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INTERIM PROGRESS REPORT

FOR THE PERIOD

16 AUGUST 1987 THROUGH 15 OCTOBER 1987

FOR THE PROJECT

"COMPOSITE CERAMIC SUPERCONDUCTING  
FILAMENTS FOR SUPERCONDUCTING CABLE"

CONTRACTOR

CERAMICS PROCESS SYSTEMS CORPORATION  
840 MEMORIAL DRIVE  
CAMBRIDGE, MASSACHUSETTS 02139

13 NOVEMBER 1987

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## ABSTRACT

→ This is the first progress report of a five month program to demonstrate the feasibility of manufacturing superconducting wires from  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , consisting of a small ceramic core with a copper cladding. The critical current will be enhanced by creating a  $\langle 010 \rangle$  fiber texture in the ceramic, using a combination of green particle orientation and controlled recrystallization. The ceramic core will be manufactured by solution dry-spinning of a mixture of the superconducting ceramic powder with appropriately chosen polymers, solvents, and additives. The dry-spun fibers will be sintered and then clad with copper or other metals by electroplating, or mechanical cladding.

The objectives of the program are to demonstrate the dry spinning process, the sintering, and the cladding process, and to determine the effect of the microstructural texturing on the critical current. The electrical and physical properties of the filaments are to be characterized.

The process for synthesizing  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  from copper oxide, yttrium oxide, and barium carbonate has been scaled up and improved. Problems involving retention of the barium carbonate have been overcome, and a sinterable powder is prepared after a single calcination reaction at  $800^\circ\text{C}$ . The powder readily sinters to around 94% of theoretical density. A study is underway to optimize the processing and microstructure. ←

The dry spinning "dope" has been improved by increasing the molecular weight of the acrylic polymer binder and by using sorbitan trioleate as a dispersant. Efforts continue to improve the spinnability of the dope, and the physical properties of the fiber. A laboratory scale continuous dry spinning apparatus has been built, and is being modified.

Indium has been selected to "pre-metallize" the ceramic fibers prior to cladding by electroplating. An alternative cladding process has been identified, in which the superconducting ceramic fiber is mechanically clad with indium coated foils.

COMPOSITE CERAMIC SUPERCONDUCTING  
FILAMENTS FOR SUPERCONDUCTING CABLE

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## INTERIM PROGRESS REPORT

COMPOSITE CERAMIC SUPERCONDUCTING FILAMENTS FOR SUPERCONDUCTING CABLE

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CERAMICS PROCESS SYSTEMS CORPORATION, CAMBRIDGE, MASSACHUSETTS

## 1 INTRODUCTION

This is the first Interim Progress Report on a program at the Ceramics Process Systems Corporation to develop practical manufacturing methods for composite superconducting wires using the ceramic superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . This research is supported with a five month contract from the Office of Naval Research (Contract Number N00014-87-C-0789) starting 16 August 1987 and expiring 15 January 1988.

## 1.1 PROGRAM OBJECTIVES

This development program is aimed at the fabrication of composite superconducting filaments consisting of a core of high  $J_c$  ceramic superconductor, and a cladding of strong, high conductivity copper metal. The approach is to fabricate  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ceramic in the form of a monofilamentary fiber by dry spinning, sinter the fiber to an optimum microstructure for superconducting properties, adjust the oxygen content, and subsequently clad the fiber with copper or other metals with an ambient temperature process.

Specifically, the objectives of this program are to:

1. Define and demonstrate fiber drawing and sintering processes with potential for continuous fiber manufacture,
2. Demonstrate the production of a textured microstructure
3. Correlate microstructure with critical current measurements, and
4. Demonstrate proof-of-principle for copper cladding.

The strategy of making a wire from a ceramic fiber exploits a rather conventional means of rendering an oxide in a continuous length. It provides an opportunity to optimize ceramic microstructure and properties in isolation, without the complicating factor of a metallic phase. The bare ceramic wire can be annealed to create a highly oxidized state in the ceramic before compositing it with a reduced metallic phase.

This Interim Progress Report covers the period 16 August through 15 October 1987. Research effort in the first quarter was principally focussed on producing consistent  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder and determining its sintering behavior, developing dry spinning dope formulations, and building equipment for producing green fiber. Activities in the other key areas of

the program aimed at preparing the groundwork for laboratory activities in the following quarter. The principal research team for this report period included L. J. Klemptner, R. J. Picerno, K. Venkataswamy, and J. Halloran.

## 2 YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> POWDER PROCESSING

We have considerably improved our process for producing YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> powder by the mixed oxide method. We now are able to produce a consistent phase pure sinterable powder, in 0.5 kg lots, with a single calcination reaction at 900°C.

### 2.1 SCALE-UP OF CALCINATION

Our first effort was to scale-up from our previous practice of making 50-gram batches in a controlled atmosphere tube furnace. The tube furnace lacked capacity, and considerable time was spent on replacing it by adapting existing box furnaces for controlled atmosphere operation, and in acquiring new controlled atmosphere furnaces. At present our capacity is adequate.

The first problem encountered during scale-up was the persistence of barium carbonate in the larger batches. Some effort was diverted to explore the use of barium hydroxide as a raw material. Initial results were very encouraging, as we found small batches of the hydroxide-derived powder to give a nearly phase pure YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> with a desirable platy morphology. Unfortunately, upon scaling up to larger batches, we found that the barium hydroxide was partially converted to the carbonate by heating in air, so the calcined product was invariably contaminated with carbonate and carbonate-hydroxide phases. Emphasis returned to the simple barium carbonate process.

Early work on the carbonate process used very shallow beds during calcination to achieve complete conversion to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>. This was intolerable upon modest scale-up. Going to deep beds in crucibles required repeated calcination reactions to effect complete reaction of the barium carbonate. While the first few millimeters of the material was uniformly black phase-pure YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, the interior of the crucible had incompletely reacted grey-green material. Moreover, the material in the center of the crucible was often worse after re-calcination than it was before. Apparently the high partial pressure of carbon dioxide inside the crucible could decompose the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> by recarbonation of the barium.

The solution was to improve mass transfer to remove the carbon dioxide. We chose to do this by granulating the raw batch to improve permeability and by introducing a modest flow of oxygen or air from the crucible bottom through a lance. By constantly flowing fresh gas through the permeable bed we assure that the carbon dioxide reaction product is swept away and the entire crucible load experiences a uniform environment. This seems to work very well. A single calcination reaction (currently 900°C for 15 hours) produces phase-pure YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> which is uniform throughout the crucible. We were able to more than double crucible volume, and simultaneously react four crucibles, without any change in the process.

## 2.2 PREPARATION OF RAW MATERIALS

To improve the control of the solid-state calcination reaction we have spent considerable time developing convenient techniques to mill the raw materials to consistent particle size and achieve better homogeneity during mixing. Several attempts were necessary to develop a satisfactory process.

Our initial plan was to mill the cupric oxide, barium carbonate, and yttria separately to a controlled particle size and surface area, mix homogeneously, and granulate the mixed batch. Initially we tried aqueous wet milling with an ammoniated polyelectrolyte dispersant<sup>1</sup>. This presented several problems. The dispersant reacted with the copper oxide, creating the deep blue tetra-amine-Cu<sup>+2</sup> soluble complex. At that time the milled slurry was de-watered by filtration, and the soluble copper complex was lost to the filtrate. Mixed slurries tended to segregate upon filtration and drying. Wet milling was temporarily abandoned while dry vibromilling was explored. Dry milling was successful for cupric oxide and yttria, using sorbitan trioleate<sup>2</sup> as an anti-caking agent. Barium carbonate could not be consistently dry milled, so was wet milled and dried. The milled raw materials were then batched and mixed by dry ball milling. This mixed batch was laboriously granulated by forming a paste with toluene and an acrylic binder, crushed, and sieved to collect -14/+35 mesh granules. These granules were satisfactory for calcination. However, the calcined granules were hard and, at 14 mesh, too large to be directly charged into the vibromill, so they had to be ground to -70 mesh by hand with a mortar and pestle before vibromilling. The powder so-produced was phase-pure and sinterable, but the process was inconvenient.

To overcome these difficulties, we now directly granulate a wet vibromilled mixture by spraying the slip in a refrigerant bath (currently liquid nitrogen, for convenience), and drying the frozen droplets by freeze drying. By freeze drying, any solubilized copper complexes are recaptured, instead of being lost to the filtrate, preserving the composition of the batch. The uniform mixing of the wet milled slip is preserved during freezing by pumping the slip directly from a vigorously stirred vessel. The spray freezing method eliminates several handling steps. More importantly, the freeze-dried granulated raw powder has a very low bulk density (12%), which is favorable for mass transport during calcination. The black calcined granules are quite friable, and can be easily crushed during dry pressing, or directly charged into the dry vibromill. Our present freeze drying capacity is adequate for preparing about two kilograms of raw powder per week. This process is readily scaled-up, using either the present freeze-spray/ freeze dry approach, or a direct spray drying process.

---

1) Narlex LD-45, from National Starch and Chemical Company, Bridgewater, N.J.

2) SPAN-85, ICI Americas, Inc., Wilmington, DE.

Figure 1A shows an X-ray diffraction pattern after a standard calcination reaction for 16.5 hours at 900°C, followed by a two hour anneal at 500°C, in this case in air. Barium carbonate is absent, and all peaks can be indexed as orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . In the calcined powder the peaks are too broad to clearly resolve (013) from the (103)/(110). After pressing the as-calcined powder into a pellet and sintering 15 hour at 960°C, followed by a slow cool in oxygen, the x-ray diffraction peaks are sharper and more clearly resolved, as shown in Figure 1B.

Some characteristics of the powders are presented in Table I, which gives the surface area of the original raw materials, the wet milled raw batch, and the calcined product. Figure 2 is an SEM micrograph showing the freeze dried granule before calcination. The calcined  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  is shown in Figure 3. Notice the open structure of the friable calcined granules, and the rather fine primary particles produced by the 900°C calcination. The particle size and shape seems to be easily variable by changing the calcination conditions, and we are currently investigating the effect of these conditions on the calcined product. The powder is readily milled to submicron particle size by either dry vibromilling or wet milling in cyclohexane. We are presently investigating the particle size distributions required for fiber spinning, sintering, and superconducting properties.

### 2.3 POWDER CHARACTERISTICS AND SINTERING BEHAVIOR

We are currently engaged in a study of sintering and microstructure development in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powders. When dry vibromilled to a median particle size (stokes diameter) near 0.8 micron, the powder can be sintered to 95% density in one hour at 910°C in oxygen. Figure 4 shows the as-fired surface of a 150 micron diameter  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fiber sintered one hour at 910°C in oxygen. The density has not been directly measured for this fine fiber, but appears to be at least 95%. The typical grain size is 1-2 microns in the short direction. Presently we are determining the relation between powder characteristics, sintering conditions, and microstructure. By using both milled and as-calcined powders we can produce a range of porosity/grain size combinations. This study is still underway, but for illustration, Figure 5 compares the microstructures of two pellets sintered to 94% density. Figure 5A shows that dry vibromilled powder, sintered at 925°C for 15 hours in oxygen, has grains 1-2 microns in short dimension at this density. The as-calcined powder reached this density at 960°C in 15 hours in oxygen, but has very large tabular grains up to 30 microns in short dimension. Figure 6 compares these two powders sintered to only 63% density. The dry milled powder was barely bisqued at 800°C, and retained the submicron grains of the similar to the original powder. The as-calcined powder required sintering at 925°C for 15 hours to achieve 63% density, at which point the grain size was 2-5 microns.

A detailed study is underway to determine the density and microstructure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x} + 5 \text{ wt}\% \text{ CuO}$  materials, as a function of sintering temperature, time, and atmosphere, for powders either unmilled or milled to various particle sizes, and surface areas. These results will be presented in the next report.

Sample Name : 24729

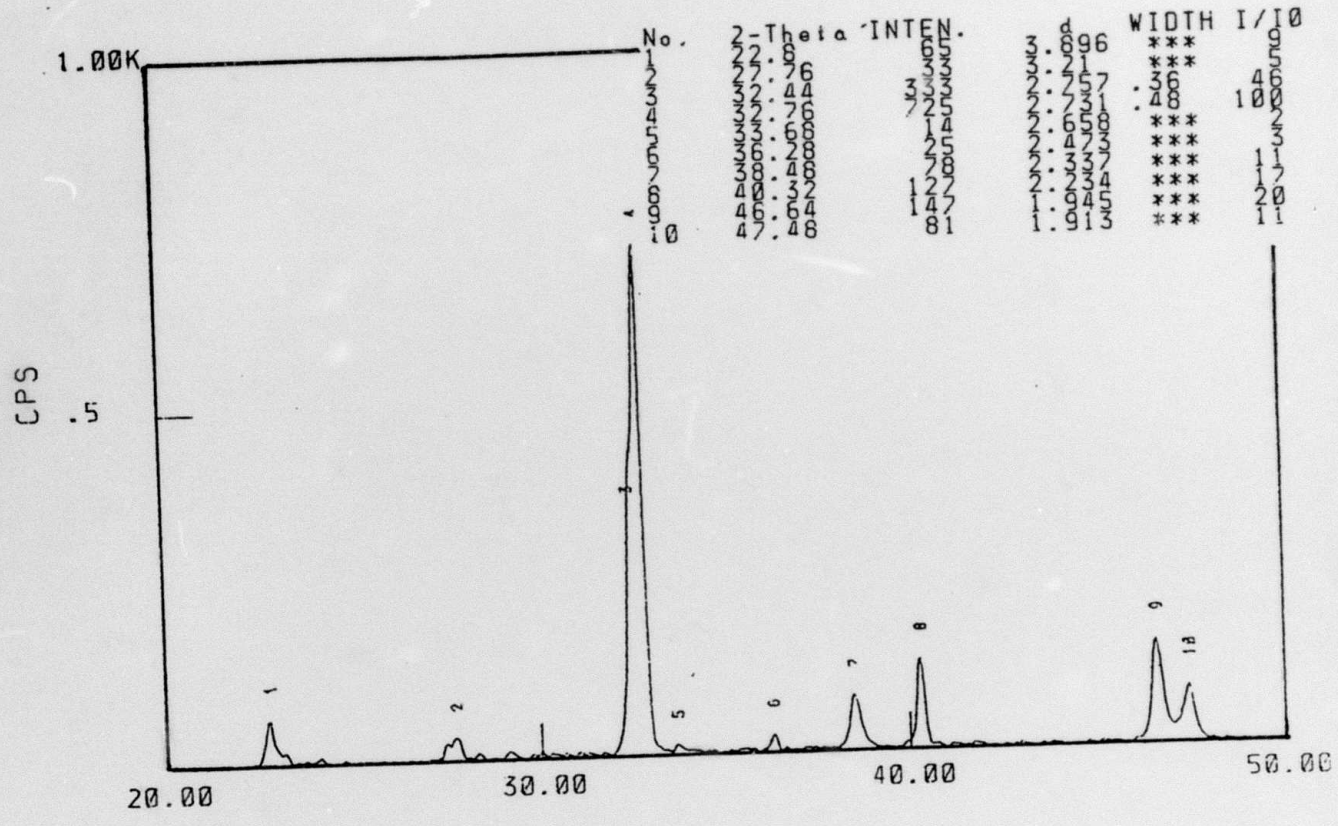


Figure 1A X-ray diffraction pattern of powder calcined 16.5 hours at 900°C in air

Sample Name : 24729

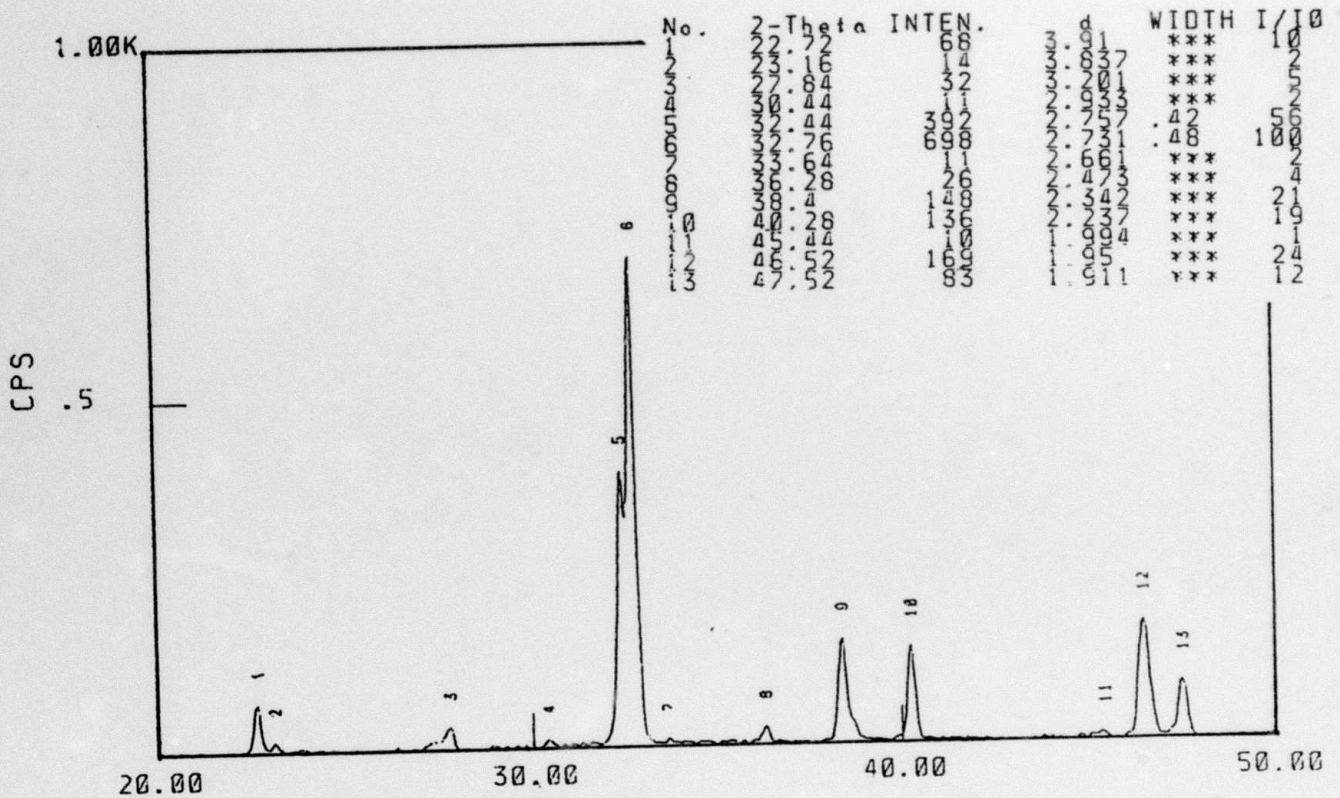


Figure 1B X-ray diffraction pattern of a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  pellet sintered 15 hours at  $960^\circ\text{C}$  and cooled slowly in oxygen

TABLE I  
CHARACTERISTICS OF POWDERS

POWDER	SPECIFIC SURFACE AREA $\text{m}^2/\text{g}$	COMMENTS
-----		
Raw Materials		
Cupric Oxide Baker Lot 302343	0.38	5-15 micron hard agglomerates of 1-3 micron primaries
Yttrium Oxide Research Chemicals Lot YO-3-245	8.3	10-25 micron friable agglomerates of 0.5 micron primaries
Barium Carbonate	1.46	agglomerates of 1 micron blocky particles, with some 10 micron particles
Raw Batch before milling 15.09 wt% $\text{Y}_2\text{O}_3$ 32.10 wt% $\text{CuO}$ 52.81 wt% $\text{BaCO}_3$	2.1	--
Raw Batch Wet Vibromilled 22 hours Freeze dried	5.6	very soft 1 mm granules
Calcined Granules 900°C 15 hours	0.7	friable granules of 0.5-5 micron particles
Dry Vibromilled Powder 22 hours	12.5	wide size range 0.1 - 5 microns

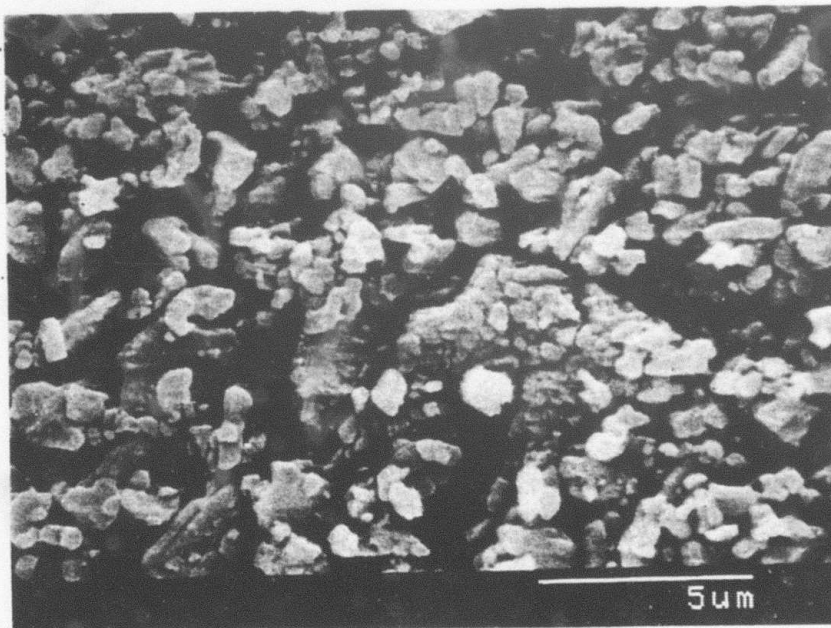
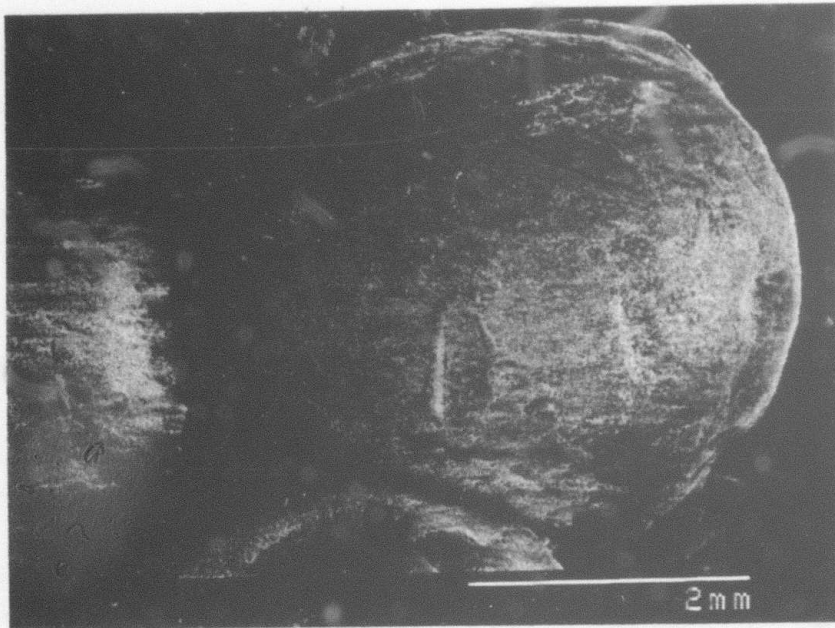


Figure 2 Freeze dried granule before calcination  
Top: 20X Bottom: 6000X



Figure 3 Primary  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  particles in granule  
after calcination at  $900^\circ\text{C}$  5000 X

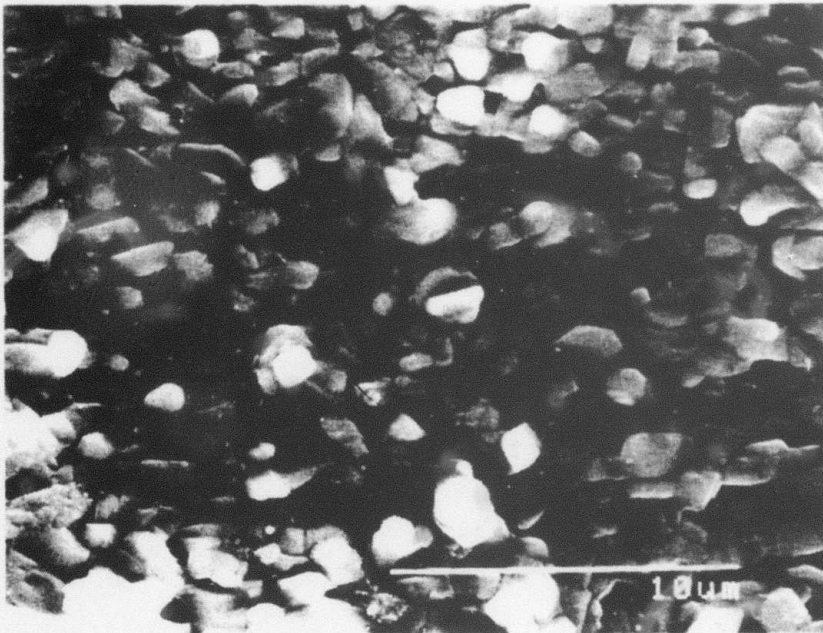


Figure 4 As-fired surface of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fiber  
sintered one hour at  $910^\circ\text{C}$  in  
oxygen 5000X

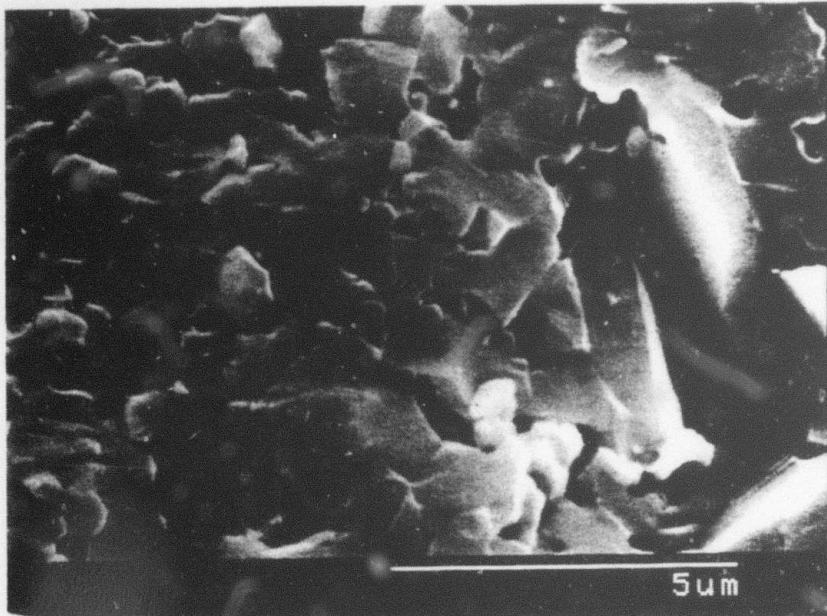


Figure 5A Fracture surface of 94% dense  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  from powder dry vibromilled 22 hours, sintered  $925^\circ\text{C}$  15 hours in oxygen  
10,000 X

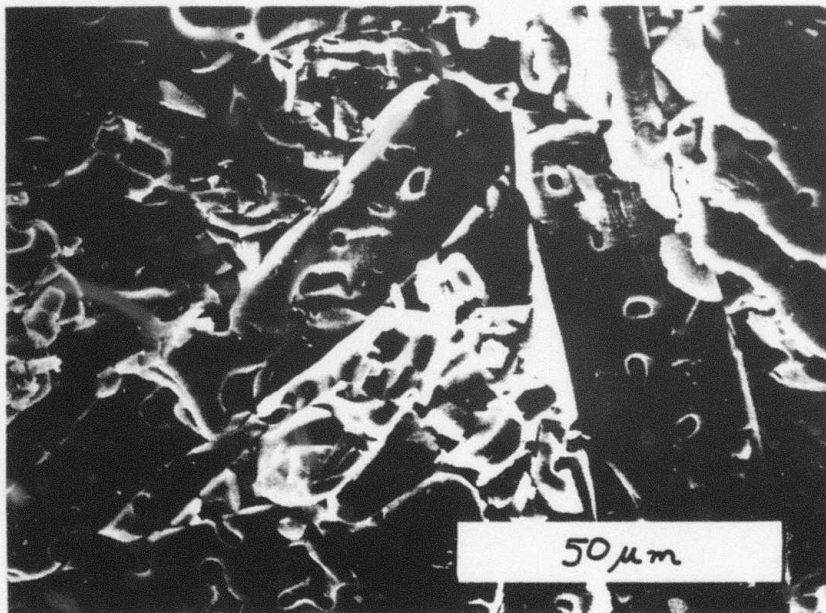


Figure 5B Fracture surface of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  pellet from as-calcined powder sintered 15 hours at  $960^\circ\text{C}$ . 94% dense 1000X

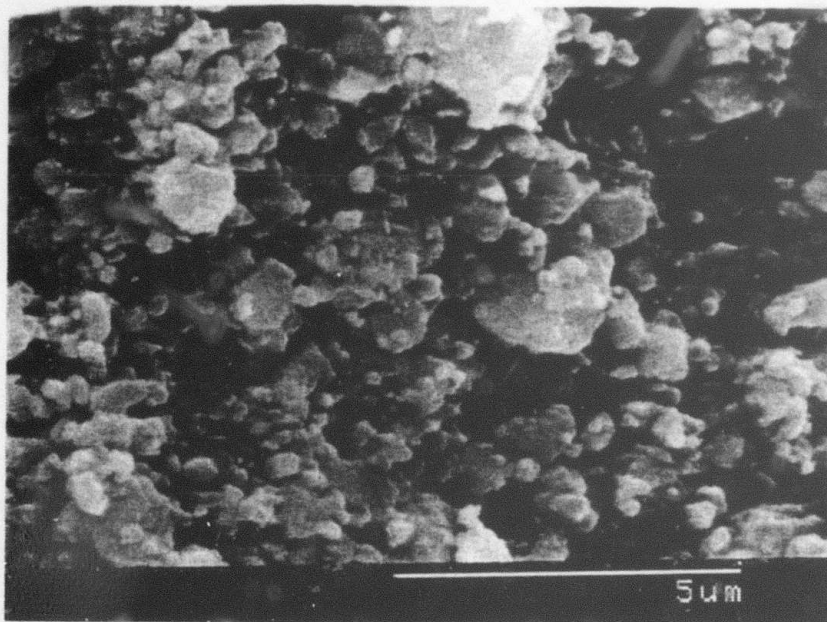


Figure 6A Fracture surface of 63% dense YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> pellet from dry vibromilled powder sintered 800°C for one hour 10,000 X

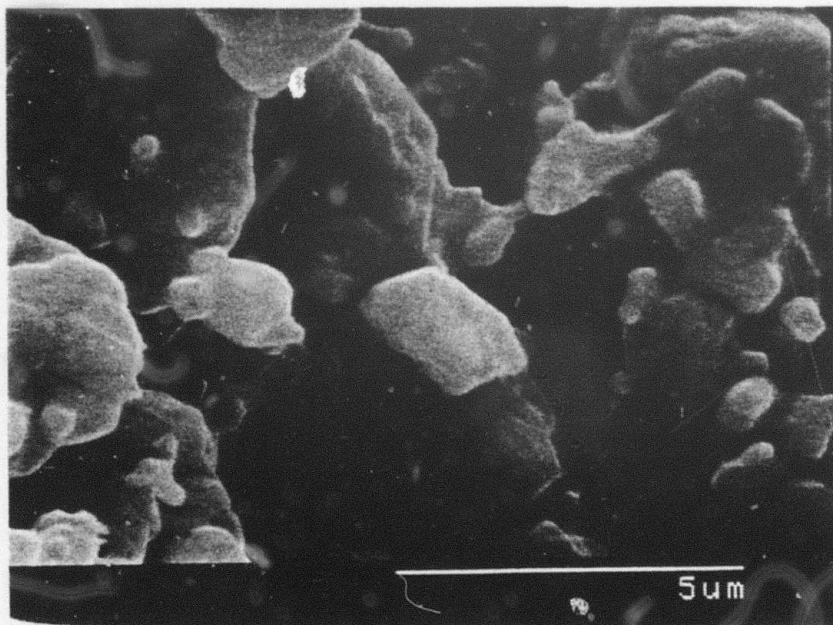


Figure 6B Fracture surface of 63% dense YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> pellet from as-calcined powder sintered 15 hours at 925°C 10,000X

### 3 TEXTURE

A major objective of this research program is to demonstrate the production of high transport critical currents in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fibers with strong  $\langle 010 \rangle$  fiber texture. Two independent methods will be explored to create such a texture. Preferred particle orientation will be created in the green fiber by the shear conditions of dry spinning. The wet fiber diameter is attenuated by about a factor of ten during the spinning process, and this elongational flow can orient nonequiaxed particles. This green texture is to be amplified during sintering by promoting directional recrystallization to align the  $\langle 010 \rangle$  fast growth directions along the fiber axis. Grain texture will be characterized by microscopy and x-ray diffraction.

We have no results to report in this area for this quarter. Efforts in both fiber spinning and sintering have been addressed as more basic issues up to this time. However, we now have in hand the capability to spin  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fibers on a nearly routine basis, and anticipate beginning concerted efforts on enhancing green texture as soon as possible. Also, now that  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fibers are becoming available, we will be able to begin experiments to define the directional recrystallization process. These results will be reported in the next quarterly report.

### 4 ELECTRICAL MEASUREMENTS

We have deliberately neglected this area during the First Quarter to allow more concentrated efforts in powder and fiber processing. Consequently we have no data to report. Underway at present are efforts to measure resistance vs. temperature in a simple apparatus cooled by liquid nitrogen. Methods are also being developed to devise fixtures to measure critical currents in bulk samples and fibers at liquid nitrogen temperatures. Data is too preliminary to report at this time.

We anticipate collecting electrical data during the second quarter to permit us to determine preferred microstructural features for superconductivity. Our very preliminary indications suggest that fine grained materials have inferior properties, so we are very eager to compare their transport currents.

For more detailed electrical measurements at controlled temperature, we are acquiring a cryostat<sup>3</sup>, in which we can do measurements either immersed in liquid nitrogen, or in nitrogen vapor at controlled temperatures between 80 and 300°K. The cryostat is designed to accept bulky specimens or fiber coils up to 1.75 inches in diameter. Delivery is expected in December.

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<sup>3</sup>) Janis Research Company, Wilmington, MA, Model 8CND-NVT

## 5 FIBER PRODUCTION

Efforts in production of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fibers during the first quarter focussed primarily on the dry spinning dope development, and the construction of the laboratory-scale continuous fiber spinning apparatus. To permit the dope formulation to progress while the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder processing was being developed, barium titanate was adopted as a "surrogate powder" for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , so the green fiber research could continue unimpeded by the limited supply of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder. The dry spinning dope has undergone several modifications, most importantly by using higher molecular weight polymers and a better dispersant. Formulations developed with barium titanate have much improved spinnability, stability, and strength in the green state. The same formulations appear to be satisfactory for use with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Green fibers of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and barium titanate appear to present no problems during binder removal and sintering.

Dopes are currently evaluated on a lab bench by extrusion from a syringe. This method is only satisfactory for short lengths. The continuous dry spinning apparatus is being used, and is in a state of constant improvement. Two problems have caused some delay. The apparatus suffered considerable downtime for installation of more adequate ventilation, and the acquisition of the take-up spooler was delayed. Our original vendor<sup>4</sup> suffered a serious fire, so was unable to build our spooling equipment. A spooler built by a second vendor<sup>5</sup> did not arrive in time to impact the progress during this quarter. Nevertheless, we have been able to run a number of experiments in the continuous dry spinning apparatus. These pointed out the need for a better dope delivery system, which was installed, and design changes in the drying column, which are ongoing.

### 5.1 DRY SPINNING DOPE DEVELOPMENT

Ceramic fiber dope development focused on achieving the proper polymer binder burn-out behavior and the improved polymer properties for continuous fiber formation.

Dispersion studies were carried out for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder in methylethylketone (MEK) and toluene solvents to identify improved dispersing agents. Table II lists the candidate dispersants and their performance based upon minimum sedimentation volume. The best surface active agents for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in MEK-toluene solvents, in their order of effectiveness, were SPAN-85, GAFAC RE-610, EMCOL CC55, and menhaden fish oil. The SPAN-85 (sorbitan trioleate) was chosen for its superior dispersing power and non-ionic nature. The GAFAC RE-610 was effective, but is a phosphate ester so has the undesirable side effect of potential

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4) EJR Engineering, Lowell, MA

5) Chase Machinery Company, West Warwick, RI

TABLE II  
 SURFACE ACTIVE AGENTS USED IN DISPERSION STUDIES ON  
 $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  POWDER

NAME	CLASS	DISPERSING ABILITY		
		POOR	GOOD	EXCELLENT
1. Stearic Acid	weak acid	X		
2. Triethanolamine	amine-alcohol	X*		
3. p-Hydroxybenzoic acid	weak acid	X*		
4. Fish oil	oxidized triglycerides			X
5. SPAN 20	sorbitan monolaurate	X		
6. SPAN 85	sorbitan trioleate			X
7. Triton X-100	alkylpolyethoxy alcohol	X		
8. Igepal DM-430	dialkylpoly- ethoxy alcohol		X	
9. Clindrol 100-0	diethanolamine	X*		
10. OLOA 1200	sterically hindered amine	X		
11. 4-nitrophenylacetic acid	weak acid	X*		
12. EMCOL CC55	quaternary amine, cationic			X
13. Dow Z6030	methyl silane ester	X		
14. Dow Z6020	amino silane ester	X <sup>^</sup>		
15. GAFAC RE610	phosphate ester			X
16. KA 301	aluminate	X		
17. KR TTS	titanate	X		
18. LICA 01	titanate	X		

\* NOTE: Reacted with copper in powder to yield blue solutions.

<sup>^</sup> NOTE: Reacted with powder to form white layer on top of sedimented volume. Suspect reaction with barium or yttrium.

phosphorous contamination of the material. The EMCOL CC55 showed no evidence of reaction with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , but has the potential to attack the copper to form amine complexes. SPAN-85 showed good dispersion stability in these solvents and did not degrade the superconducting powder. This dispersant also works well for  $\text{BaTiO}_3$ .

A screening test was undertaken to assure that the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder would not be adversely affected by reaction with the binder or intermediate products generated during binder burnout. The acrylic binders included QR1074 and AT63 from Rohm and Haas, and DuPont's Elvacite 2046, in either MEK-toluene or n-butanol. The interaction of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with the binders and the solvent was studied with thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and powder x-ray diffraction (XRD) to search for phase changes in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder.

First derivative plots of the DTA data in air for samples with MEK-toluene solvent systems showed localized superheating effects in the 300-375°C temperature range. This superheating effect is believed to be due to the interaction of powder with the binder system, creating a rapid exothermic event. The superheating effect was suppressed by slower heating rates, and eliminated by heating in nitrogen. Apparently, the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder catalyzes the binder oxidation reaction in air. This is a very unusual behavior for ceramic powders during binder burnout, and perhaps reflects that the orthorhombic powder, which contains trivalent copper, is a strong oxidizing agent.

This corroborates other scattered observations in which compacts of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder containing stearate or oleates as binders often ignited upon heating in air above about 250°C. The vigorous combustion disrupts the compact, but does not cause changes in the powder detectable by XRD. This problem can be avoided by conducting the initial heating in nitrogen, to remove the binders by pyrolysis rather than oxidative processes. This does not seem to damage the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder.

The sample with an alcohol solvent system did not show a superheating effect at comparable heating rates. It was noted that under prolonged contact the alcohol dissolved the powder particles.

One sample containing QR1074 was crosslinked with Cymel 370<sup>6</sup>, to increase the integrity of the binder residue during burnout. The crosslinked sample required more energy to burn-off the binder than non-crosslinked samples. This data is summarized in Table III.

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<sup>6</sup>) Cymel 370, a methylated melamine formaldehyde resin, American Cyanamid, Wayne, NJ

TABLE III

## THERMAL ANALYSIS OF POLYMER POWDER MIXTURES

<u>SAMPLE</u>	<u>SOLVENT</u>	<u>POLYMER</u>	<u>CROSSLINKED</u>	<u>AREA OF DTA CURVE</u>
22126	MEK/TOL	QR1074/2046	NO	2.566 °C/mg*min
22127	n-Butanol	QR1074/2046	NO	2.972 °C/mg*min
22128	MEK/TOL	AT63/2046	NO	2.561 °C/mg*min
22129	MEK/TOL	QR1074	YES	4.616 °C/mg*min

The TGA results in air showed initial weight loss of approximately 18 wt% up to 400°C, followed by a weight gain in the temperature range 400-750°C and then a weight loss after 750°C. Correlation of the TGA and DTA data indicate that binder burnout is complete by 400°C. The weight gain of approx. 3 wt % in the 400-750°C range is believed to be due to the reoxidation of copper ions in the sample.

The XRD study comparing the original powder to the powder after binder burnout showed no important changes in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  phase. This indicates that an acrylic binder will not destroy the 123 oxide powder upon binder burnout.

## 5.2 BARIUM TITANATE FIBER SPINNING

Ticon HPB barium titanate powder<sup>7</sup> was adopted as a surrogate powder for fiber processing development until consistent  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder becomes plentiful. Barium titanate was chosen because its highly basic barium-dominated surface chemistry was expected to mimic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , and because of its ready availability. Table IV compares the properties of both powders. It appears that this was a good choice, and dope formulations developed with barium titanate work well with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

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<sup>7</sup>) Ticon HPB, TAM Ceramics, Niagara Falls, NY

TABLE IV

COMPARISON OF BaTiO<sub>3</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> POWDERS

PROPERTY	BaTiO <sub>3</sub>	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7-x</sub>
Theoretical Density	6.06 g/ml	6.2 g/ml*
Surface Area of Bulk Powder	2.9 sq.m/g	0.7-13 sq.m/g
Average Particle Diameter	1.24 microns	0.8-1.5 microns
Particle Size Distribution	0.6-2.4 microns	0.5-3 microns***
Powder surface pH	basic	very basic
Reactivity with Solvents	can use H <sub>2</sub> O	Dec. in H <sub>2</sub> O and Alcohol
Production Method	chemical precipitation	solid state rxn
Supplier	TAM Ceramics	made at CPS

\* Density measured by Helium Picnometry = 5.947 grams/cc.

\*\*\* Based on SEM information

Initial dry spinning fiber formulations were based on binder systems commonly used in tape casting technology. These polymers typically have low molecular weight (less than 50,000), but can form fibers in dopes containing 40 volume percent powder solids. However, these fibers were not strong enough for convenient handling. We have evaluated several higher molecular weight polymers (approx. 500,000) to improve the fiber forming properties, fiber green strength, and allow an increase in the powder solids loading. Acryloid B-7MEK, from Rohm & Haas Co., is currently being used as the high molecular weight polymer for most of our studies. Fiber formulations having a mixture of high and low molecular weight polymers have produced the strongest fibers. Currently barium titanate fibers are made with up to 55 volume percent dry powder solids (upon solvent evaporation). These fibers were easy to handle.

Table V lists the polymers being used to make fibers from BaTiO<sub>3</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> powders. The current best dope formulation is presented in Table VI. The main polymer binder is a mixture of the high molecular weight B-7 with the low molecular weight AT-63. A mixture behaves much better than either end member. The AT-63 also has a hydroxyl functionality to react with the Cymel 370 to add a component of crosslinking. We presently believe that crosslinking can be beneficial to binder burnout and enhance green strength. Experiments are planned to

TABLE V

## POLYMERS USED IN FIBER PRODUCTION

<u>Rohm &amp; Haas Product</u>	<u>Molec. Wt. Range</u>	<u>Wt. % Solids</u>	<u>Functionality</u>	<u>Solvent</u>
QR-1074	15,000-20,000	75	Hydroxyl	n-butylacetate
AT-63	approx. 40,000	50	Hydroxyl	xylene
Acryloid B-7MEK	300,000 to 400,000	30	None	methylethylketone

test this supposition. A plasticizer is included in the current formulation to improve the flexibility of the binder system, although probably at the cost of some green strength. The actual role of the plasticizer is now being determined. The solvent system is designed to incorporate a fast evaporator (MEK) and a slow evaporator (toluene), as is conventional to promote stable drying behavior, although the fast evaporating xylene as the carrier solvent for the AT-63 affects the balance. In the future we will reexamine the solvent system design. At present our main thrust is evaluating higher molecular weight polymers for improved dope formulations.

A syringe extruder was used to form the fibers from the dry spinning dope. The fiber is slowly withdrawn and dried in air by natural convection. No attempt is made to wind the fiber in these bench top experiments. The component order of addition to the formulation is important to insure that the powder intimately mixed with the polymer resin. The high molecular weight polymer requires filtering before use, otherwise, flakes of undissolved polymer were found on the fiber surface.

Figure 7 shows a Scanning Electron Microscope (SEM) photo of a BaTiO<sub>3</sub> green fiber of the formulation shown in Table VI. Even with the simple syringe extrusion, a surface is smooth and the diameter is uniform at around 50 microns. The barium titanate powder is largely free of agglomerates and particles coarser than about three microns. This is very important for fiber spinning. When an early dry vibromilled YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> powder (lot 21496B) was substituted in this formulation to make fibers, the fiber diameter varied erratically. Agglomerates and a wide particle size distribution in the powder contributed to the formation of clumps on the fiber surface, as shown in Figure 8.

Further processing of the superconductor powder is being pursued to improve fiber characteristics. In particular, it seems essential to exclude all particles larger than 2 -3 microns to prevent surface instabilities during dry spinning. We intend to control particles both by milling and by stokesian separation of particles. Figure 9 illustrates a powder fraction collected from milled  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by stokesian separation, featuring a very uniform particle size at about 0.5 micron.

TABLE VI

$\text{BaTiO}_3$  GREEN FIBER FORMULATION 24424-#1

<u>COMPONENT</u>	<u>FUNCTION</u>	<u>WEIGHT %</u>	<u>VOLUME %</u>
BaTiO <sub>3</sub> Powder	Powder	74.63	31.07
Toluene	Slow drying solvent	2.60	7.57
Methylethylketone	Fast drying solvent	4.52	14.17
Xylene	AT-63 Solvent	6.42	18.65
SPAN 85	Dispersant	1.60	4.24
AT-63 Polymer	Low MWt. Polymer	6.41	15.09
B-7MEK Polymer	High MWt. Polymer	1.94	4.54
Paraplex G51	Plasticizer	0.94	2.49
Cymel 370	Crosslinking Agent	0.94	2.18

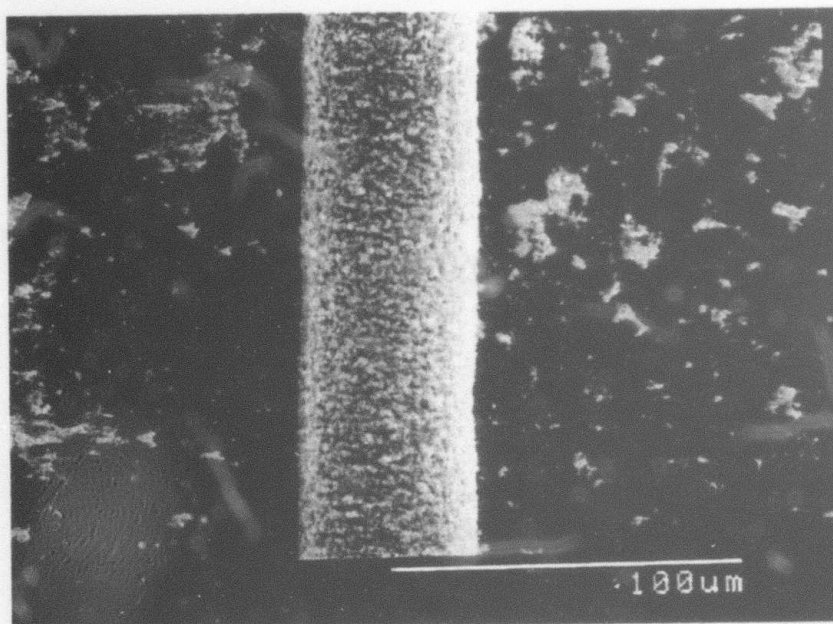


Figure 7 SEM of  $\text{BaTiO}_3$  Green Fiber 24424-#1

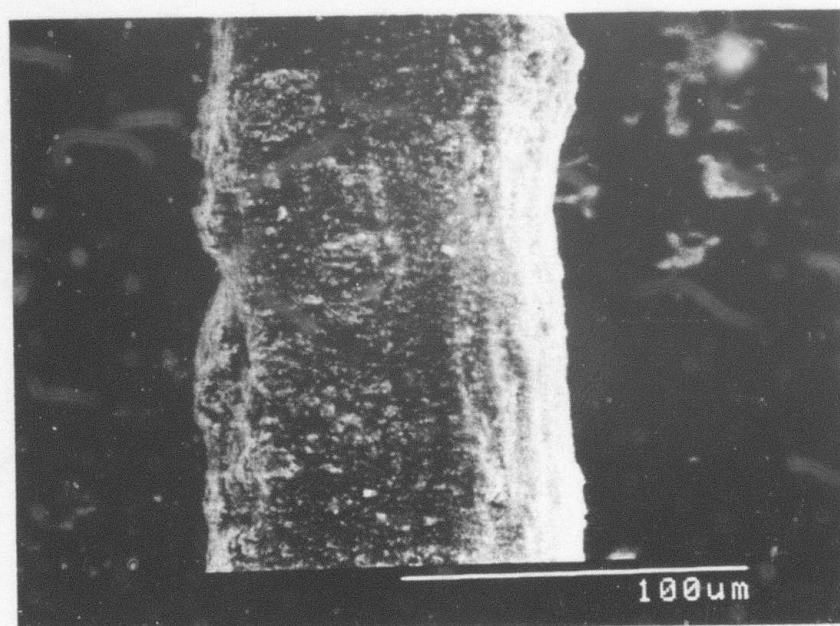


Figure 8 SEM of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  Green Fiber 24434

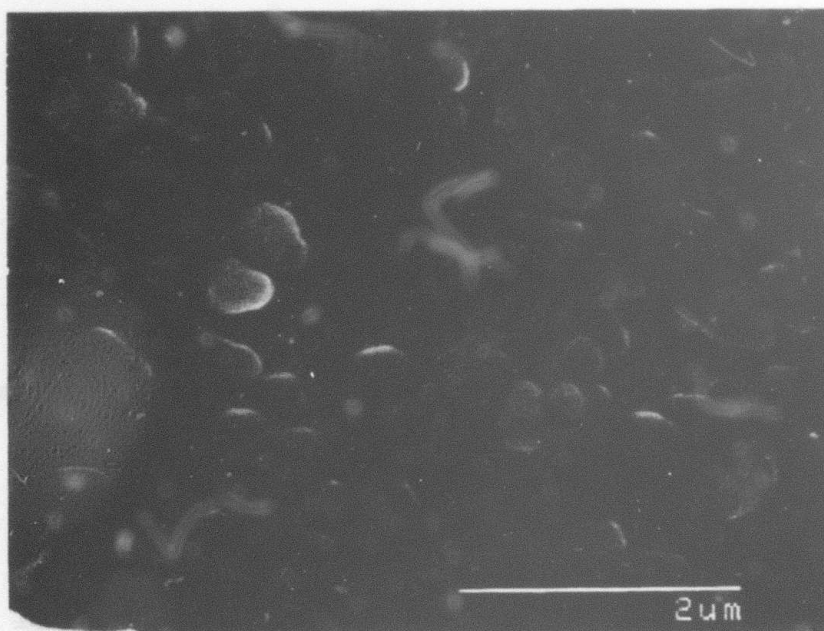


Figure 9  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  Powder Fraction from Stokesian  
Separation of Coarse Particles from Dry  
Vibromilled Powder

### 5.3 SPINNING PROCESS DEVELOPMENT

We have adopted the solution dry spinning process to prepare continuous green fiber from the superconducting material. During this quarter, we have built and are continuously up-grading a laboratory scale continuous dry spinning apparatus.

Solution dry spinning is the oldest manufacturing process for man-made fibers, and is still used in the manufacture of polymeric fibers which are not thermally stable but are readily dissolvable in highly volatile solvents. This procedure has been adopted to spin ceramic fibers<sup>8</sup>. The dope consists of finely dispersed ceramic powder in a polymeric solution. The function of the polymer is to impart "spinnability" and to be a binder for the ceramic particles. The solvent (or mixture of solvents) is very volatile (the formulation efforts of the spinning dope is discussed in the earlier sections). The dope is extruded through fine spinnerete holes and drawn into a fiber, which solidifies as the solvents are evaporated by suitable gas currents.

A spinning apparatus was designed and built in-house to demonstrate continuous filament winding of green fibers from the dope containing the superconducting material. The apparatus consists of three major components:

1. Dope delivery system
2. Drying chamber and
3. Filament take-up unit

The spinning apparatus is schematically shown in Figure 10. The dope delivery system consists of a polypropylene disposable barrel with 30 cc capacity. This barrel is used for storage and delivery of the spinning dope. The neoprene barrel piston pushes the spinning dope due to air pressure. This piston is air tight to prevent entrapment or dissolution of air in the spinning dope. The barrel is end capped and clamped to a pressure tube through an o-ring/clamp arrangement. The tube is connected to an air supply through a valve to regulate air pressure (max 30 psi). The air is passed through a trap to remove moisture. The end of the barrel has a luer lock to accept the spinnerete, which in this case is a smooth flow tapered polyethylene disposable tip (1.5" long and 22 gauge or 410 microns diameter), which snugly fits at the end of the barrel.<sup>9</sup> The dope passes through the

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<sup>8</sup>. "Production of Continuous Ceramic Fibers", P. Alan, and C. Hart, U. S. Patent 4,071,594, 1978.

<sup>9</sup>) Components for the dope delivery system were purchased from EFD, Inc., East Providence, RI

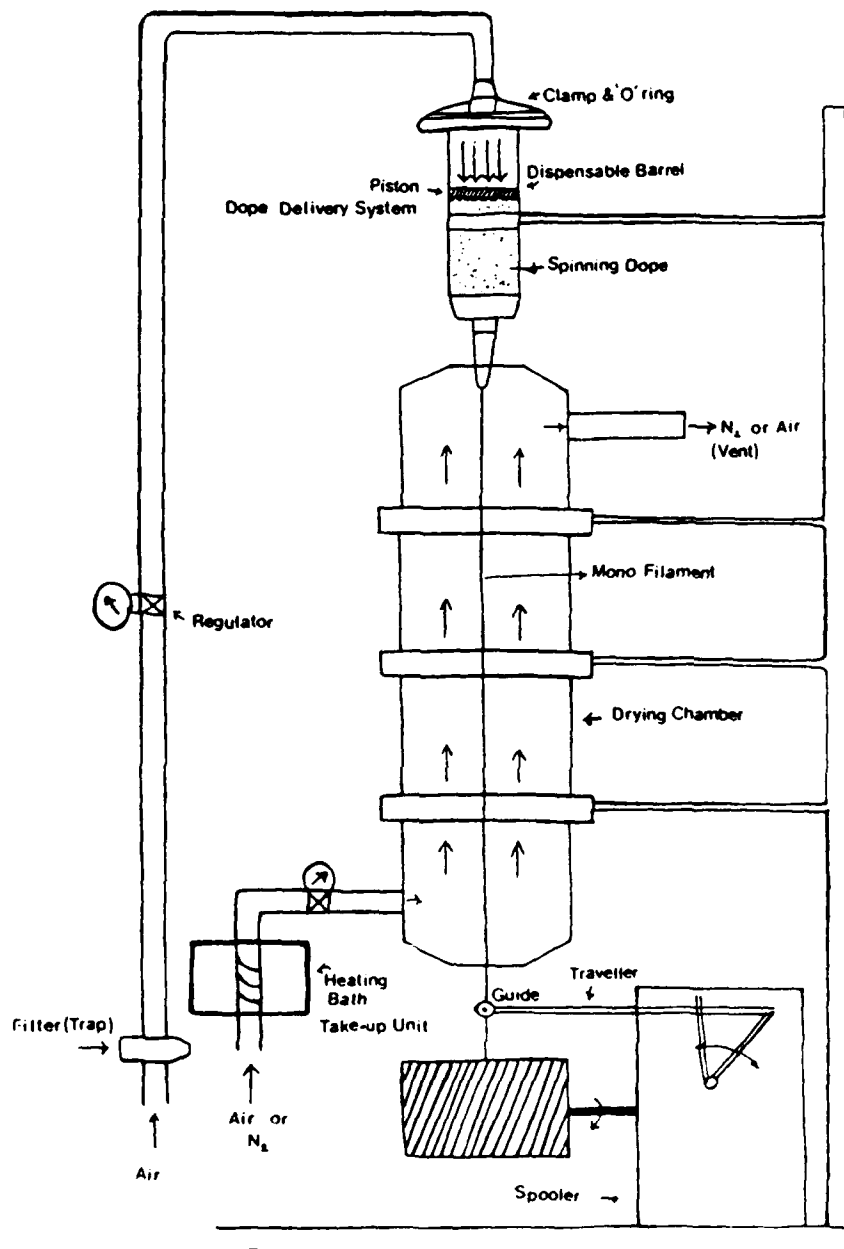


Figure 10 Schematic of the Laboratory Scale Dry Spinning Apparatus

spinnerete and extrudes into a monofilament stream, which is attenuated to a fine fiber with a diameter dependent upon the spinning conditions.

The drying chamber consists of several pyrex glass sleeves which are 12 inches long and 2 inches in diameter. The individual sleeves are clamped, and the length of the drying chamber is adjustable (the present arrangement is 5 feet long). The drying chamber is connected to an inlet tubing to allow hot gases through the chamber. Air or nitrogen passes through the heating coils immersed in mineral oil which can be externally heated. In the drying chamber, the air flows countercurrent to the direction of spinning, and facilitates in drying the filament. The effluent gas saturated with the solvents is vented from the top of the chamber.

The takeup unit is a specially built low-speed spooler which was purchased from the Chase Machinery Company Inc., RI (to be delivered in mid-October). This unit is a monofilament winder, with 1 inch diameter spindle on which spools can be mounted. It has a motor with a 0.5 HP drive connected to a gear box unit to step down the drive. The rotating speed can be adjusted from 0 to 30 rpm. A mechanical traveller guides the filament onto the spool.

The current experimental efforts include testing the spinning dope formulations through the spinning apparatus. Using ambient air as the drying gas, several meters length of the green fiber have been spun, and collected at the bottom of the drying column. Figure 11 shows some of the fibers collected with this apparatus. The fibers are long and fairly uniform in diameter. The dopes we have tested are 'spinnable'. Upon the arrival of the filament winder system, fibers will be wound on spools.

The future work consists of fiber spinning and winding of filaments complementing the spinning dope development efforts. The experimental variables include dope temperature before spinning, metering speed (air pressure), length of the drying column, drying conditions (counter current or co-current flow, temperature of the gas and nature of the circulating gas etc), and take up speed. All these parameters will affect the fiber diameter, smoothness, and uniformity, and so will determine the processing window for the dopes in this apparatus. Primary emphasis will be on discovering and overcoming those problems which limit the length of the continuous filaments. We also must define the desirable fiber characteristics for convenient handling, spooling, and sintering. If there is a need for the fiber to go over many stationary guides during spinning or further processing operation, we will examine spin finish (fatty oils) on the fiber which could act as a lubricant. Efforts will be focussed on optimizing the process conditions for the dry spinning.

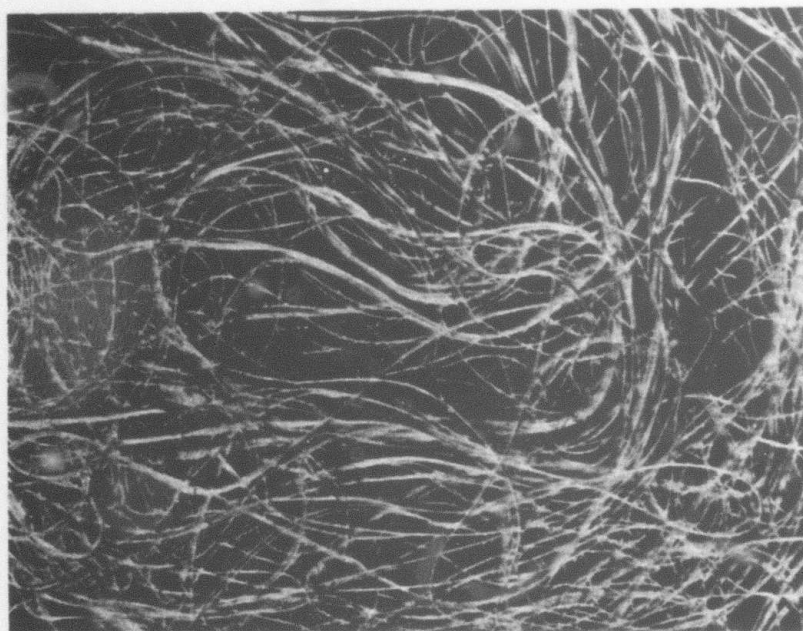


Figure 11 Optical micrograph of green fibers formed in the laboratory scale dry spinning apparatus from barium titanate formulation 24424 (6.5 X)

## 6 METAL CLADDING

Activities during this first quarter relevant to metal cladding of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fibers were largely focused on laying the groundwork for future progress. The major accomplishments were to

- 1) identify indium as a premetallization material;
- 2) begin organizing meetings with vendors and consultants in the electroplating industry;
- 3) explore a mechanical cladding concept;
- 4) develop concepts for handling fragile fibers during cladding.

### 6.1 PREMETALLIZATION AND ELECTROPLATING

Indium is being investigated as a candidate for the premetallization for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  to protect it from aqueous electroplating baths and promote adhesion. Some preliminary experiments have shown good adherence of indium on a sufficiently clean  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  surface. Presently we are attempting to clean the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  surface by heating it to 300-500°C, to simulate its condition immediately after sintering. A freshly heated sample was not wet by molten indium at 300°C, and exhibited no adhesion upon cooling. However, under the same conditions, the molten indium spontaneously spread over and wetted the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  surface when the indium drop was touched with an ultrasonic probe. After cooling, the pellet was covered with a strongly adherent indium coating. Attempts to remove the coating caused cohesive failure of the indium, rather than adhesive failure at the interface. We are now extending our investigations to develop reliable procedures for indium coating of pellets, and intend to adapt this process to sintered fibers in the next quarter.

Our present concept for treating the as-sintered indium fibers is to premetallize them immediately upon exit from the furnace. This could be done, for example, by taking up the emerging fibers onto a stainless steel belt coated with a continuously replenished film of liquid indium. Adhesion is assisted by ultrasonic agitation of the steel belt. At this point it may also be convenient to bond the fragile  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fiber (with the indium solder) to a metallic carrier wire (e.g., Ni) to carry it through subsequent plating operations. In a variant of this idea, the carrier wire itself could be coated with the indium, rather than a belt, and upon contact with the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fiber, deliver the indium to the fiber as it is being bonded. The premetallized fiber is then coated with the desired thickness of copper in a reel-to-reel electroplating bath.

Our experimental program for electroplating is currently in the planning stage. In this area we are being assisted by Mr. Dan Schachter, a Senior Plating Engineer at the CPS Watertown manufacturing facility. While Mr. Schachter is not a project member, he is actively advising us in the area of electroplating processes, techniques, and industrial equipment. In particular, he is assisting us in locating vendors in the electroplating area who would be interested in working with us to develop plating processes and baths for copper plating on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

We also have begun to investigate the feasibility of electroplating from a molten salt electrolyte. The advantage of a molten salt lies not in the metal deposition, but rather in a "coulometric titration" step done after sintering and before plating to adjust the oxygen stoichiometry. For this concept, the sintered fiber is exposed to molten nitrates or sulfates, which act as the oxygen electrolyte. The oxygen stoichiometry is adjusted by anodically biasing the fiber and "charging" the ceramic to a desired oxygen stoichiometry. This approach is an alternative to a solid state process using a zirconia electrolyte. If the molten salt coulometric titration proves successful, it would then be convenient to apply the metal electrodeposit from the same molten salt electrolyte by simply cathodically biasing the fiber.

## 6.2 MECHANICAL CLADDING OF THE FIBERS

We have also begun working on an alternative cladding strategy based on the "pressure bonding" property of indium, whereby a hermetic seal can be created between indium and a suitably clean oxide surface. Ljung and Koper show that a seal can be created by flattening an indium gasket between clean oxide surface by gently squeezing them together.<sup>10</sup> This seems to work quite well with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Our preliminary results indicate that a freshly heated pellet can be given an adherent indium coating with this press-sealing method. A sintered  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  pellet was ground flat with 600 grit abrasive paper and degreased by heating to 400°C in air. Immediately after cooling, a piece of 30 gauge indium wire was pressed onto the surface by squeezing it between the pellet and a glass slide. The indium spread over the pellet surface. Adhesion was good. Determined scraping with a razor blade was required to peel off the indium coating, which failed adhesively along the bond.

We believe that the complete cladding operation can be carried out by pressure bonding the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fiber to indium clad metal foil strips. These would be, for example, 10-20 mil Ni

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<sup>10</sup>) B. H. G. Ljung and J. G. Koper, "Hermetic Bonded Seal" U. S. Patent 4,159,075, June 26, 1979

or Ni-clad Cu foils clad with 20-50 microns of indium, which are commercially obtainable. At room temperature, pure indium is very soft, with a yield stress of only about 100 psi, so it should easily flow around a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fiber at stresses far below the compressive strength of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . When the fired fiber is sandwiched between the indium surfaces of two such clad foils, the indium should flow around the fibers, bonding to the ceramic, and also bonding the two foils together. We envision this bonding being done by simple rollers at the furnace exit.

It seems probable that the bonded sandwich could be subjected to higher forces, to shape the copper into a round wire, without damaging the fiber inside. The ceramic core, cushioned by the indium, should survive shear stresses applied to the outer metal layers, provided there is no tensile force acting to elongate the wire in the axial direction. The low shear strength indium layer should act like a hydrostatic liquid, and prevent transmission of shear stresses from the outer layers to the underlying ceramic.

Figure 12 illustrates the fiber exiting the belt furnace at right, and being sandwiched between two indium-clad Cu strips. These then are bonded and formed into shape by a simple roller mill. The details of the process are shown in Figure 13, which shows an array of sintered fibers between two foils (A), which are bonded to form a single layer strip (B) when the indium creates the metal-ceramic bond and pressure welds the two foils. This foil may itself be a product, or may be passed through a set of rolls to cut and form it into individual monofilament wires.

An advantage of this process is the ability to clad the fiber in a single dry step immediately after firing, minimizing the need to handle the fragile sintered fiber. It exploits a known ceramic-metal joining technology, and is based on the simple production process of metal rolling. Note that one could substitute just about anything for the copper foil-- Ni, Ag, Cu with imbedded high modulus reinforcement, etc., available as custom products from commercial firms. At present we are discussing our requirements with two firms<sup>11</sup>, to obtain experimental quantities of either copper strip with 10 mils of roll bonded indium, or nickel strip with a molten reflow coating of indium.

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<sup>11</sup>) Technical Materials, Inc., Lincoln, RI, and Metallon Engineered Materials Corp., Pawtucket, RI

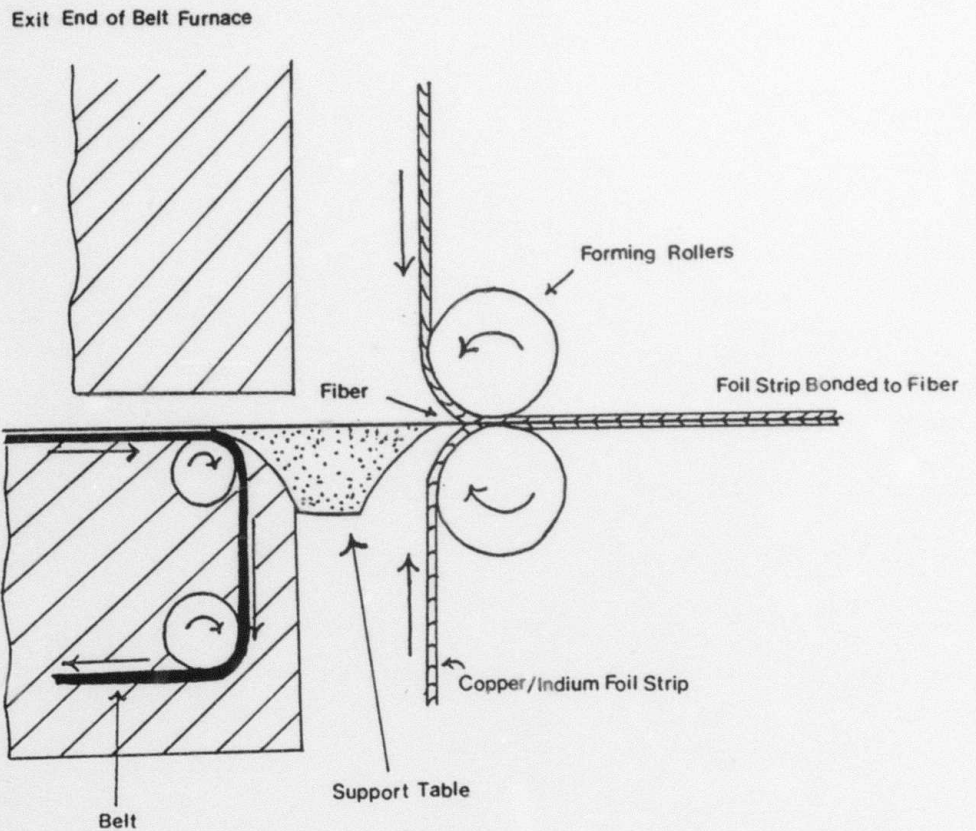


Figure 12 Schematic illustration of mechanical cladding concept. Sintered fiber emerges from belt furnace on left, and is guided between two strips of copper foil clad with indium. Forming rollers bond the ceramic to the indium, and weld together the metal strips.

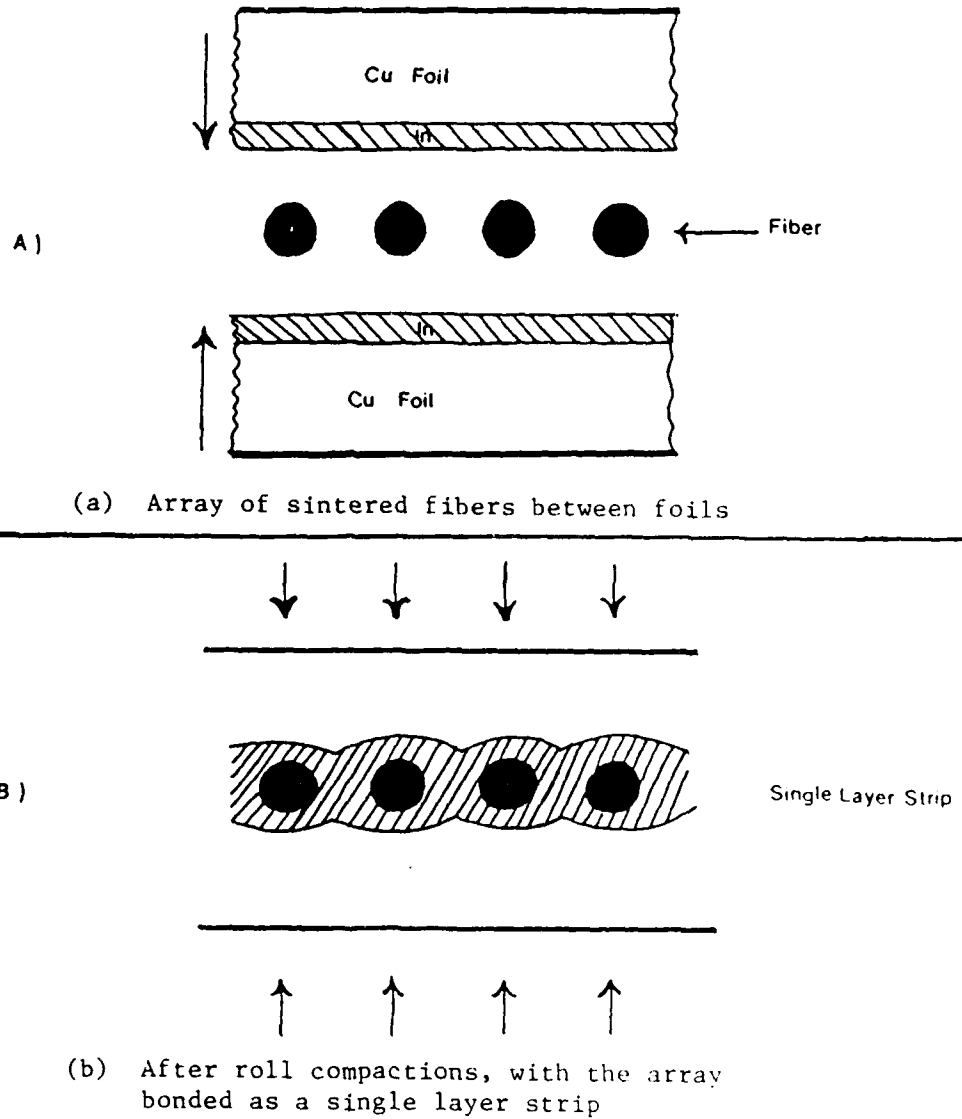


Figure 13 Detail of mechanical cladding concept

## 7 SUMMARY AND CONCLUSIONS

Freeze granulation and freeze drying have been found to be convenient processes for treating a milled raw batch so that it can be entirely reacted to phase pure  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in a single  $900^\circ\text{C}$  calcination process. This powder is satisfactorily sinterable, achieving 94% density with either as-calcined or dry vibromilled powder. Preliminary results of a study of microstructure as a function of processing conditions show significant flexibility in grain size and porosity achievable with these powders. Investigations are underway on the effect of microstructure on the superconducting properties of these ceramics.

An improved dry spinning dope has been developed with higher molecular weight acrylic polymer binders. Sorbitan trioleate has been identified as a preferred dispersant in MEK-toluene based solvent systems. Spinnability and green strength have been enhanced with the improved dope. This is an ongoing effort.

A laboratory scale ceramic fiber dry spinning apparatus has been built and used to spin longer fiber lengths. Continuous fiber spinning will be possible upon the arrival and installation of a specially built low-speed spooler, expected late October.<sup>12</sup>

Indium has been identified as a premetallization material for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Indium can be made to wet and adhere to a freshly heated ceramic surface in the presence of ultrasonic agitation. Plans are underway for electrodeposition. Promising results have been obtained for pressure bonding of indium to the clean ceramic surface. A mechanical bonding scheme for cladding has been developed, in which the ceramic fibers are rolled between indium-coated copper or nickel foils.

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<sup>12</sup>) By the date of this report, the spooler had arrived and had been installed.

ATTACHMENT IREPORT SUMMARYCOMPOSITE CERAMIC SUPERCONDUCTING FILAMENTS FOR  
SUPERCONDUCTING CABLE

First Quarterly Interim Progress Report on  
Contract Number N00014-87-C-0789

13 November 1987

J. W. Halloran, et al., Ceramics Process Systems Corporation,  
Cambridge MA 02139

This is the first progress report of a five month program to demonstrate the feasibility of manufacturing superconducting wires from  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , or another high critical temperature ceramic superconductor. These wires will consist of a small ceramic core, about 50-200 microns in diameter, covered with a copper cladding of similar thickness. The current carrying capacity of these wires will be enhanced by creating a high degree of texture in the ceramic core. Such a textured core has most or all of its grains aligned so that the crystallographic direction of high critical current runs parallel with the wire axis.

The ceramic core will be manufactured by solution dry-spinning of a mixture of the superconducting ceramic powder with appropriately chosen polymers, solvents, and additives. The dry-spun fibers will be sintered to produce a ceramic fiber with the proper microstructure and texture for high critical current. These sintered fibers will clad with copper or other metals by electroplating, or mechanical cladding.

The objectives of the program are to demonstrate the dry spinning process, the sintering, and the cladding process, and to determine the effect of the microstructural texturing on the critical current. The electrical and physical properties of the filaments are to be characterized.

The process for synthesizing  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  from copper oxide, yttrium oxide, and barium carbonate has been scaled up and improved to allow 0.5 kilogram batches to be made. Problems involving retention of the barium carbonate have been overcome, and a sinterable powder is prepared after a single calcination reaction at  $800^\circ\text{C}$ . The powder readily sinters to around 94% of theoretical density. A study is underway to optimize the processing and microstructure.

The dry spinning "dope" has been improved by increasing the molecular weight of the acrylic polymer binder and by using sorbitan trioleate as a dispersant. Efforts continue to improve the spinnability of the dope, and the physical properties of the fiber. A laboratory scale continuous dry

(ATTACHMENT I page 2)

spinning apparatus has been built, and is being modified.

Indium has been selected to "pre-metallize" the ceramic fibers prior to cladding by electroplating. Arrangements are being made to begin electroplating experiments in the coming quarter. An alternative cladding process has been identified, in which the superconducting ceramic fiber is mechanically clad with indium coated foils. This method will be explored experimentally in the coming quarter.

A cryostat has been ordered to permit electrical measurements at controlled temperatures between 77 and 300°K. This will be used for measurements of resistance and critical current of the superconducting filaments.

ATTACHMENT II

ARPA ORDER NUMBER: 6214

PROGRAM CODE NUMBER: 7Y10

CONTRACTOR: Ceramics Process Systems Corporation  
840 Memorial Drive  
Cambridge, MA 02139

CONTRACT NUMBER: N00014-87-C-0789

CONTRACT EFFECTIVE DATE: 8/16/87

CONTRACT EXPIRATION DATE: 1/15/88

SHORT TITLE OF WORK: Ceramic Superconductor Filaments

PRINCIPAL INVESTIGATOR: John W. Halloran  
(617) 354-2020

During the reporting period 16 August through 15 October 1987, major progress was made in improving the quality and production rate of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder, by improving the uniformity of the calcination reaction of the copper and yttrium oxides with barium carbonate. A sinterable powder can now be produced in adequate quantities to supply the needs of the program. The relations between powder characteristics, processing conditions, and microstructure are being explored. Process improvements have been made for the dry spinning process to make  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fibers. The composition of the dry spinning dope has been improved by the use of a better dispersant and higher molecular weight polymer. A dry continuous dry spinning apparatus has been built and is being refined. Important progress was made in the metal cladding process for the fibers. A candidate for the essential premetallization was found to be indium. Plans were made for experimental work on electroplating. An important new concept was developed for cladding, involving mechanical bonding of indium coated metal foils to the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fibers.

A specially built low-speed spooler was ordered for the continuous spinning apparatus. Delivery is due late October. A controlled temperature cryostat was ordered for electrical measurements of the filaments. Delivery is expected in December.

Feasibility of each of the process steps should be demonstrated by the end of the contract period.

ATTACHMENT III

ARPA ORDER NUMBER:6214

PROGRAM CODE NUMBER: 7Y10

CONTRACTOR: Ceramics Process Systems Corporation  
840 Memorial Drive  
Cambridge, MA 02139

CONTRACT NUMBER: N00014-87-C-0789

CONTRACT AMOUNT: \$298,533.00

EFFECTIVE DATE OF CONTRACT: 16 August 87

EXPIRATION DATE OF CONTRACT: 15 January 88

PRINCIPAL INVESTIGATOR: John W. Halloran

TELEPHONE NUMBER: (617) 354-2020

SHORT TITLE OF WORK: Ceramic Superconductor Filaments

REPORTING PERIOD: 16 August 87 through 15 October 87

DESCRIPTION OF PROGRESS

During the reporting period 16 August through 15 October 1987, progress was made in improving the quality and production rate of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder, by improving the uniformity of the calcination reaction of the copper and yttrium oxides with barium carbonate. A sinterable powder can now be produced in adequate quantities to supply the needs of the program. The relations between powder characteristics, processing conditions, and microstructure are being explored. Process improvements have been made for the dry spinning process to make  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fibers. The composition of the dry spinning dope has been improved by the use of a better dispersant and higher molecular weight polymer. A dry continuous dry spinning apparatus has been built and is being refined. Important progress was made in the metal cladding process for the fibers. A candidate for the essential premetallization was found to be indium. Plans were made for experimental work on electroplating. An important new concept was developed for cladding, involving mechanical bonding of indium coated metal foils to the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  fibers.

A specially built low-speed spooler was ordered for the continuous spinning apparatus. Delivery is due late October. A controlled temperature cryostat was ordered for electrical measurements of the filaments. Delivery is expected in December.

SUMMARY OF SUBSTANTIVE INFORMATION DERIVED FROM SPECIAL EVENTS

Project members attended conferences on high temperature superconductors sponsored by the Department of Energy, American Chemical Society, and American Ceramic Society. The information gathered was much too voluminous to summarize here, due to the continued rapid pace of progress worldwide in this field.

CHANGE IN KEY PERSONNEL

No change

PROBLEMS ENCOUNTERED AND/OR ANTICIPATED

We anticipate demonstrating the feasibility of each element in the program, as outlined in the Objectives.

ACTION REQUIRED BY THE GOVERNMENT

No action is needed.

FISCAL STATUS

- 1) Amount currently recieved on contract: \$ 0.00  
(No funds have yet been recieved on this contract)
- 2) Expenditures and commitments to date: \$ 88,002.00  
(As of 10/31/87, \$ 88,002.00 has been expended)
- 3) Funds required to complete work: \$ 298,533.00