongly influences powder packing and subsequent sinterability. Another factor influencing the state of aggregation is the stability of dispersion against coagulation. Thin film, on the other hand, requires a homogeneous and stable sol. In general, this requires a very slow rate of hydrolysis.

During the reporting period, we have experienced instability of the stock solutions and/or precursor sols as a function of time for the powder production as well as for thin film applications. For this reason, it was decided to spend additional time to perhaps understand and identify the chemical aging phenomena, which is affecting the electrochemical instability of the selected precursor sols to be used under the program. (Exhibit A presents the well known electrochemistry, as related to dispersion and coagulation).

2.1.1. Materials Process Refinement

In our previous experiments, attempts were made only to control the alkoxide water molar ratios and not to monitor the effect of the solution pH change with time on the solubility of 123 constituents. While conducting a literature search in preparation for doing a more systematic study, it was found, for example, that Ba^{2+} or Sr^{2+} at a surface of e.g., TiO_2 particle, changes the surface properties of TiO_2 significantly. BaO has an isoelectric point (IEP) of 12, and $BaTiO_3$ has an IEP ≈ 9, thus the presence of Ba^{2+} at the surface, whether in the form of an adsorbed ion or a carbonate, shift the IEP of the TiO_2 surface from 5.5 toward 12. Also, it has been reported that attempts to disperse Ba^{2+} doped TiO_2 at pH 9 to 10 were unsuccessful, but a pH $\leq$ 8 yielded stable dispersion.

As indicated in Section 2.1, in order to pinpoint the 123 sol and/or solution instability issue, three 10 ml alkoxide solutions [$Y(i\text{-}OPr)_3$, $Ba(i\text{-}OPr)_2$, and $Cu(MeO)_2$], each with a concentration of 0.05 M, were prepared in three separate vials. They were allowed to hydrolyze in open air, and the onset of hydrolysis was recorded. Table 1 shows the results. As the table shows, all three alkoxides exhibit vastly different rates of hydrolysis.

Even if the rate of hydrolysis could be matched, it was found that another critical issue must be addressed. During the hydrolysis and polycondensation of the sol, a suspension must be prevented from being formed. The supernatant above the settled powder may appear colorless, thus giving the impression that all metals have been hydrolyzed. However, in actuality, it was found, through emission spectroscopy, that supernatant contains a large amount of dissolved Ba and Cu, especially in highly basic solutions such as the one being utilized in this case.

The dissolution of Ba and Cu puts a rigid restriction on the nature of the sol-to-powder transition. In order to maintain 123 stoichiometry and minimize chemical segregation, the hydrolysis and polymerization of the precursor compound must be rapid and complete and not remain in the liquid.

TABLE 1
ONSET OF HYDROLYSIS OF 0.05 M ALKOXIDE SOLS

Alkoxide	Elapsed Time
$Y(i\text{-}OPr)_3$	8 min
$Ba(i\text{-}OPr)_2$	3 hr
$Cu(MeO)_2$	26 hr

To match the hydrolysis rates, one could either slow down Y and Ba, speed up Cu, or speed up both. As a preliminary set of experiments, prior to a more systematic and detailed experiment, a broad range of hydrolysis conditions were chosen to observe whether there were any significant differences in resulting reaction kinetics. In order to speed up the rate of hydrolysis of Cu, H_2O_2 was added, since it was found to be an efficient rate enhancer. To slow down Y and Ba, less than a stoichiometric amount of water was added, either directly or by further diluting with methanol. A total of six tests were performed. All six sols were prepared from the same stock sol. Each sol was hydrolyzed differently and, the resulting powders were heated to 900°C in flowing oxygen (200 cc/min) for 75 min. Figure 1 shows the hydrolysis conditions and the associated XRD patterns.

If we use the same relative amount of 123, as compared to the amount used in other phases, as a qualitative indication of the homogeneity in the starting powder, it is clear that the monolithic gel forms are superior to particle suspensions. Also, it is clear that either too fast or too slow of a hydrolysis leads to large inhomogeneities and that an intermediate rate is optimal. Currently, an effort is underway to examine what concentrations of water, alkoxides, and H_2O_2 are required to best match the rates of hydrolysis.

2.1.2. Rare Earth Substituted 123

Work on the preparation and characterization of the $RBa_2Cu_3O_{7-\delta}$ series, using sol-gel process, continues. An improved $LuBa_2Cu_3O_{7-\delta}$ powder was prepared that exhibited a very clean X-ray spectrum and an orthorhombic structure. Differential thermal analysis revealed low concentrations of impurity phases. In the process of pressing and annealing the powder into pellet form, the sample quality degraded. Experience has shown that the formation of the $LuBa_2Cu_3O_{7-\delta}$ compound is impeded by the small size of the Lu ions. Work is continuing on improving the annealing procedure.

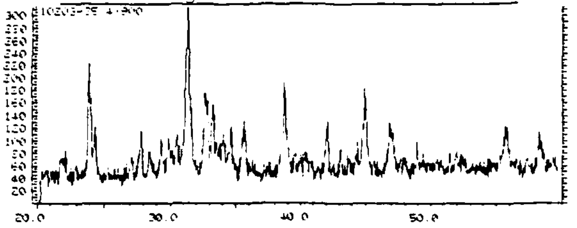
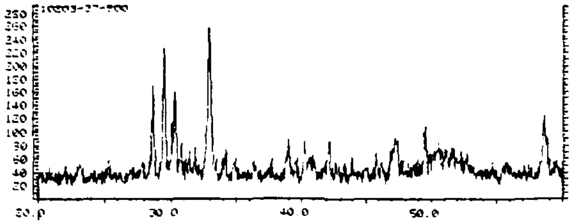
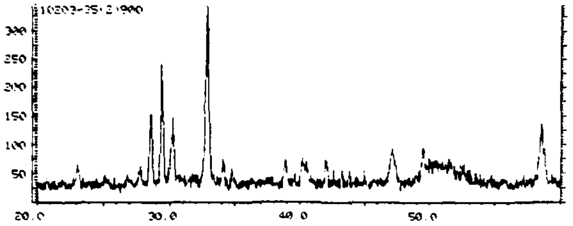
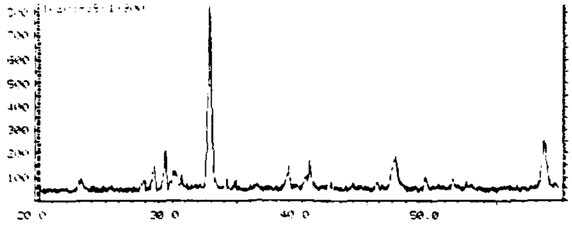
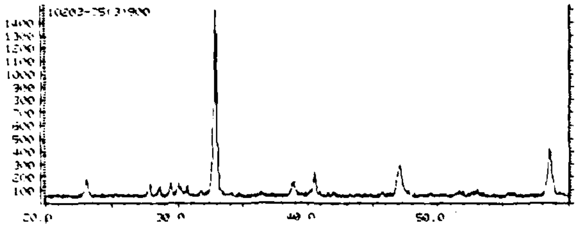
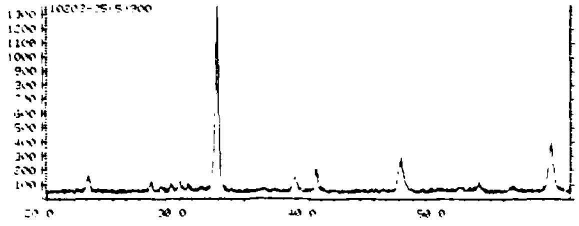
Hydrolysis Condition	State	Resulting XRD Pattern at 900 C
excess water	suspension resulted immediately	
$Cu(MeO)_2$ is partially hydrolyzed with H_2O_2 for 2 min. before adding $Y(i\text{-}OPr)_3$ and $Ba(i\text{-}OPr)_2$	some ppt's formed, but gelled eventually	
excess H_2O_2/H_2O	suspension resulted immediately	
hydrolysis induced via exposure to atmospheric water	gelation started in 26 min. & completed in 113 hr.	
less than stoichiometric amount of H_2O_2/H_2O	some ppt's formed, but gelled eventually	
less than stoichiometric water diluted with methanol	gelled homogeneously in 15 hr.	

Fig. 1. Effect of hydrolysis conditions on the phase assemblage of the YBCO powder heated to 900°C for 75 min in O_2

2.1.3. Electromagnetic Properties Characterization

In order to investigate mechanisms for the enhancement of the critical field and the critical current density, we are studying the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system for possible flux pinning by the praseodymium ions. A series of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ powders has been prepared with x = 0, 0.1, 0.2, and 0.4. The $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_{7-\delta}$ sample has been found to be superconducting with a critical temperature of $T_c = 59.7$ K. The expected value for the critical temperature is $T_c = 88$ K (Ref. 1). Additional samples are currently being annealed. Routine measurements will include the electrical resistivity as a function of temperature, X-ray diffraction analysis, and iodometric titration to determine oxygen content. Subsequently, we plan to make specimens in which the grains are aligned in an applied magnetic field. The magnetization of these grain-aligned samples will be measured as a function of the temperature, T, and the applied field, H, for the c-axis parallel and perpendicular to H. From these measurements, the critical field, $H_{c2}(T)$, and the induced critical current density, $J_c(T)$, can be estimated for both c-axis orientations. We also plan to study flux creep phenomena by observing the time dependent decay of magnetization and to compare our results with relevant theoretical models.

3. THIN FILM AND FIBER PROCESSING

During the last quarter, homogeneous solutions have been prepared using $Y(OR)_2$, $Ba(OR)_2$, and the copper (II) mixed-ligand species $(C_5H_7O_2)_2Cu_2(u\text{-}OR)_2$, where R = $CH_2CH_2OCH_2CH_2OCH_2CH_3$ and $C_5H_7O_2$ = 2,4-pentanedionate. Since the copper species with the 2-(2-ethoxyethoxy)ethoxide moiety is more soluble than the earlier compounds used, the solids content of the solutions is significantly higher than in the earlier preparations.

3.1. EXPERIMENTAL PROCEDURES

Yttrium tris-2-(2-ethoxyethoxy)ethoxide was prepared by alcohol exchange of yttrium isopropoxide with 2-(2-ethoxyethoxy)ethanol. In an oven dried 125 ml erlenmeyer flask was added 3 g yttrium isopropoxide (0.0113 mole) and 10 ml (0.0745 mole) dry 2-(2-ethoxyethoxy)ethanol. The flask was fitted with a drying tube and a N_2 inlet. The mixture was heated at 100° to 120°C until all the isopropoxide had dissolved. Heating was continued for 6 hr under a N_2 purge to remove isopropyl alcohol as it was formed. After cooling, the solution was centrifuged and decanted to remove a small amount of residue. A clear, pale yellow solution resulted. EDTA titration of the yttrium content verified the concentration and showed that the solution was stable for several weeks.

The copper compound was synthesized by reaction of Di-Cu(II)-u-methoxo-2,4-pentanedionate with 2-(2-ethoxyethoxy)ethanol following a similar procedure used for the preparation of the yttrium compound. EDTA titration again indicated that the solution was stable for several weeks.

Barium 2-(2-ethoxyethoxy)ethoxide was prepared by reaction of barium metal granules (Alfa inorganics) with dry 2-(2-ethoxyethoxy)ethanol. Typically, 3.96 g (0.0288 mole) of barium was reacted with about 30 ml (0.223 mole) of dry alcohol. After the reaction was complete, as evidenced by the cessation of hydrogen evolution, the solution was filtered to remove a small amount of residue.

3.1.1. Preparation of 123 Precursor Solution

A septum bottle containing the required stoichiometric solution of yttrium, barium, and copper was prepared by weighing aliquots of the stock alkoxide solutions. Hydrolysis (using less than 2 moles of water per mole of metal) was accomplished by injecting a dilute solution of the required amount of water in 2-(2-ethoxyethoxy)ethanol into the alkoxide solution.

3.1.2. Dip Coating

Thin strips of yttria stabilized zirconia polycrystal were coated with the homogeneous 123 precursor solutions. Dip coating is accomplished under a controlled atmosphere with a small bench top coater constructed at GA. The strips are vertically dipped for 10 sec, removed from the solution at 0.38 mm/sec, and fired at 400° to 600°C for 3 min before the cycle is repeated.

3.1.3. Heat Treatment

Coated sample strips were heated in flowing ultra-pure oxygen at 1°C/min to 880° to 960°C. They were then held for 60 min and cooled at 5°C/min to 482°C. After holding for an additional 60 min, the chips were cooled to room temperature at 5°C/min.

3.1.4. Results and Discussion

The microstructure, homogeneity, and superconducting properties of the coatings formed on YSZP were found to depend on the conditions used during the hydrolysis of the initial reaction mixture. Solutions that were hydrolyzed with more than 2 moles of water per mole of metal precipitated barium and the coatings prepared from this solution were, thus, low in barium.

When the reaction conditions were such that either the extent of hydrolysis was low or the viscosity of the solution did not change due to polymerization, the final coatings showed segregation of the individual constituents, with copper being present as nodules of CuO. Figure 2 is an SEM photograph at a magnification of 4000X showing the microstructure of this type of coating and a CuO nodule at the top of the picture.

Figure 3 shows a SEM photograph of a coating that was prepared from a solution containing about 17 wt % equivalent 123 compound and that had polymerized sufficiently to increase the solution viscosity. EDAX line measurements show that the coating stoichiometry is homogeneous. Furthermore, the coating shown in Fig. 3 has less void than the coating shown in Fig. 2. Magnetic flux measurements (Fig. 4) showed that this coating exhibited a Meissner effect beginning around 90 K.

The coated sample heat treatment is important in establishing the final microstructure of the coating. Figure 5 shows a coating prepared from the same solution used to form the coating shown in Fig. 3. However, the firing temperature was increased from 882° to 958°C. Significant amounts of grain growth were observed of the finer grains obtained at the lower firing temperature, during the 958°C anneal. Magnetic flux measurements showed that this coating was semiconducting and was not superconducting.

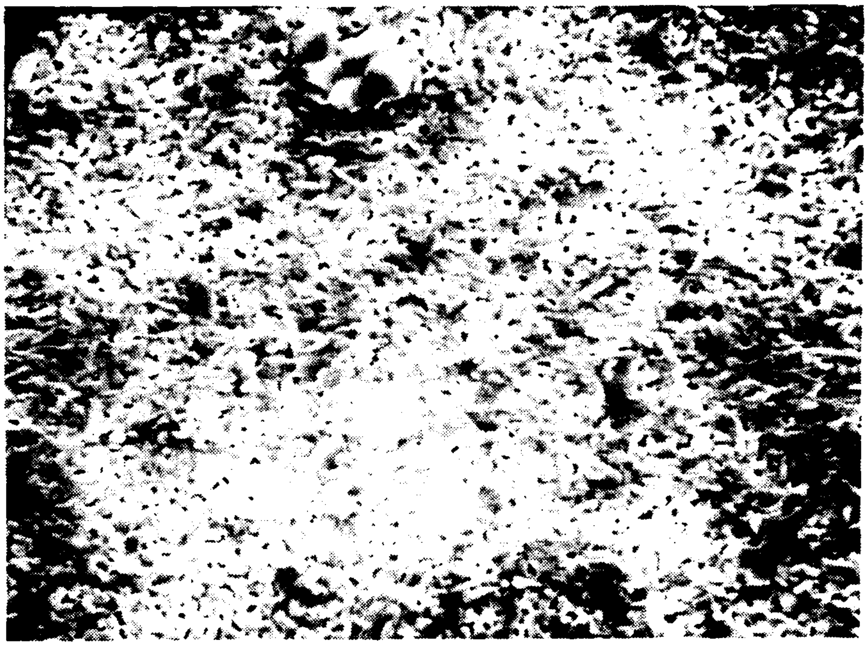


Fig. 2. SEM of Y123 thin film showing CuO nodules

Fig. 3. SEM of higher density Y123 film with no evidence of CuO nodules

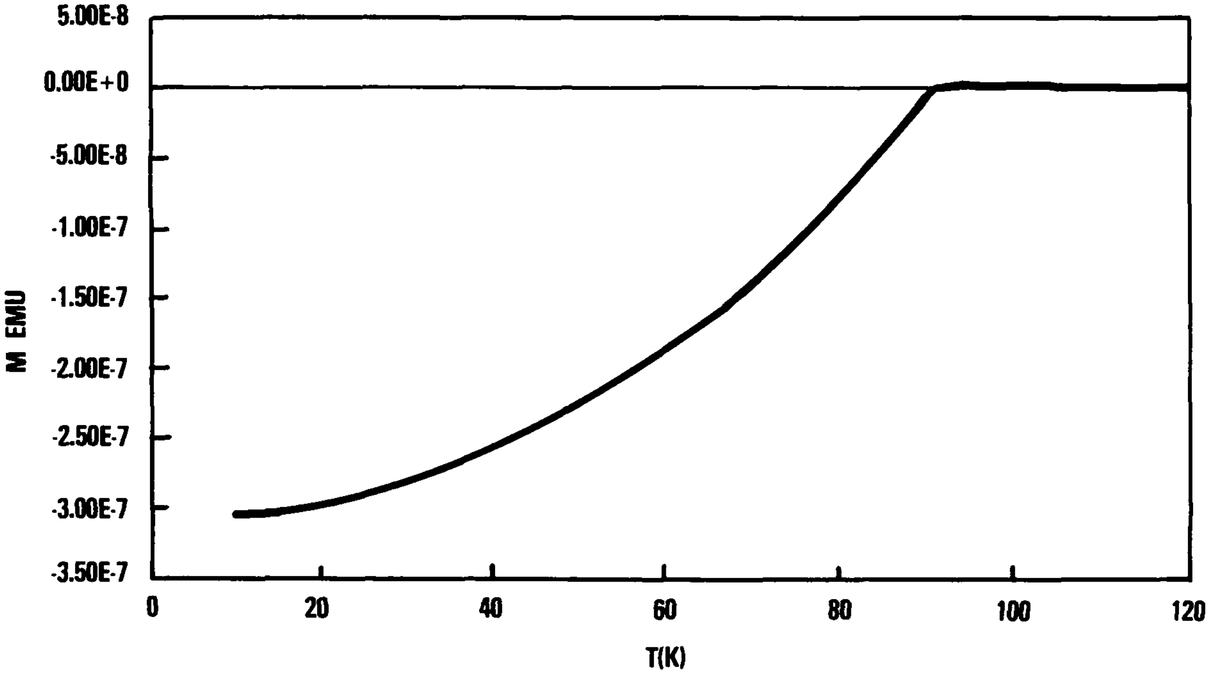


Fig. 4. Magnetic susceptibility measurement of Y123 coating on YSZP substrate

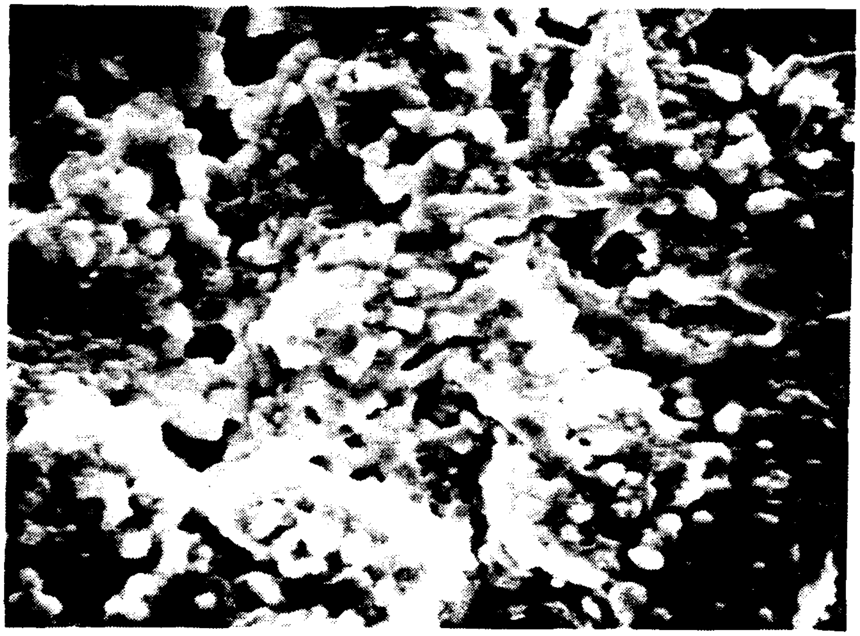


Fig. 5. SEM of Y123 coated on YSZP fired at 958°C for 1 hr with semiconducting properties

The length of time at the firing temperature also affects the coating microstructure and the stoichiometry. Annealing the coating shown in Fig. 3 for an additional 42.6 hr at 882°C resulted in the formation of nodules (Fig. 6) that were rich in barium. Whether this is due to loss of copper or to some reaction to form a different phase containing a higher barium content is not yet known.

3.2. FIBER PROCESSING

3.2.1. Detailed Evaluation of BaYCuO High-Temperature Superconductor Preparation

We have experimentally identified a few processing parameters that can have substantial influences on the final properties of the BYCO fibers. They are indicated numerially in the flow diagram, as shown in Fig. 7. These parameters are as follows:

1. The temperature and time used for refluxing the precipitates.
2. The amount of water required for hydrolysis.
3. The solution temperature during hydrolysis and afterward.

These process parameters are being systematically and iteratively investigated such that the effect of process variations on the final properties can be predicted. The limits of each variable and some initial results are described in the following paragraphs:

1. The refluxing condition: The 3-neck flask has been used so that the solution temperature can be closely monitored during the entire preparation. In the earlier sample preparations, it was noted that when the solution was subjected to a vigorous refluxing condition, a small amount of precipitate formed upon the completion of reflux. The formation of precipitates could be eliminated by a gentler refluxing condition. It is anticipated that by using different combinations of time and refluxing rates, phase separation and solution instability are

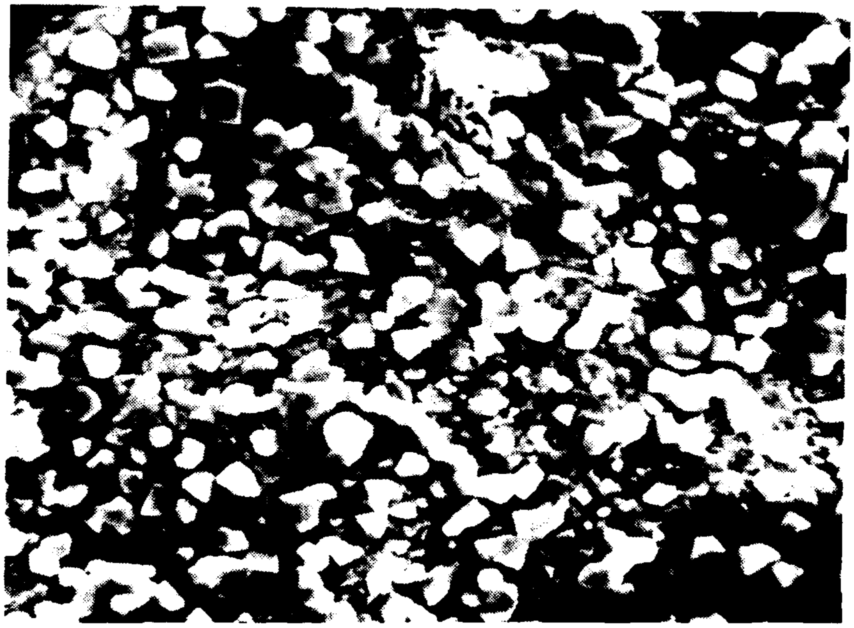


Fig. 6. SEM of Y123 coated on YSZP fired at 958°C for ~43 hr showing segregation of CuO throughout the sample

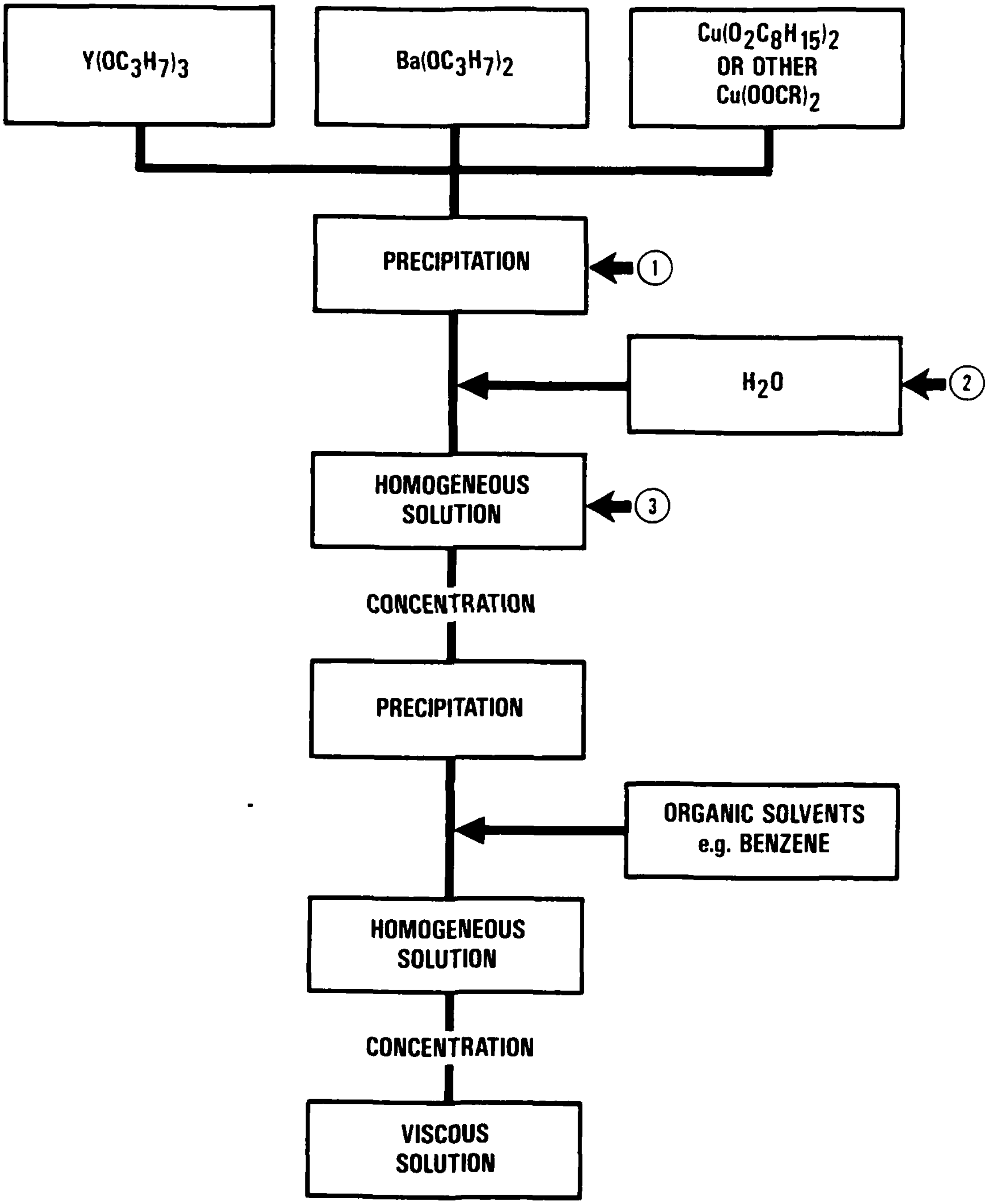


Fig. 7. Flow diagram for preceramic BYCO fiber preparation

eliminated, which will produce samples with desired fiberizability properties.

2. Hydrolysis: The molar ratios of 4/1, 7/1, and 10/1 of water to 123 compounds have been chosen for investigation. From the preliminary results obtained so far, no definite conclusion can be drawn based on the amount of water used.

3. Solution temperature: The temperature, ranging from the reflux temperature 82.4°C to room temperature, will be employed in this phase of the investigation.

3.2.2. Further Improvement in Composition Stoichiometry

An effort to improve the consistency of phase purity in the process is continuing. In order to avoid formation of $BaCuO_2$, which is a liquid at approximately 960°C, the compositions of precursor solutions have been tailored such that the maximum molar concentration of yttrium is 1.03 M and the minimum molar concentration of copper is 2.97 M. Increasing the yttrium concentration addresses the issue of presence of $BaCuO_2$, and decreasing the copper concentration addresses the overall stoichiometric integrity of the sample. However, the results of the XRD and DTA data obtained from the fiber samples (Fig. 8) are unexplained at this time.

3.2.3. Resistivity and Magnetic Susceptibility Measurements

The dc magnetic susceptibility measurement of fiber sample (10228-39) prepared from the solution precursor is described in Section 3.2.2; however, the indicated T_c onset is 91 K [Fig. 9(a)], which represents an improvement from the previous result [Fig. 9(b)].

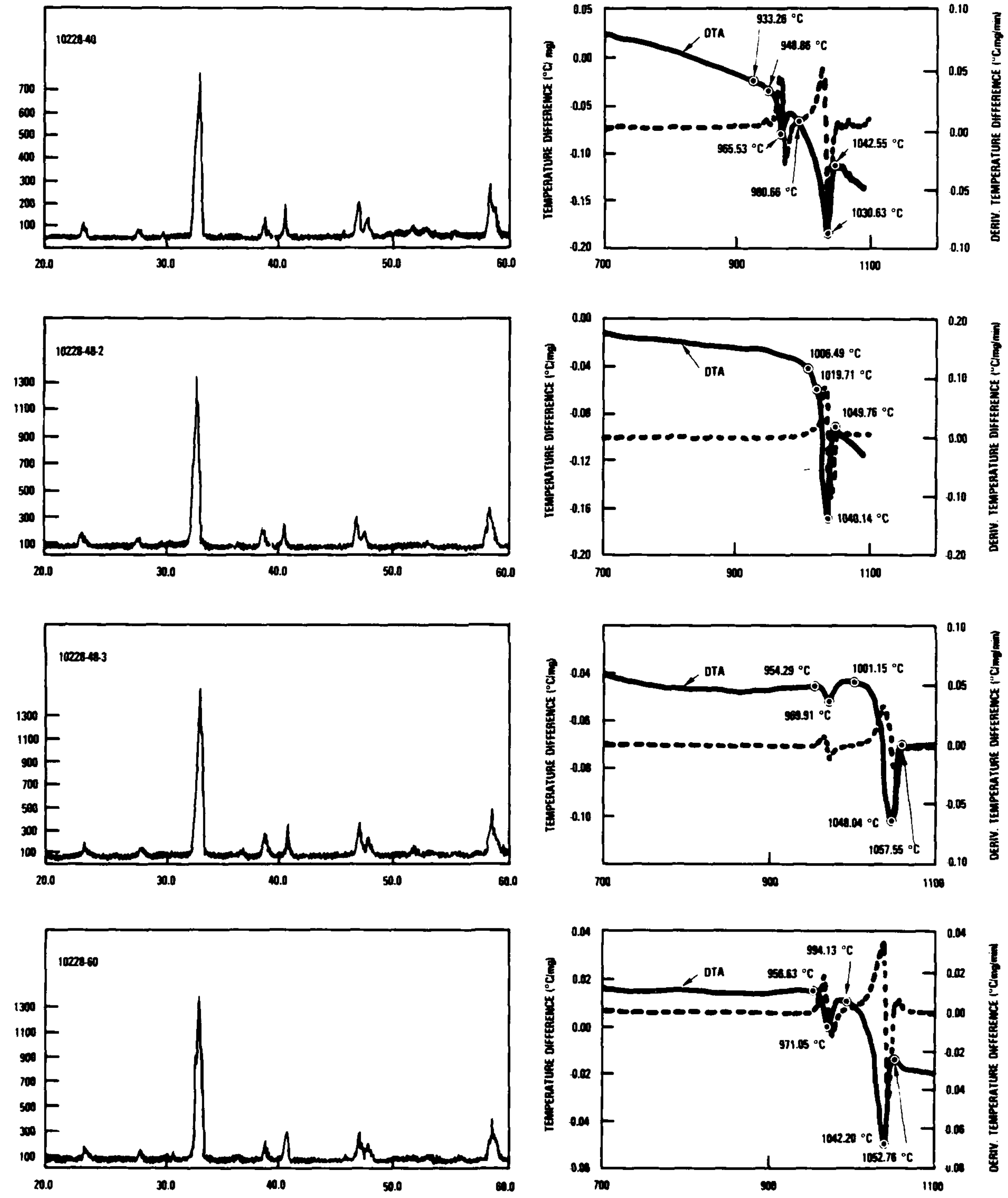


Fig. 8. XRD and DTA data of some of the fiber samples

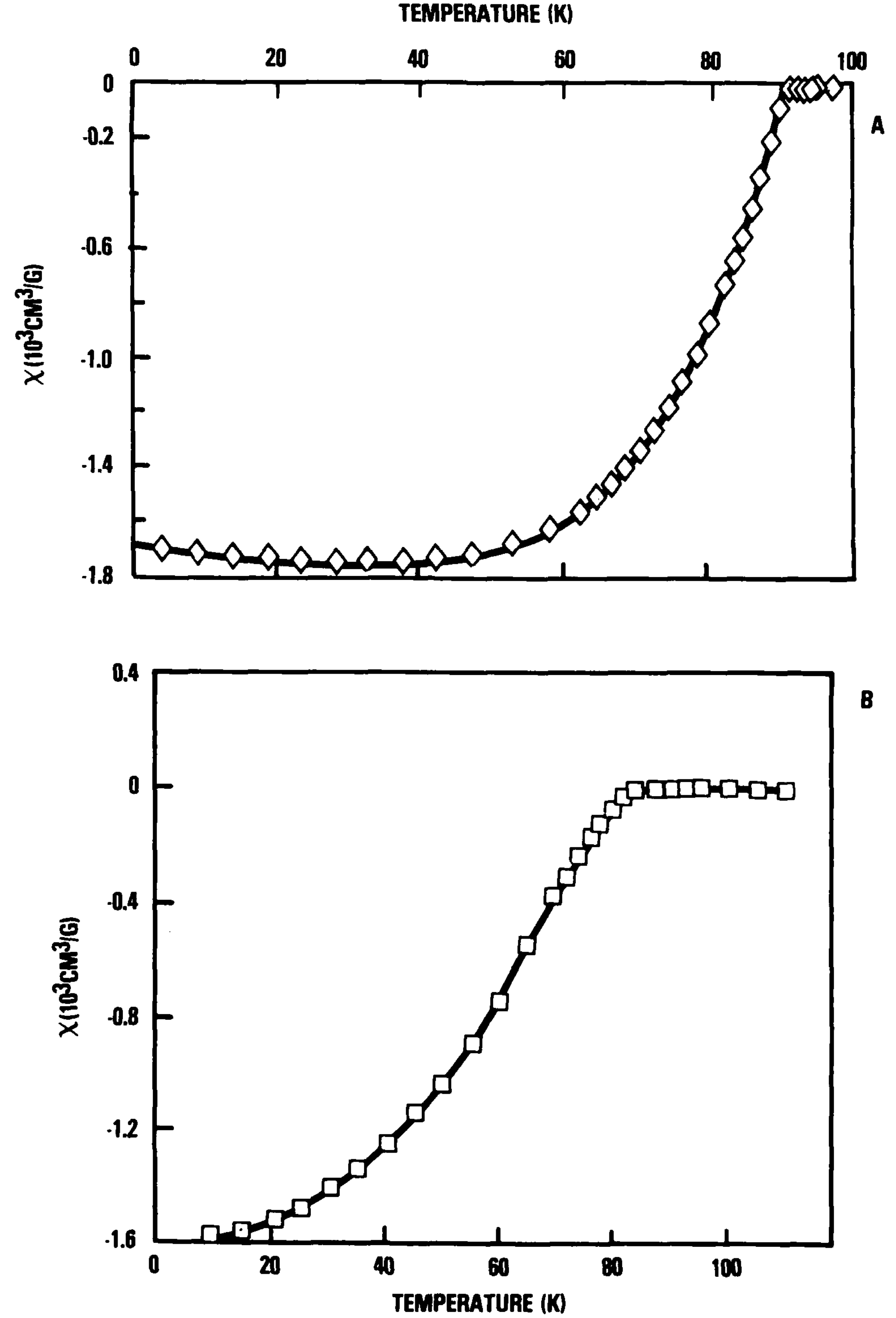


Fig. 9. Comparison of the magnetic susceptibility measurements
(a) recent result (b) previous result

3.3. IN-SITU PREVENTION OF BARIUM CARBONATE FORMATION BY MODIFICATION OF THE SOLUTION CHEMISTRY

During the course of this program, a method was developed to prepare a homogeneous stable solution that can be converted to viscous liquid or solid resin states for fiber drawing. Many associated chemistry problems, which influence the stoichiometry of the starting solution and phase purity in the final superconducting ceramics, have been successfully resolved. It was found that it is possible to control microstructure to incorporate minor 211 phase inclusions in the fibers by a slight adjustment in the solution stoichiometry at an early stage of the solution preparation. The solution chemistry was further improved to avoid stable barium carbonate formation. This has been accomplished by partial substitution of copper ethylhexanoate with copper trifluoroacetate.

In replacing of some of the copper ethylhexanoate with copper trifluoracetate to provide 4 to 6 moles of fluorine per formula of Y123, it was discovered that no barium carbonate was found during the pyrolysis of the preceramic fibers. In these fibers, barium fluoride and copper oxide were found at intermediate temperature range [Fig. 10(a)]. By calcining at 850° to 900°C in a flowing oxygen saturated with water, single phase Y123 was produced in these fibers [Fig. 10(b)]. The optimal temperature and duration of heat treatment have not yet been established. These two parameters, together with the resulting microstructure, need to be evaluated for continuous fiber processing before the copper trifluoroacetate containing solutions can be adapted for the final fiber processing.

3.3.1. Effect of Solvent Mixtures on the Rheology Behavior of the Resin

It has been found that the rheology of the resin was strongly influenced by the presence of different kinds of solvents as well as their relative amounts. In certain combinations, a minute change in

- **STARTING COMPOUNDS**

$$1\ \mathrm{Y(OP_r^i)_3} + 2\ \mathrm{Ba\ (OP_r^i)_2} + 2\frac{1}{3}\ \mathrm{Cu(EH)_2} + \frac{2}{3}\ \mathrm{Cu(CF_3COO)_2}$$

- **REACTION SEQUENCE**

$$\mathrm{AMORPHOUS} \xrightarrow[\text{2 HR}]{\text{500°C}} \begin{bmatrix}\mathrm{BaF_2}\\ \mathrm{CuO}\end{bmatrix} \xrightarrow[\text{900°C, 12 HR, Dry } O_2]{\text{900°C, 3 HR, WET } O_2} \begin{bmatrix}211\\ \mathrm{BaF_2}\\ \mathrm{CuO}\end{bmatrix} \xrightarrow[\text{900°C, 20 HR, Dry } O_2]{\text{850°C, 18 HR, WET } O_2} \mathrm{Y123}$$

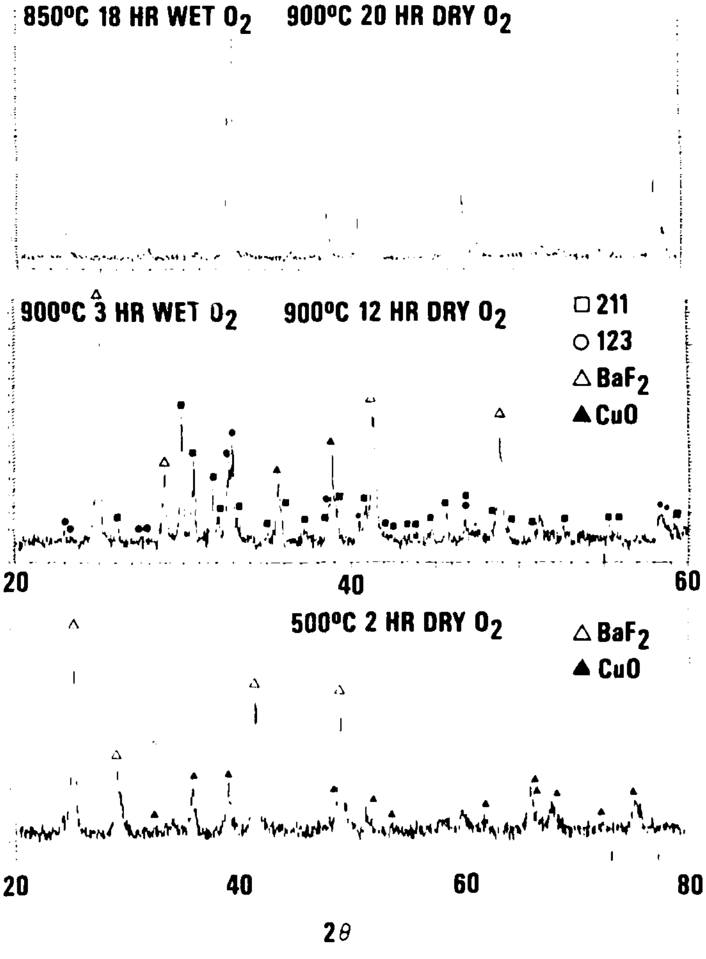


Fig. 10. X-ray diffractions of fibers calcined at (a) 500°C for 2 hr and (b) 850°C for 18 hr in dry O_2 then at 900°C for 18 hr in wet O_2 atmosphere

the solvent ratio has a profound influence on the viscosity. Therefore, the effects of the solvent concentration in the resin on the rheological behavior of the resin was closely examined. The purpose of this study is to define the volume fraction of solvent mixtures in the resin that are necessary to obtain a certain viscosity. Once the conditions are found, the resin can be readily converted to suitable viscosities for either film or fiber processing.

3.3.2. Behavior of the Y123 Resin in Benzene-Isopropanol Binary Solvents

First, the qualitative rheology behavior of the dry resin in different combinations of benzene and isopropanol was examined (Fig. 11). In this ternary phase diagram, there are six major regions. In region I, the resins are viscous, and the viscosity decreases with increasing amounts of benzene (e.g., point 1 is more viscous than point 2). Fibers or thick films are made within certain combinations of benzene and isopropanol within this region. However, on the tie line between the dry resin and toluene, resin is cohesive (Fig. 12).

3.3.3. Behavior of the Y123 Resin in Xylene-Isopropanol Binary Solvents

The behaviors of resin in the xylenes-isopropanol binary system have also been studied (Fig. 13). As in the previous systems, there are also similar regions. A similar viscous range was found in the benzene-isopropanol system. There exists a much larger homogeneous solution region. On the tie line between the dry resin and xylene, the cohesive property of the resin is again observed. Two unique features of this system are that, (1) the solution viscosity in the homogeneous region is higher than those homogeneous solutions in either benzene-isopropanol and toluene-isopropanol systems and, (2) the evaporation rate of solvents is slightly slower. As a result, the xylenes-based solutions are better for thick film applications.

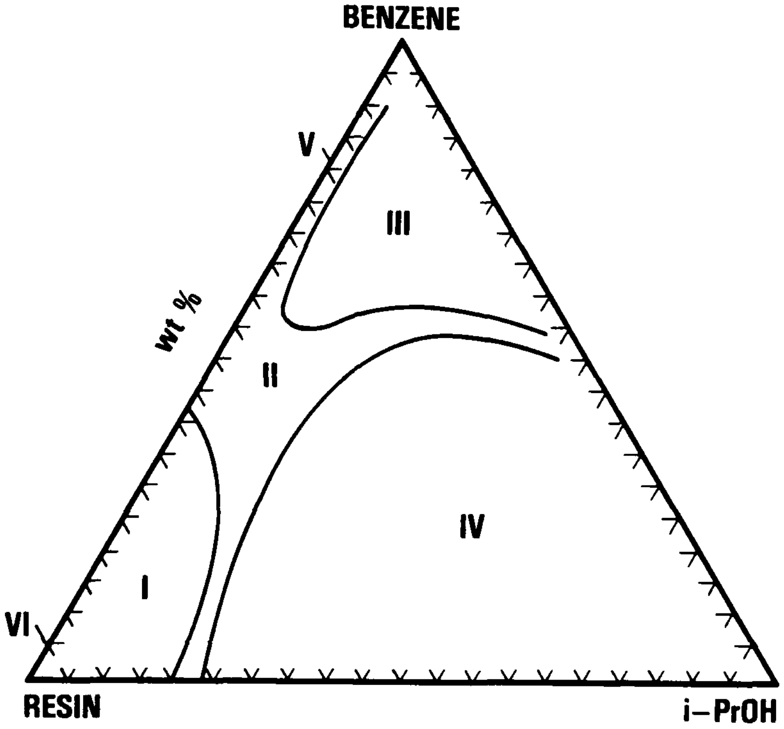


Fig. 11. Characteristics of the Y123 resin in benzene-isopropanol binary solvents

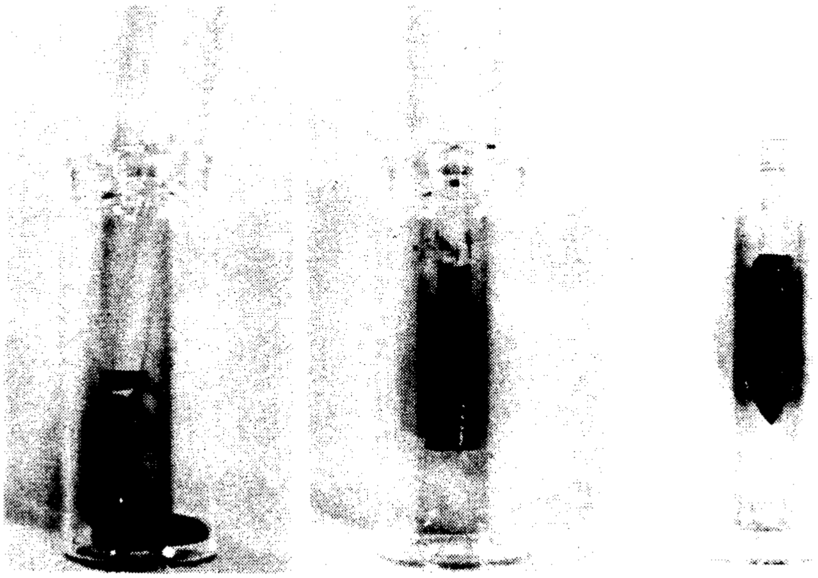


Fig. 12. The cohesive property of resin in benzene enables it to be molded into different shapes

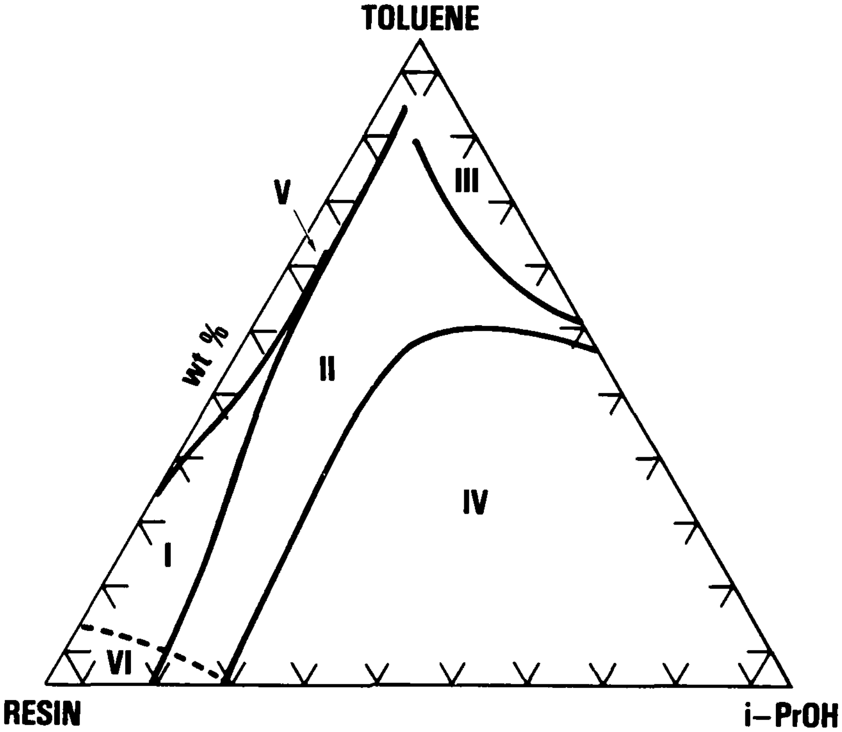


Fig. 13. Characteristics of the Y123 resin in toluene-isopropanol binary solvents

3.3.4. Behavior of the Y123 Resin in Hexane-Isopropanol Binary Solvents

As in the xylene/isopropanol-based system, the hexane-isopropanol system has a similar wide range of homogeneous solutions, a large precipitation region, and a small viscous region located close to the apex of dry resin (Fig. 14). Compared to three previous systems, however, this system has the smallest cohesive region, and that region does not coincide on the dry resin-hexane tie line.

3.4. RESIN SPINNING PROPERTIES AS A FUNCTION OF SOLVENT CONSTITUENTS

While it has been shown in the last annual report that the fiber can be continuously spun from the resin, the refinement of the solvent content in the resin and its effect on spinning processes have not yet been examined. The spinning properties that are critical for continuous fiber spinning include the rheology and the plasticity of the resin, die-swelling of the resin, surface smoothness of the fiber after extrusion, drying rate and flexibility of the fiber, possible collapse of the fiber after solvent evaporation or deformation under its own weight, green strength, and pressure needed for extrusion. These must be examined concurrently or simultaneously before a process flow sheet is constructed.

While it is not conclusive at the present time which of the viscous regions in the above four systems is better for the continuous spinning requirements, it was found that only a very narrow combination of solvents and resin in the viscous regions in each system is possible. As an example, some results in the toluene-isopropanol system are given in Table 2.

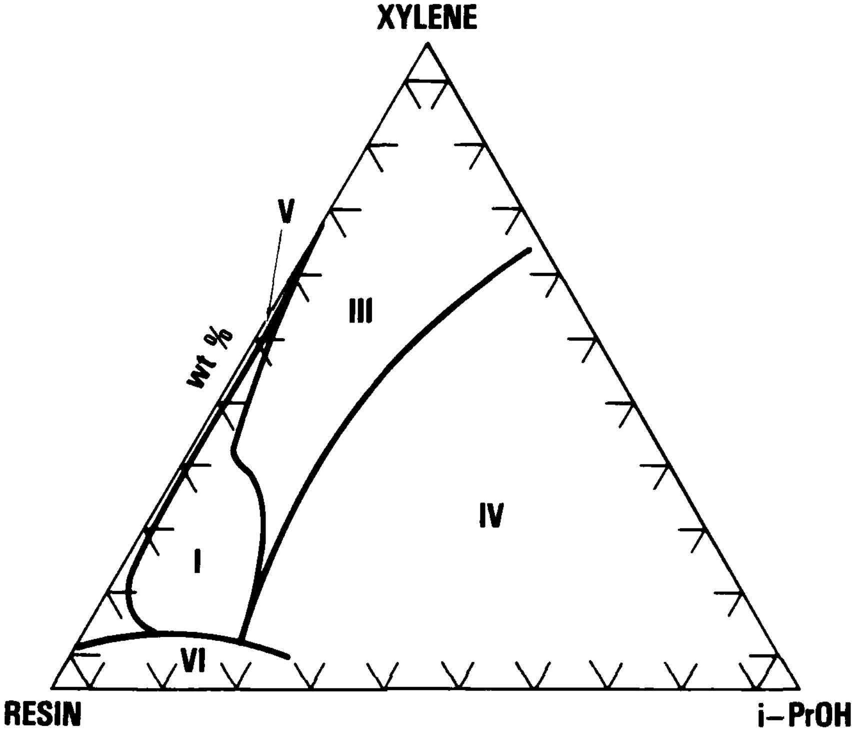


Fig. 14. Characteristics of the Y123 resin in xylene-isopropanol binary solvents

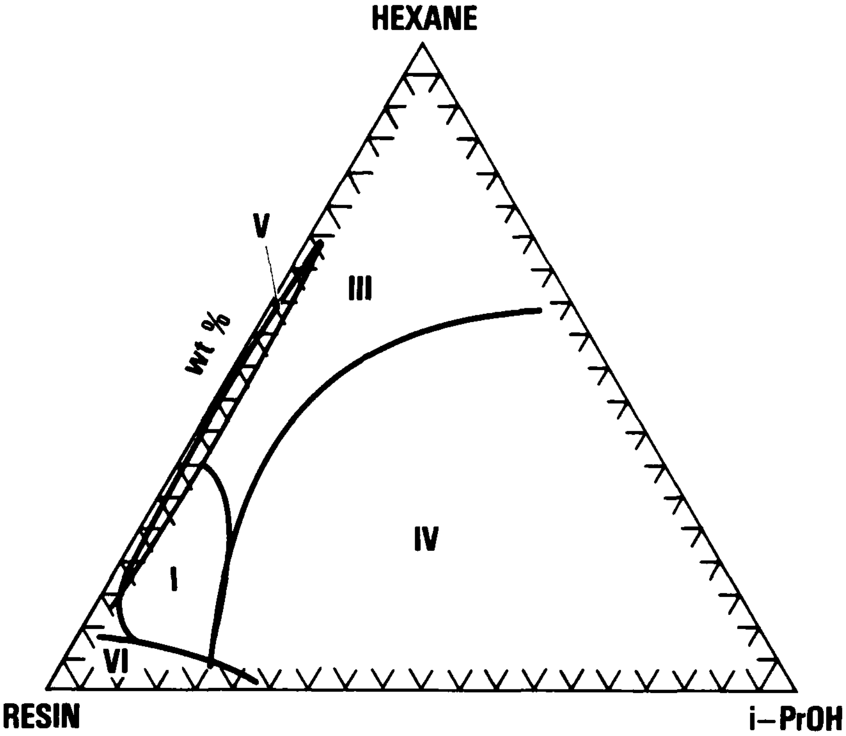


Fig. 15. Characteristics of the Y123 resin in hexane-isopropanol binary solvents

TABLE 2
CHARACTERISTICS OF RESINS IN DIFFERENT SOLVENT COMBINATIONS

Test Run	Resin Constituents (wt %)			Resin Characteristics						Figure of Merit
	Xylene	I-Propanol	Dry Resin	Cohesive	Surface Smoothness	Die Swell	Flexibility	Collapse	Extrusion Pressure	
1	5.7	0.0	94.3	Yes	Yes	Small	No	Slightly	High	B^-
2	30.0	0.0	70.0	Yes	Yes	Slight	No	Slightly	High	B^-
3	9.7	3.4	86.9	Yes	Yes	Large	Yes	Some	High	C^-
4	42.3	1.0	56.6	Yes(a)	Yes	Slight	No	Yes	High	C^+
5	29.0	1.0	70.0	Yes(a)	Yes	No	Some	Some	Medium	B^-
6	19.8	1.2	79.0	Yes(a)	Yes	No	Very slight	Very slightly	Medium-high	B^--B^+
7	17.8	1.0	81.0	Yes	Yes	No	Yes	Very slightly	Low-medium	B^+-A^-
8	16.8	1.1	82.0	Yes	Yes	Very slight	Yes	No	Medium-high	A^--A
9	15.6	1.3	83.0	Yes	No	Very slight	Yes	Very slightly	High	B^+-A^-

(a) Slightly sticky.

4. EQUIPMENT MODIFICATION

Because thin films and fibers have a high surface-to-volume ratio and are therefore more susceptible to contamination, we have set up clean furnaces in our laboratory. Degreased stainless steel gas lines and extra dry oxygen were installed to minimize the introduction of impurities into the system. The use of elastomer seals was avoided by using ground quartz coupled to stainless steel fittings. Programmable Omega oven controllers provide reproducible annealing profiles.

4.1. NEW EQUIPMENT

A piston-type extruder (Fig. 16) is currently being manufactured at a UCSD machine shop. The extruder will allow filament of constant diameter to be produced from the viscous solution.

Since the last report, GA's HP8720A Microwave Network Analyzer has been upgraded so that its frequency resolution is now 1 Hz, in order that very high Q's can be measured precisely and accurately. Using this new capability, the Q of our cylindrical cavity with a 1/8 in. thick copper end plate resting on the bottom, resonating at 10.3 GHz in the TE_{011} mode, was measured as 12,500 at room temperature (much less than the 18,000 measured with the old equipment) and 23,000 in liquid nitrogen; in the TE_{012} mode at 14.3 GHz, the Q was also 12,500 at room temperature (compared to 19,000 with the old equipment). We believe that the Q measured with the old equipment was simply inaccurate because of the poor frequency stability and severe noise problems associated with that equipment. The network analyzer contains an ultrastable frequency synthesizer, and averaging can reduce its noise floor to below -50 dB.

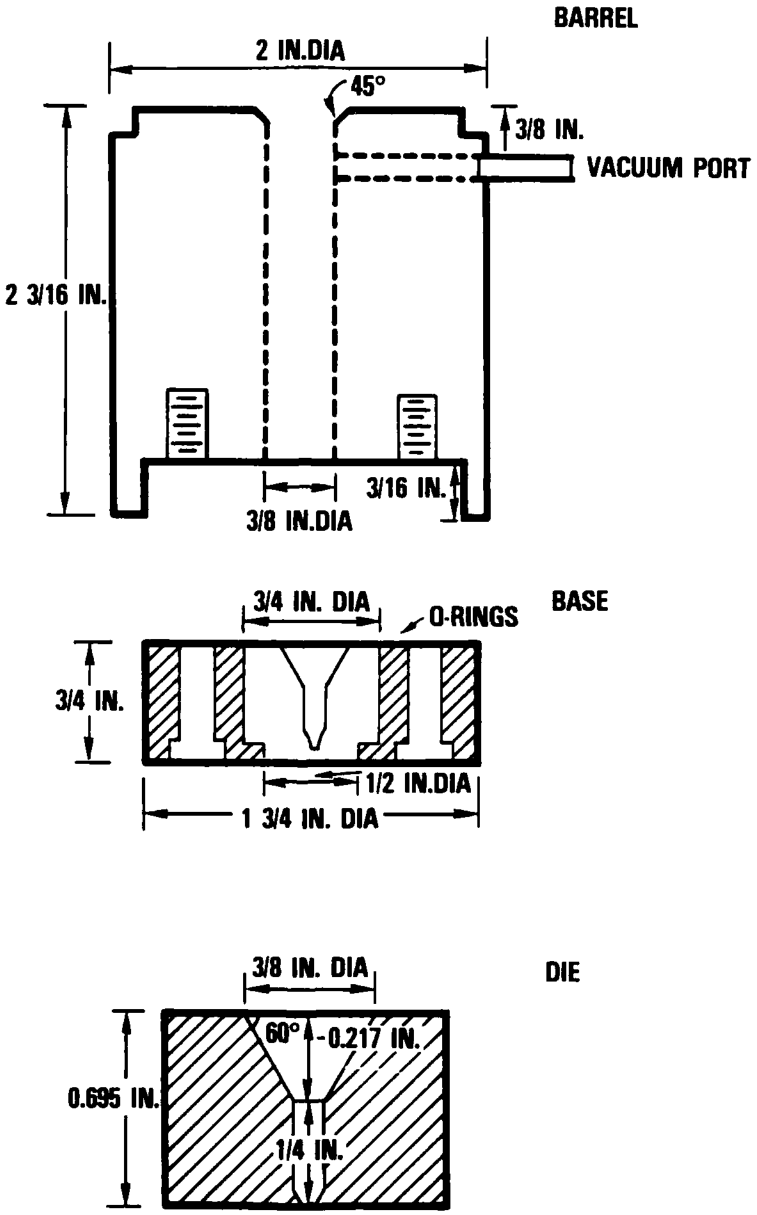


Fig. 16. Schematic of the extruder

5. REFERENCES

1. Dalichaouch, Y., M. S. Torikachvili, E. A. Early, B. W. Lee, C. L., Seaman, K. N. Yang, H. Zhou, and M. B. Maple, Solid State Comm., 65, 1001 (1989).
2. Overbeek, J. T. G., "Recent Developments in the Understanding of Colloid Stability," J. Colloid Interface Sci., 58, 408-422 (1977).
3. Ottewill, R. H., "Stability and Instability in Disperse Systems," J. Colloid Interface Sci., 58, 357-373 (1977).
4. Hamaker, H. C., Physics, 4, 1058 (1937).
5. Von Smoluchowski, M., Phys. Z., 17, 593 (1916).

EXHIBIT A

DISPERSION

Particle Interactions

The state of aggregation of a dispersed powder, which strongly influences powder packing and subsequent sinterability, depends on the stability of the dispersion against coagulation. The approach of two particles, from Brownian motion, sedimentation, or processing forces, results in coagulation when the particle interactions are not sufficiently repulsive. The theory describing these interactions (DLVO theory) was recently reviewed (Refs. 2 and 3). The basic equations are given in the following discussion.

The general equation describing the two-body interactions consists of attractive and repulsive terms,

$$V_T = V_A(\text{van der Waals}) + V_R(\text{electrostatic}) + V_R(\text{others}) \quad . \qquad (1)$$

The van der Waals attraction between two spherical particles of radius a and center-to-center distance r is given by (Ref. 4)

$$V_A = -\frac{A}{6}\left(\frac{2a^2}{r2 - 4a^2} + \frac{2a^2}{r^2} + \ln\frac{r^2 + 4a^2}{r^2}\right) \quad , \qquad (2)$$

where A, the Hamaker constant, depends on the properties of the particles and the dispersion medium ($A \sim 10^{-12} - 10^{-13}$ ergs). The electrostatic repulsion, arising from the interaction of the electrical double layers surrounding the dispersed particles, has the general form

$$V_R \propto \epsilon\epsilon_0 \psi_d \exp(-kH) \quad , \qquad (3)$$

where ϵ is the medium dielectric constant, H the particle separation, and ψ_d the Stern (diffuse layer) potential. The quantity 1/k is the Debye-Huckel length given by

$$1/k = \left(\frac{\epsilon\epsilon_0 RT}{F^2 \Sigma_i c_i z_i^2} \right)^{1/2} \quad , \qquad (4)$$

where F is Faraday's constant, and c_i and z_i are the counterion concentration and valence, respectively (Ref. 2).

Coagulation

The rate of coagulation of a dispersion depends on the sign and magnitude of the interaction energies; the frequency of Brownian encounters determines the maximum rate of coagulation in the absence of forces. Coagulation is retarded by the presence of repulsive interactions, as the maximum repulsive energy ($V_T$max) acts as an activation energy for the process.

Coagulation has been modeled as a biparticle reaction obeying the rate equation

$$\frac{dn}{dt} = kn^2 \quad , \qquad (5)$$

where n = particle number density and k = coagulation rate constant. The rate constant for rapid coagulation, based on mutual particle diffusion, was given by Smoluchowski (Ref. 5) as

$$k_r = 8\pi D n_0 \quad , \tag{6}$$

where $_0$ is the initial particle concentration and D is the particle diffusion coefficient given by

$$D = kT/6\pi\eta a \quad , \tag{7}$$

where η is the dispersion medium viscosity.

The retardation of coagulation owing to repulsive interactions was evaluated in 1934 by Fuchs through the introduction of the stability factor, W, given as

$$W = \frac{k_r}{k_{slow}} = 2a \int_{2a}^{\infty} \exp\left(\frac{V_T}{kT}\right) \frac{dr}{r^2} \quad , \tag{8}$$

where k_{slow} is the rate constant for slow coagulation. Although this theory is restricted to the formation of pairs from primary particles (singlets), stability factors can be experimentally obtained through measurements of the time rate of change of n (or the average particle size). The stability factors not only reveal the behavior of the solution/particle electrochemistry but are also useful in predicting coagulation behavior in slurries of ceramic powders.

EXHIBIT B

During this period, the following paper under the subject contact was presented at the fall meeting of the MRS in Boston. The paper was well received and 52 requests for reprint were received.

HIGH T_c SUPERCONDUCTOR FIBERS FROM METALLO-ORGANIC PRECURSORS

K.C. CHEN AND K.S. MAZDIYASNI
General Atomics, PO Box 85608, San Diego, CA 92138-5608

ABSTRACT

Homogeneous solution for Y-Ba-Cu-O superconductor was prepared from yttrium i-propoxide, barium i-propoxide, and copper ethylhexanoate. The solution was converted to a resin-like material and was readily dissolved in organic solvents. The resin possesses a cohesive property in a number of solvents, such as benzene and xylene. Single-phase superconducting $YBa_2Cu_3O_{7-x}$ fibers have been continuously spun from the viscous solution. Controlled amounts of Y_2BaCuO_5 phase in the fibers were made possible by slight adjustments in the solution compositions. Partial substitution of copper ethylhexanoate with copper trifluoroacetate prevents barium carbonate formation in the fiber during curing and organic pyrolysis.

INTRODUCTION

For the new high T_c superconducting ceramics to be useful, they must be made into desirable shapes. Specifically, the magnetic applications critically depend on the fabrication of fibers or tapes that carry sufficiently high electrical current. Fabrication of $YBa_2Cu_3O_{7-x}$ superconductor ceramic fibers or wire with adequate strength, modulus, and electromagnetic properties is a formidable task because the yttrium barium cuprate ceramic material is brittle and is not easily drawn into the desirable fine fiber geometry. Such fiber property requirements demand high chemical and phase purities as well as crystallographic orientation in the a or b direction, uniform microstructure, and clean grain boundaries.

Various methods have been used to prepare superconducting fibers [1]. The powder-in-binder [2], powder-in-sol [3], sol-gel and metallo-organic [4-8] methods adopt the spinning process, which has been established for ceramic fiber-making. In this paper, we discuss the method involving the preparation of single phase $YBa_2Cu_3O_{7-x}$ fibers and fibers with minor Y_2BaCuO_5 phase inclusions from metallo-organic precursors. We also describe modification of the solution chemistry to overcome barium carbonate formation.

EXPERIMENTAL PROCEDURES

Yttrium i-propoxide/i-propanol solution was prepared by the method described by Mazdiyasni, et al. [9]. Barium i-propoxide/i-propanol solution was prepared by reacting barium metal chips (Alfa Products) with dry i-propanol. Copper ethylhexanoate/i-propanol solution was made by dissolving copper ethylhexanoate (Alfa Product) in dry i-propanol. Copper trifluoroacetate was synthesized by reacting copper ethoxide (Alfa Products) with trifluoroacetic acid.

Stoichiometric ($YBa_2Cu_3O_{7-x}$) or off-stoichiometric ($YBa_2Cu_3O_{7-x}$ + y Y_2BaCuO_5) solutions were obtained by pipetting the calculated volumes from each stock solution. In cases where copper trifluoroacetate were used, 2/3 to 1 mole of copper trifluoroacetate per mole of yttrium was added to partially substitute for copper ethylhexanoate. A green precipitate formed when copper solution was introduced. This precipitate was hydrolyzed by adding water/isopropanol solution. The greenish precipitate gradually dissolved after adding water, and a clear dark green solution formed. This solution was further concentrated in a vacuum oven or a rotary evaporator until it became highly viscous liquid or completely dry resin-like mass. The dried resin could be dissolved to a prescribed viscosity in a number of solvent mixtures, such as benzene-isopropanol or xylene-isopropanol solutions. Fibers were prepared either by hand-drawing or mechanical spinning from these viscous liquids.

RESULTS AND DISCUSSIONS

The dry resin is readily dissolved or "softened" by using proper ratios of benzene-isopropanol mixtures. The characteristics of the resin in these solutions are shown in Figure 1. There are several regions in this ternary phase diagram. Transitions across boundaries are gradual. The transition between regions is reversible and can be done by adding or removing solvents. In the low benzene, low isopropanol region (region V), the resin becomes viscous. Within this region, fibers can be easily prepared by hand-drawing or mechanical spinning (Figure 2). In the high isopropanol region (region P), precipitation occurs. In region L_c, a solution with a very small amount of colloid exists. A stable solution can be obtained in region L. Similar results were observed in a xylene-isopropanol system.

In the tie line between the benzene-resin, resins possess an interesting cohesive property, i.e., they do not stick to glass vials. This property enables resins to be molded into different shapes (Figure 3). The fibers spun from the resin have adequate mechanical strength prior to pyrolysis and sintering and are flexible. After calcination, some fibers of 20 microns diameter were able to be bent into a circle of 1 to 2 cm radius.

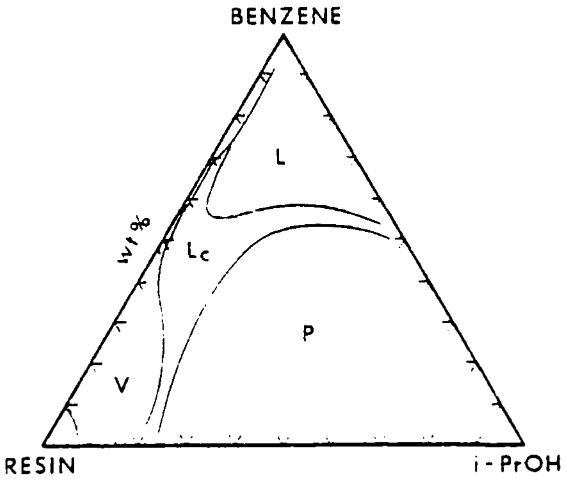


Figure 1. Characteristics of the "123" resin in binary benzene-i-propanol mixtures. (see text for legends)

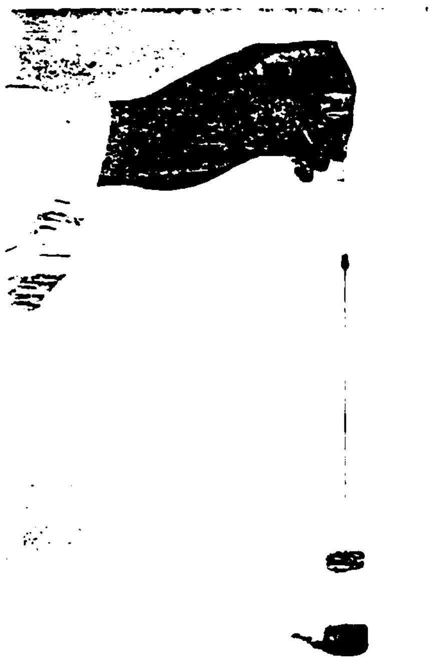


Figure 2. Preceramic fibers drawn from viscous solutions.

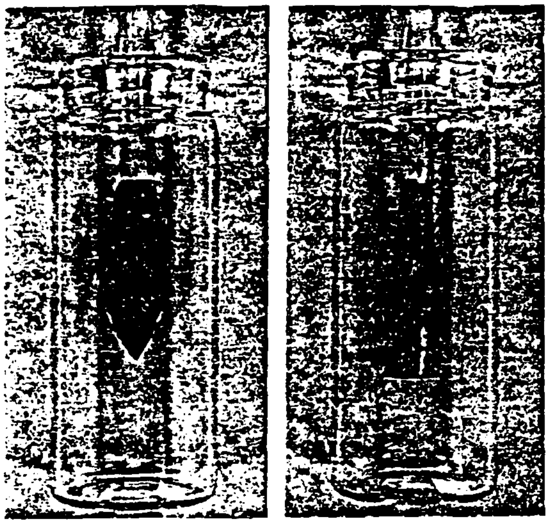


Figure 3. Cohesive property of resin in benzene enables it to be molded into different shapes.

The phase purity of the fibers was examined by X-ray and DTA. The X-ray indicates only single phase $YBa_2Cu_3O_{7-x}$ in the fiber. By using DTA, no low-melting impurities at 950°C were observed in the fibers [Figure 4(a)]. In order to obtain a controlled amount of fine Y_2BaCuO_5 phase in the fibers for possible flux pinning centers, the stoichiometry of the solutions was slightly adjusted so that the final compositions of the fibers were in the tie line between $YBa_2Cu_3O_{7-x}$ ("123") + y Y_2BaCuO_5 ("211"). Figures 4(b) and (c) show X-ray and DTA curves with y values equal to 0.02 and 0.05. The ease of tailoring the phase in the fibers by the metallo-organic process is clearly demonstrated.

The dc magnetic susceptibility of the fiber indicated the T_c onset is 87K. The electrical resistivity measurement shows the fibers have T_c (R = 0) at 81K (Figure 5).

Prevention of stable barium carbonate formation was achieved by partial substitution of copper ethylhexanoate with copper trifluoroacetate. During heat treatment, barium fluoride formed in the fibers instead of usual barium carbonate (Figure 6). The fibers containing barium fluoride were converted to "123" phase by calcining them at 850°C for 18 hr in flowing oxygen saturated with water vapor and then switching to dry oxygen at 900°C for 10 to 24 hr.

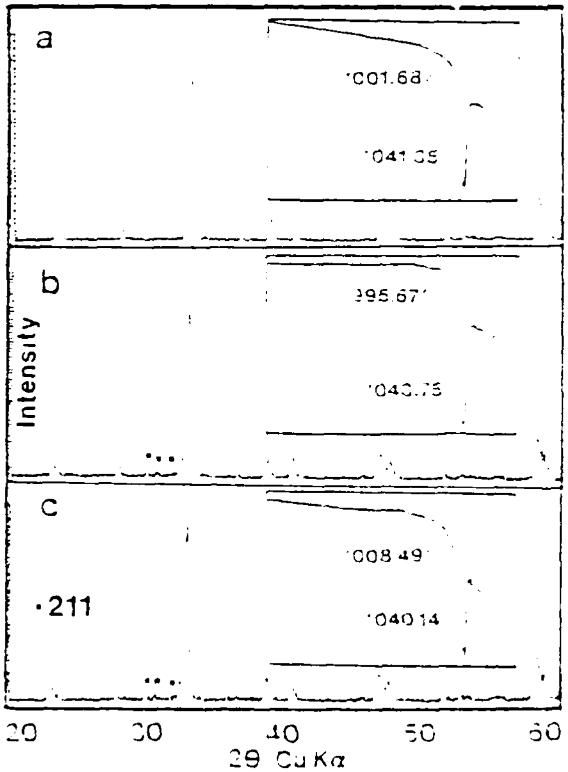


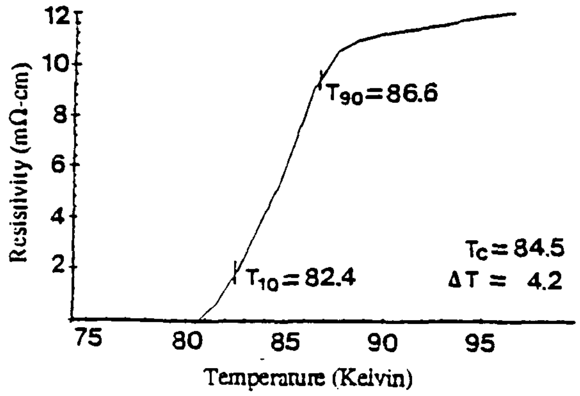
Figure 4. X-ray and DTA of fiber compositions (a) "123"; (b) "123" + 0.02 "211"; (c) "123" + 0.05 "211" (900°C, 8 hr).

CONCLUSIONS

Superconducting fibers were prepared from a soluble resin derived from metallo-organic precursors. The resin becomes either viscous, fluid, or precipitate in different benzene-isopropanol mixtures and is cohesive in benzene. Single-phase $YBa_2Cu_3O_{7-x}$ fibers with T_c (R = 0) = 81K were obtained. Substitutions of copper ethylhexanoate with copper trifluoroacetate prevents barium carbonate formation during calcination of the fibers.

ACKNOWLEDGEMENTS

This research was supported by DARPA/ONR under Contract N00014-88-C-0714.



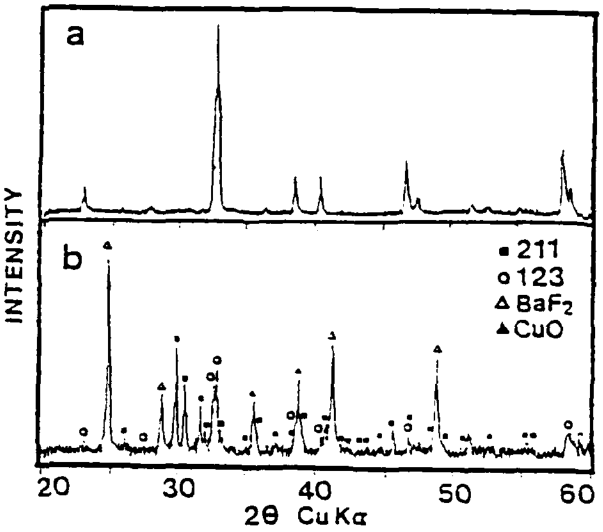


Figure 5. Electrical resistivity of the fibers calcined at 900°C for 12 hr and annealed at 450°C for 24 hr.

Figure 6. No $BaCO_3$ formation during the pyrolysis of trifluoroacetate containing preceramic fibers.

REFERENCES

1. T.H. Tiefel, et al., J. Appl. Phys. 64, 5896 (1988).
2. R. Goto and M. Kada, J. Mater. Res. 3, 1292 (1988).
3. R. Enomote, et al., Japan. J. Appl. Phys. 28, L1207 (1989).
4. T. Umeda, H. Kozuka, and S. Sakka, Advanced Ceramic Materials 3, 520 (1988).
5. J.C.W. Chien and M.M. Gong, Phys. Rev. B. 38, 11.853 (1988).
6. H. Konishi, T. Takamura, H. Kaga, and K. Katsuse, Japan. J. Appl. Phys. 28, L241 (1989).
7. R. M. Laine, et al., in Ceramic Superconductors II edited by M.F. Yan (Amer. Ceram. Soc., Westerville, Ohio, 1988) pp. 450-463.
8. H. Zheng, et al., in High Temperature Superconductor II edited by D.W. Capone II, W. H. Butler, B. Barlogg, and C.W. Chu (Material Res. Soc. 1988) Extended Abstract 93 (1988).
9. K.S. Mazdiyasni and L.M. Brown, Inorg. Chem. 9, 2783 (1970).