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Superconducting Wire Fabrication

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ADMINISTRATIVE INFORMATION

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INTRODUCTION

GENERAL

The discovery of materials that exhibit superconductivity above the temperature of liquid nitrogen (77 K) makes possible the development of devices whose previous operation was prohibitively expensive or inconvenient because earlier classes of superconductors required liquid helium refrigeration. In order to take advantage of these new high-temperature superconductors for applications involving high currents or high magnetic fields, real devices and structures must be designed. The most logical structure for the fabrication of high-current, high-field devices is wire that can be wound into the desired geometry. Unfortunately, all of the recently discovered high-temperature superconductors are brittle ceramic oxides. Some of the materials require oxygen-rich processing conditions to become properly superconducting, and all of the materials require processing at temperatures higher than 800°C. The properties of these materials make it impossible to fabricate wire by simply pulling it from bulk material. Conventional superconducting wire has, however, been fabricated in the past by drawing metal sheaths containing a powder core.¹ This process produced a multifilamented superconducting composite in a high-purity normal metal matrix. The composite was made up of tubular niobium filaments containing niobium tin powder in a copper matrix. The windings were insulated with glass braid, and the final device was reacted at 700°C.

The production of composite wire from the new high-temperature superconducting materials requires that a continuous filament of the metal oxide superconductor be formed and sintered into place in a tubular metal filament after the composite wire has been drawn to size, insulated, and wound into a useful configuration. The filament can be sintered from a powder form of the pure superconductor, or it can be synthesized from chemical precursors in powder form. The reaction of the components with the filament wall material must be controlled, and compensation for losses of components, in particular, oxygen, must be made. The entire system must be able to withstand the time and temperature of the heat treatment required to form the continuous superconducting filaments.

BACKGROUND

Wire Work

Fairly soon after the discovery of high-temperature superconductors, some composite wire was produced.² The wire did superconduct, but the critical currents were relatively poor. Later work established that there were several issues that needed to be addressed before composite wire fabrication with these materials could be successful.³ Critical among these issues were the proper choice of metal sheath material, the means of providing for the oxidation of the sintered superconductor, and the determination of optimum heat treatment conditions. Curiously, it was found that critical currents in composite wire were often higher than those attainable from the bulk polycrystalline material from which the wires were fabricated. This may be because the drawing process tends to naturally compress and orient the superconductor, providing better intergrain current links. It is commonly believed that the limitation of critical currents in bulk polycrystalline samples is due to weak links between grains.

Oxygen Enrichment

It has been found that the removal of the metal sheathing from composite wire before heat treatment improves the electrical properties of the wire.⁴ While the improved properties resulting from the removal

of the metal sheath were attributed to the elimination of cracks due to different thermal expansion characteristics between the oxide and sheath, it is also likely that the removal of the sheath improved the oxygen enrichment of the superconductor during heat treatment and annealing.

The necessity for oxygen enrichment applies only to the yttrium- and rare-earth-based superconductors. The more recently discovered bismuth-based superconductors do not appear to require special treatments to increase the oxygen content in order to maintain superconducting behavior. Consequently, the bismuth-based materials may have an advantage in wire fabrication. However, there are other considerations as well, since the bismuth-based materials are a bit more difficult to prepare as single-phase material than the yttrium-based materials.

SCOPE

Our intentions in this work were to design and fabricate a stabilized superconducting composite wire utilizing tubular filaments with cores of high-transition temperature metal oxide superconductor. There were several phases to this effort. First, it was necessary to gain experience in the fabrication and characterization of bulk superconductors. Also, experiments were done to test the chemical compatibility of potential cladding materials with the ceramic superconductors under different heat-treatment conditions. Finally, tubes were packed with superconducting powder and drawn into wires. These wires were heat-treated and their electrical properties were measured.

SYNTHESIS AND CHARACTERIZATION OF MATERIALS

FABRICATION ATTEMPTS

The production of the yttrium-based 1-2-3 material is straightforward, with either barium carbonate or barium peroxide being used as one of the starting materials. Barium peroxide has potential advantages over barium carbonate as a starting material. Long calcining times are required to decompose barium carbonate, which is a very stable compound. Very seldom is all of the carbonate removed. Experiments using the branch carbon analyzer show that even material believed to be well prepared will have up to 0.2% carbon present. Also, barium peroxide provides enough oxygen to produce material of the desired $\text{YBa}_2\text{Cu}_3\text{O}_7$ stoichiometry directly.

Batches of 1-2-3 superconductor material were processed through a calcining heat treatment series in which both barium carbonate and barium peroxide were used as starting materials. Y_2O_3 , CuO , and BaCO_3 were used as raw materials for the carbonate mix and BaO_2 was substituted for the carbonate in the peroxide mix. The weights of starting chemicals required to produce the YBa_2Cu_3 atomic ratios were used. Several calcining heat treatments of 5 hours at 950°C in air followed by grinding and remixing were used to react the constituents. The barium carbonate material lost 9 to 10% of its weight through the calcining and the barium peroxide material lost about 4%. The calcined material was ground, pressed into discs, and given a final oxygen anneal. The critical temperature of these materials was measured. The materials were shown to be superconducting at liquid nitrogen temperatures. The 1-2-3 superconducting material was ground into powder for later use in laboratory experiments.

A sample of 1-2-3 mix using barium peroxide was made up with unreacted component chemicals. The formulation was ground in a mortar and pestle and was not given any heat treatment. A 10-gram pill, 1 inch in diameter, was pressed at 10,000 psi. This pill was heated in air from room temperature to 950°C in 6 hours, held for 11 hours at 950°C , furnace cooled to 549°C , held at 549°C for 4 hours, and furnace-cooled to room temperature in 2 hours. Losing 3.37 % of its weight from the heat treatment, the

pill was sintered into a hard composite, indicating that the components will react with a heat treatment of 10 hours at 950°C.

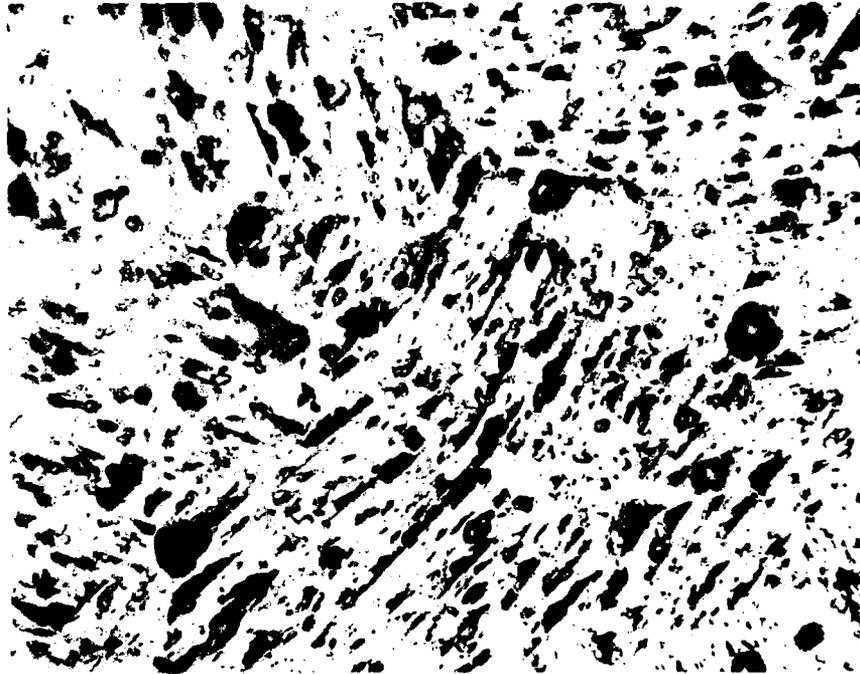
The material produced with barium peroxide as a starting material also superconducted and shows some promise as a single-step synthesis that avoids the multiple calcinings required to decompose carbonates. If the resulting overpressure of oxygen can be controlled through the proper cool-down cycle, and the correct starting mix is used, the correct oxygen composition of the 1-2-3 compound can be obtained. Initially it was felt that it might be possible to synthesize the superconductor directly inside of the wire by using a precursor mix containing barium peroxide. Later measurements suggested that this method was not likely to be successful, although additions of this precursor mix were made to prepared superconductor powder inside of the wire in order to provide additional oxygen to the system.

CHARACTERIZATION OF YTTRIUM 1-2-3 MATERIALS

A comprehensive experimental program in high-temperature superconductors requires not only the characterization of bulk materials by their electrical properties and x-ray diffraction patterns, but also the examination of the microstructure of these materials. The microstructure of these new superconducting compounds is both interesting and important for the characterization of these materials. Indeed, since the critical currents of bulk polycrystalline materials are much less than that found for single crystal materials, the microstructure is bound to be an important factor in the critical currents of bulk materials and structures such as composite wire. The microstructure of a number of bulk superconductor samples has been examined by light microscopy, scanning electron microscopy, and energy-dispersive x-ray fluorescence spectroscopy (EDS) in the scanning electron beam.

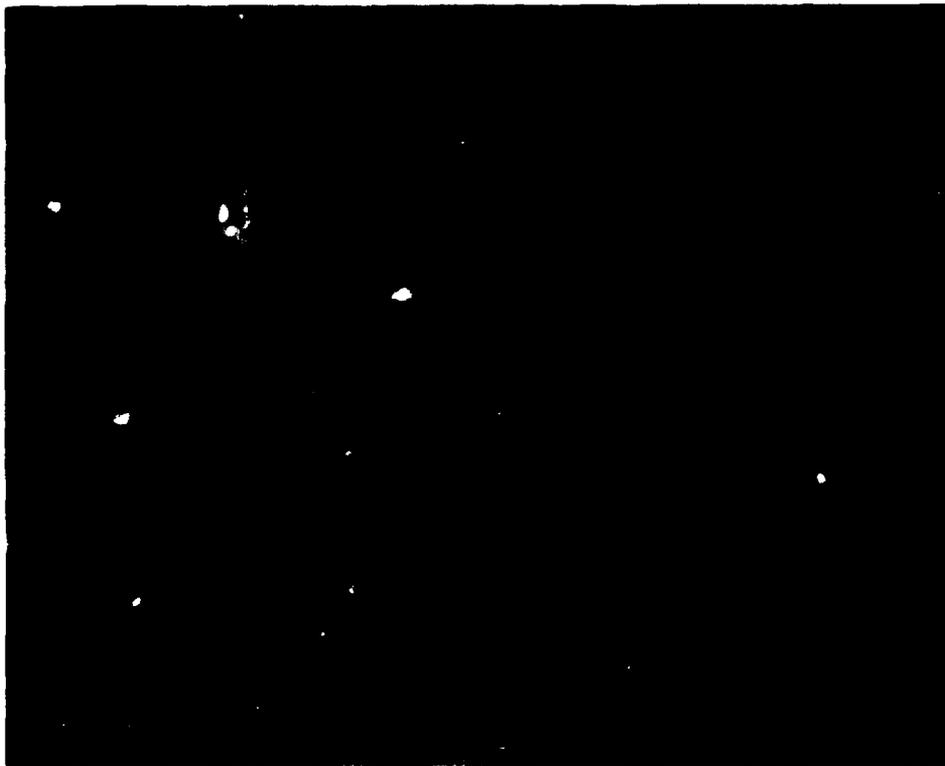
Samples are usually prepared for microstructural examination by mounting the sample in resin, then grinding the samples through 600 grit, following with a succession of diamond polishes through 1 μ , and finally finishing with a 0.05- μ aluminum oxide polish. The samples are then examined by optical microscopy. These oxide materials are very active in polarized light, which results in a distinct coloring of the image, which greatly enhances the detection of grain orientation, grain and twin boundaries, and phase types. Figures 1 and 2 are photomicrographs of a sample of yttrium 1-2-3 material viewed in white and polarized light. These pictures show the dramatic difference caused by polarized light. Figures 3 and 4 are micrographs of a sample of yttrium 1-2-3 material using polarized light. The micrographs are of the same area, the only difference being that one micrograph was taken with color film and the other with black and white film. Even in black and white, the polarized light brings out important details of the grain and twin boundaries. Grain size may have an effect on current-carrying ability. Twinning in the yttrium 1-2-3 material is indicative of the oxygenated orthorhombic phase. The lack of twins apparently indicates the presence of the nonsuperconducting tetragonal phase.

Figure 5 is a scanning electron microscope (SEM) micrograph of a region of the same sample depicted in Fig 2. The x-ray dot maps of this same region (Fig. 6) show that the bright areas in the SEM micrograph represent a different phase from the dark areas. The x-ray spectrum of the bright area (Fig. 7) is consistent with the so-called "green" 2-1-1 semiconducting impurity sometimes found with the yttrium 1-2-3 material. The x-ray spectrum of the dark area (Fig. 8) is consistent with good yttrium 1-2-3 material. Note that the optical microscopy and SEM complement each other. Grain and twinning information are only available in the optical micrographs. Surface morphology and chemical information are more readily produced by the SEM and the associated x-ray spectroscopy.



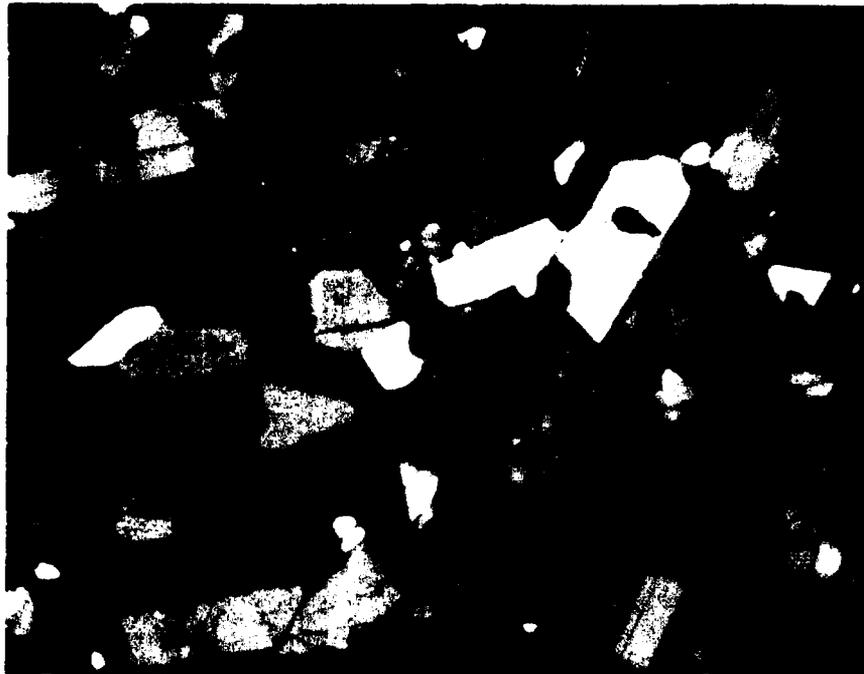
500X

Figure 1. Yttrium 1-2-3 superconductor, normal light, black and white positive film.



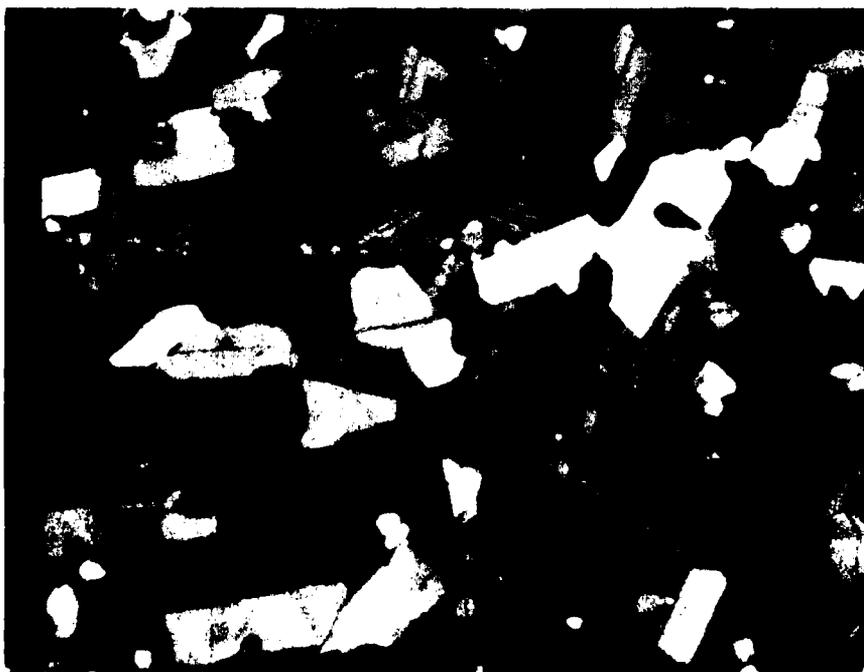
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Figure 2. Same sample as Fig. 1, polarized light, color negative film.



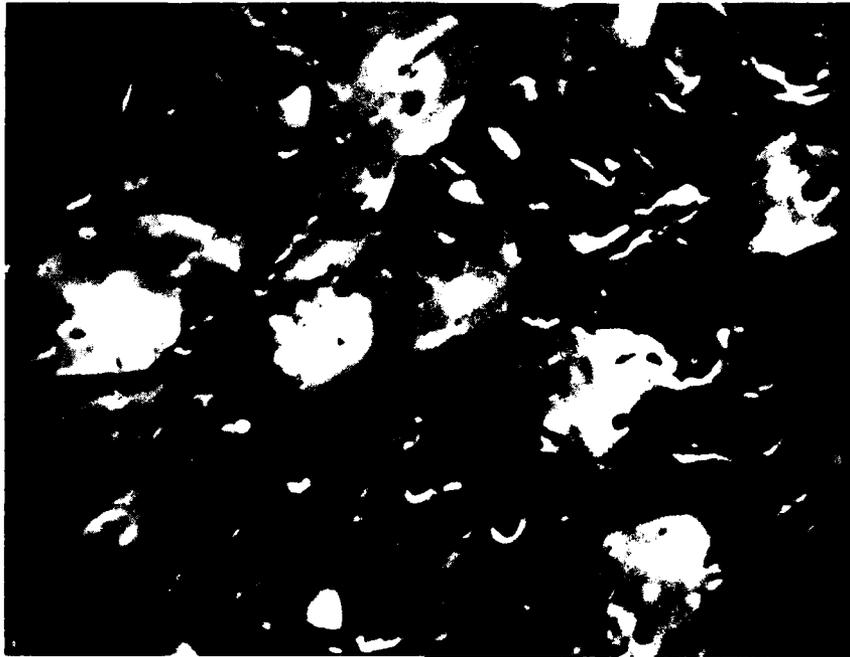
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Figure 3. Yttrium 1-2-3 superconductor, polarized light, color positive film.



800X

Figure 4. Same sample and region as Fig. 3, polarized light, black and white positive film.



1200X

Figure 5. SEM image of same sample depicted in Fig. 2.

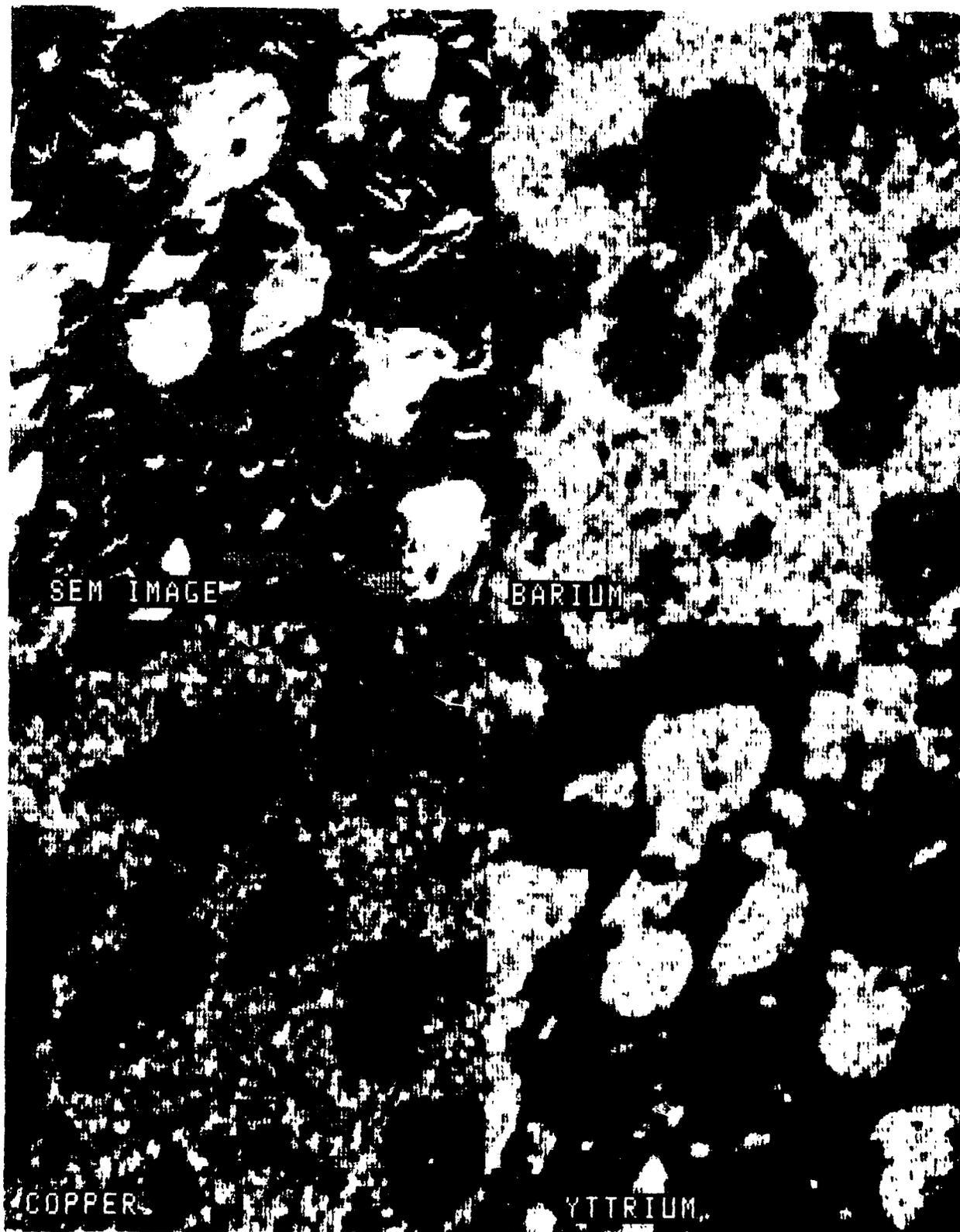


Figure 6. X-ray dot maps of the region in Fig. 5.

CHARACTERIZATION OF BISMUTH-BASED MATERIALS

The general features of the microstructure of the bismuth-based materials are all present in Fig. 9. The micrograph shows the presence of a number of phases, in particular a needle-like acicular phase. This phase is actually a cross section of the plate-like superconductor material, an example of which is shown in the digitized electron micrograph of Fig. 10. X-ray spectroscopy shows that the acicular phase in Fig. 9 is the superconductor embedded in a phase with a higher bismuth concentration. The blue phase of Fig. 9 is a calcium copper oxide. Other copper oxide phases and a Sr-Ca-Cu oxide phase are often found in bismuth-based materials as well. When lead is added to the bismuth-containing material, the 105 K T_c $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ phase (referred to as the 2-2-2-3 phase) is known to form preferentially. When the starting stoichiometry is enriched in calcium and copper, the equilibrium is driven to favor formation of the 105 K T_c phase almost exclusively over the lower T_c $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ phase (referred to as the 2-2-1-2 phase). However, the addition of copper and calcium in excess of the 2-2-2-3 phase stoichiometry leads to the inevitable production of additional calcium copper oxide phases in the bulk material. These additional phases are easily detected by the metallography of the bulk material even when evidence of the additional phases is not present in the x-ray diffraction patterns. Proper heat treatment of stoichiometric 2-2-1-2 starting materials can lead to a 2-2-1-2 superconductor that is largely free of extraneous phases.

The process for producing superconducting wire must retain good microstructural properties of the bulk material. For the yttrium 1-2-3 materials this means producing single-phase grains with good twinning. Large grains oriented in the current-carrying direction appear to provide the best critical currents. Critical currents as large as 75000 A/m² have recently been observed in bulk samples with large (1cm × 2mm × 20 μ) oriented grains. For the bismuth-based materials, it is important to maintain the chemical composition of the starting materials and avoid the formation of extraneous phases that might interrupt the superconducting path in small-diameter wire.



200X

Figure 9. Bi-Sr-Ca-Cu-O superconductor.



Figure 10. SEM image of Bi-Sr-Ca-Cu-O superconductor.

COMPATIBILITY EXPERIMENTS

YTTRIUM 1-2-3 MATERIALS

The candidates for metal sheathing were originally chosen with the yttrium 1-2-3 materials in mind. In particular, metals that would be less likely to remove oxygen from the superconductor were chosen. Copper was chosen for its ready availability and good electrical and thermal properties. Silver was selected for its electrical properties and its resistance to oxidation, particularly at high temperature. Niobium and zirconium were chosen because these materials will form a dense and stable oxide layer that under the right conditions may prevent further oxidation and the diffusion of oxygen through the layer.

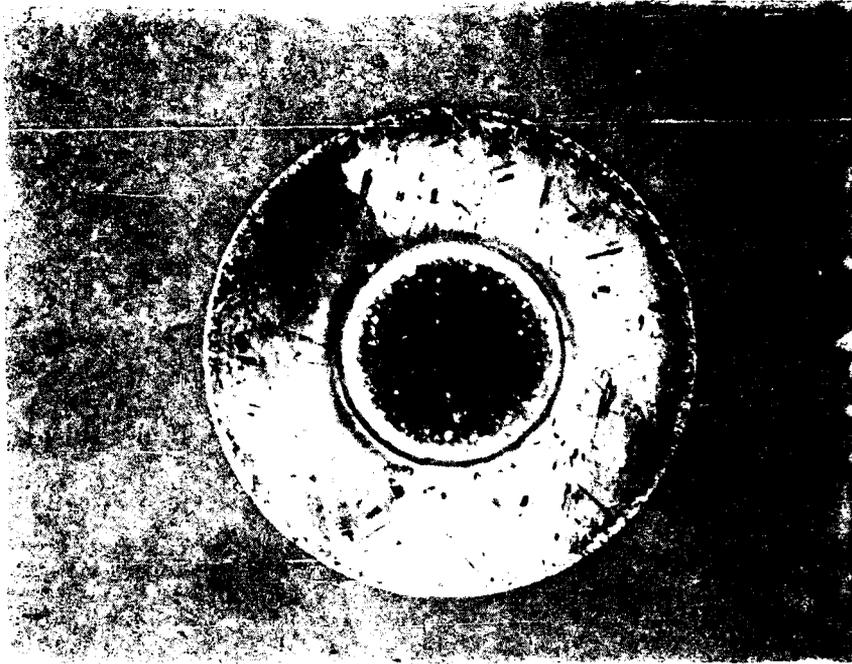
Capsules of these metals were made by drilling a 1/8-inch hole in a 1/4-inch-diameter rod and machining a plug to fit the end. The capsules were filled with oxide material by loading small amounts of powder into the capsule and tamping it in place for compaction. This operation was repeated until the capsule was loaded. The plug was then pressed in place. The capsules were typically loaded with 0.2 to 0.3 gram of powder. The capsules were loaded into a closed-end quartz tube, evacuated, and sealed. The sealed quartz ampules were heated in a box furnace, and the temperature was measured with a type K thermocouple adjacent to the capsule. After cooling, the ampule was opened and the reaction capsules were removed. Each capsule was cut in half, mounted in epoxy mounting compound, ground, and polished. The powder and the powder-to-metal interface were examined with the optical metallograph and then in the SEM.

In the initial experiment, one capsule of each material was filled with the "standard" 1-2-3 compound that was previously synthesized. All four capsules were placed in the same quartz ampule that was then evacuated and sealed. The ampule was slowly heated to 910°C over a 5-hour period, and was periodically observed to see if it was intact or if any unusual reaction had occurred. The ampule was held at temperature for an hour and furnace-cooled over 5 hours.

As can be seen in Fig. 11 and 12, copper formed several different reaction layers with the superconductor, ranging from copper oxides to barium copper oxides. Copper is clearly unacceptable as a cladding metal for yttrium 1-2-3 material. Niobium formed a broken oxide layer (Fig. 13 and 14) and is probably unsuitable also. Zirconium was interesting because it formed a very thin (0.0006 inch) oxide layer that may be a good diffusion barrier (Fig. 15 and 16). As can be seen in Fig. 17 and 18, silver formed no reaction layer with the superconductor (although the heat treatment did cause large-grain growth in the silver) and appears to be the best candidate cladding material. The powder core was lightly sintered and had the 1-2-3 x-ray spectrum.

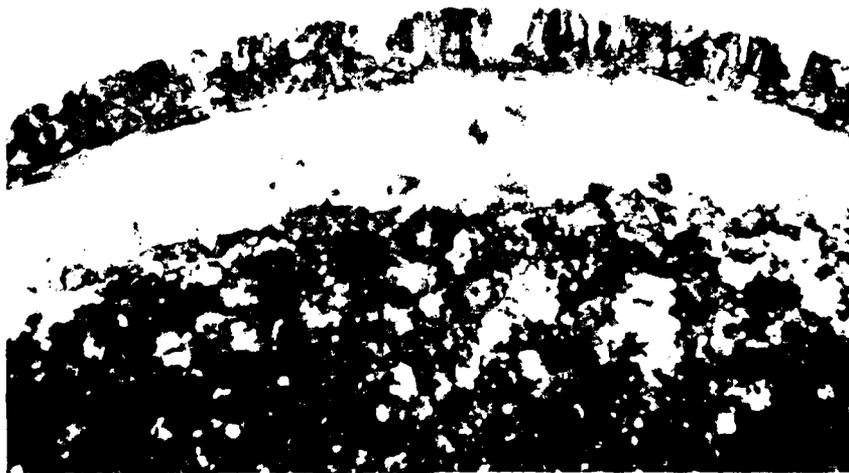
A second experiment was run at a higher temperature and a much longer time in order to get a much more severe heat treatment cycle. The unreacted barium peroxide mix was used to provide excess oxygen. Four capsules were filled with barium peroxide mix that had not been prereacted and were sealed in the same evacuated ampule. The ampule was heated to 930°C in 2 hours, held for 22 hours, and furnace-cooled in 5 hours.

The copper reacted considerably, increasing the apparent diameter of the powder core. Near the copper-to-powder interface, a great number of orange-colored copper barium oxides were present. Further, inside the core there was evidence that a phase approaching the composition of the 1-2-3 superconductor had formed, but with a higher copper concentration.



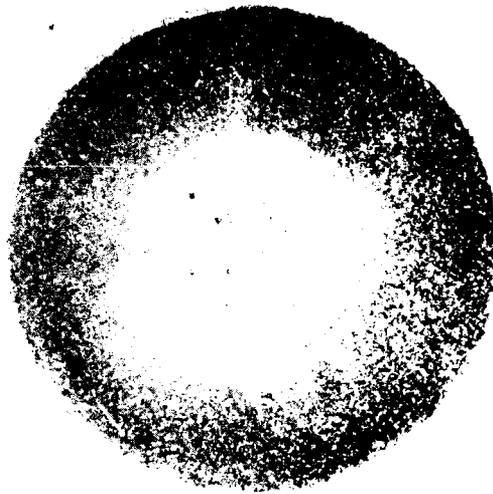
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Figure 11. Copper container, prereacted 1-2-3 powder core, 1 hour at 910°C, etched with dichromate.



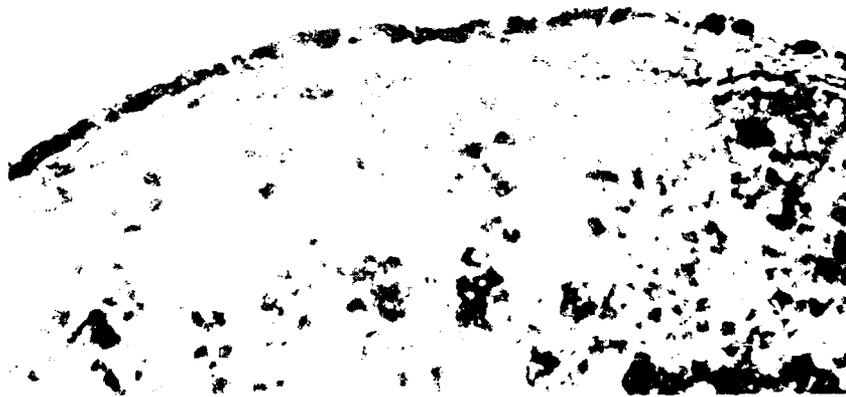
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Figure 12. Copper container, prereacted 1-2-3 powder core, 1 hour at 910°C, as polished.



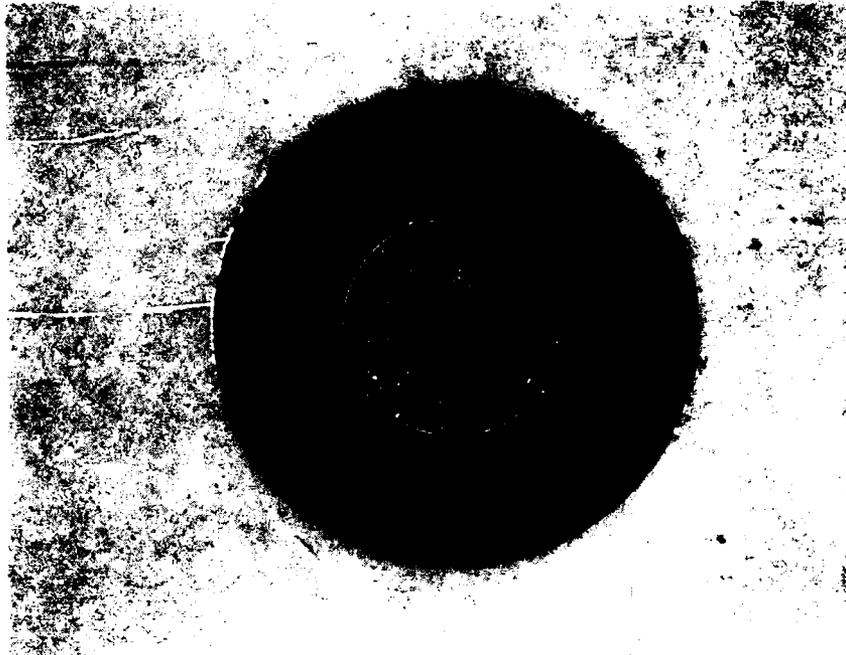
10x

Figure 13. Niobium container, prereacted 1-2-3 powder core, 1 hour at 910°C, etched with nitric and hydrofluoric acid.



100x

Figure 14. Niobium container, prereacted 1-2-3 powder core, 1 hour at 910°C, as polished.



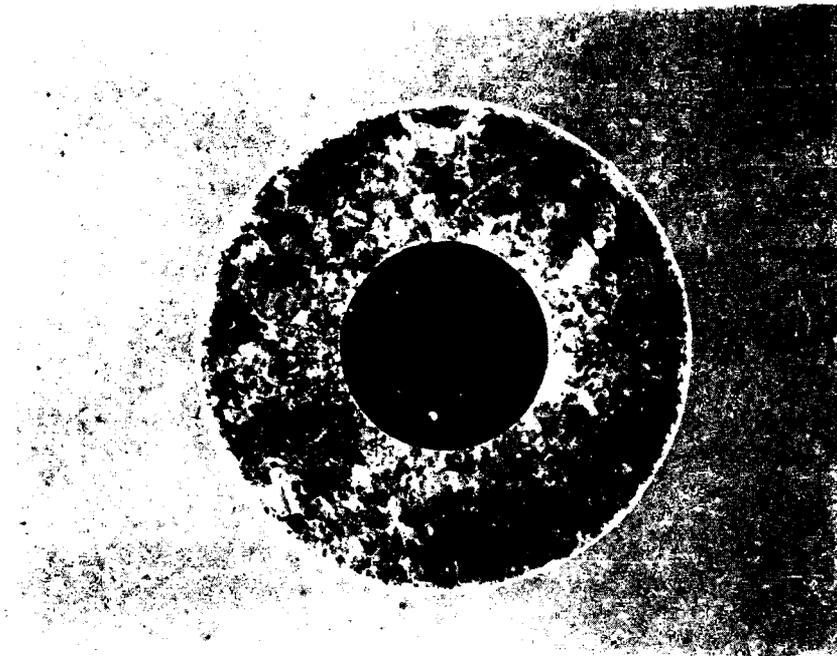
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Figure 15. Zirconium container, prereacted 1-2-3 powder core, 1 hour at 910°C, etched with nitric and hydrofluoric acid.



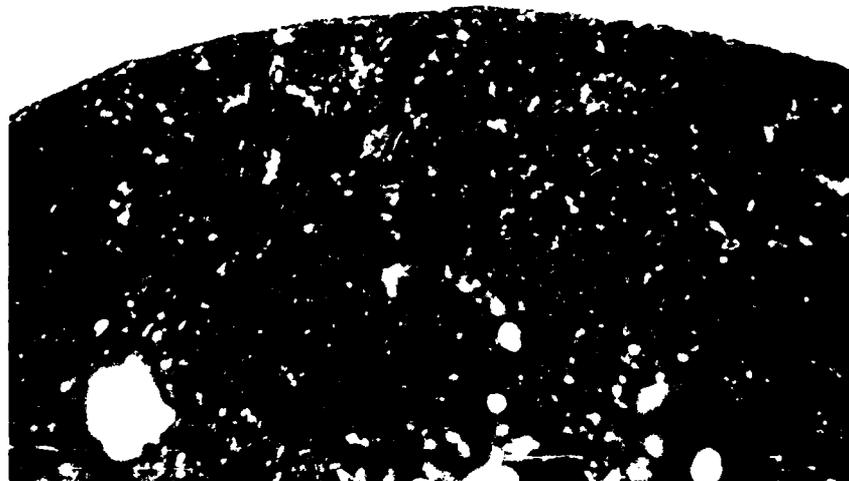
400x

Figure 16. Zirconium container, prereacted 1-2-3 powder core, 1 hour at 910°C, as polished.



10x

Figure 17. Silver container, prereacted 1-2-3 powder core, 1 hour at 910°C, etched with ammonium hydroxide, hydrogen peroxide solution.



100x

Figure 18. Silver container, prereacted 1-2-3 powder core, 1 hour at 910°C, as polished.

The SEM micrograph in Fig. 19 shows that the zirconium cladding suffered severe attack under these conditions. Orange reaction products (copper oxides and barium copper oxides) were present in the interior. There was also evidence of copper metal formation among the superconductor. The attack of the zirconium is probably due to the excess oxygen present in the oxide mixture. The formation of copper metal among the superconductor was probably due to the reduction of copper oxides by the zirconium and may be attributable to the longer reaction time compared to that of the previous experiment.

A heavy broken oxide layer was formed near the powder core interface in the niobium capsule. Inside of this region was some orange phase which contained niobium. Some regions of pure copper and regions of the 1-2-3 phase were identified.



Figure 19. SEM image of zirconium container, unreacted 1-2-3 mix, 22 hours at 930°C.

The SEM micrograph of the silver-clad sample in Fig. 20 shows that the oxide mix reacted to form a mixture of insulating material (the lighter appearing material in the ceramic region) and conducting material (the darker regions). The insulating material was found to contain undesirable extraneous phases. This indicates that the one-step synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_x$ inside of drawn wire is probably not feasible. In general, the long-term heat treatment at 930°C is quite severe on all the materials except silver, and the reactions of the capsules and powder cores in this experiment were affected by the presence of the zirconium and niobium.

In another experiment, a silver capsule loaded with unreacted barium peroxide mix was sealed in an evacuated quartz ampule about 5 cm long. The ampule was placed in a preheated oven at 930°C for 1 hour and quenched in water. A visual inspection of the ampule revealed that the outer surface of the silver capsule had melted and the resultant "slush" had slumped to the bottom of the ampule. The ampule was opened and the capsule was sectioned and examined. Metallic silver was dispersed throughout the powder core, indicating that melting had occurred in the core. An EDS spectrum showed that the material was essentially metallic silver with no metallic alloying. The melting point of silver is 960°C, yet considerable melting of the capsule was observed. The phase diagram of silver and oxygen and a

pressure-vs-temperature diagram of silver and oxygen show that the melting point of silver in 1 atmosphere of oxygen is 939°C and that 0.01% oxygen is soluble at this temperature. The considerable amount of melting observed at 930°C indicates that the pressure of oxygen in the ampule was greater than 1 atmosphere, and as the melting began, the oxygen dissolved in the melt, reducing the pressure to the equilibrium pressure at 930°C. This would be just above 1 atmosphere. The reason that no melting was observed in the second experiment, conducted at 930°C, is that the refractory alloys, zirconium and niobium, reacted with and absorbed the oxygen as it was released from the powder core and kept the pressure below 1 atmosphere in the ampule. Additional experiments lead to the conclusion that the oxygen pressure in closed ampules is difficult to control, resulting in an unexpected melting of the silver capsules. The lowering of the melting point of silver by oxygen leads to uncertainties in the heat treatment of silver-clad yttrium 1-2-3 materials. This problem has been recognized elsewhere.³



Figure 20. SEM image of silver container, unreacted 1-2-3 mix, 22 hour at 930°C.

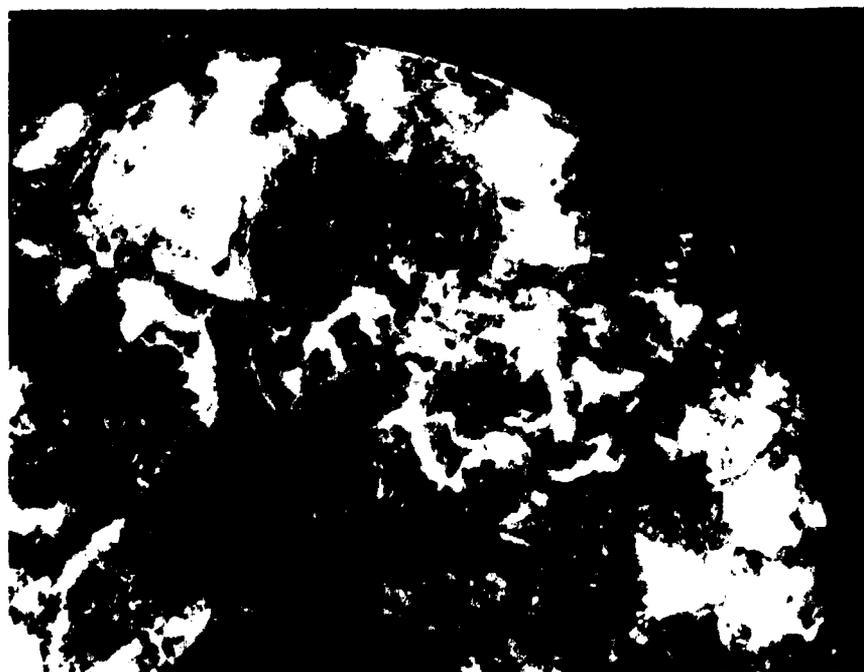
BISMUTH MATERIALS

Drilled rods of niobium, zirconium, copper, and silver were packed with 2-2-1-2 bismuth-based superconductor. The samples were capped with metal plugs and placed in a ceramic boat inside the inconel retort of the tube furnace. The retort was sealed and pumped to a vacuum of $<10^{-5}$ torr. The furnace was heated to 850°C and then rolled over the retort. The furnace was maintained at temperature for at least 4 hours, then allowed to cool overnight, with the furnace rolled away from the retort. The samples were removed, then sectioned, mounted, and polished.

A color micrograph of the zirconium section is shown in Fig. 21. The reddish colors indicate that severe reactions have occurred. The micrograph was taken with dark field illumination, so what is visible is the core area of the section. The metal portion appears dark. Dark islands in the core are actually metallic copper. Similar severe reactions are obvious for the copper (Fig. 22) and niobium (Fig. 23). The silver sample (Fig. 24) showed less reaction, but still showed significant amounts of white crystalline material on the surface. Examination with x-ray spectroscopy in the SEM showed that significant phase separation occurred and that no material with an x-ray spectrum matching the 2-2-1-2 phase could be found. This may indicate that the processing temperature was slightly too high, perhaps resulting in the melting and reforming of the superconductor.

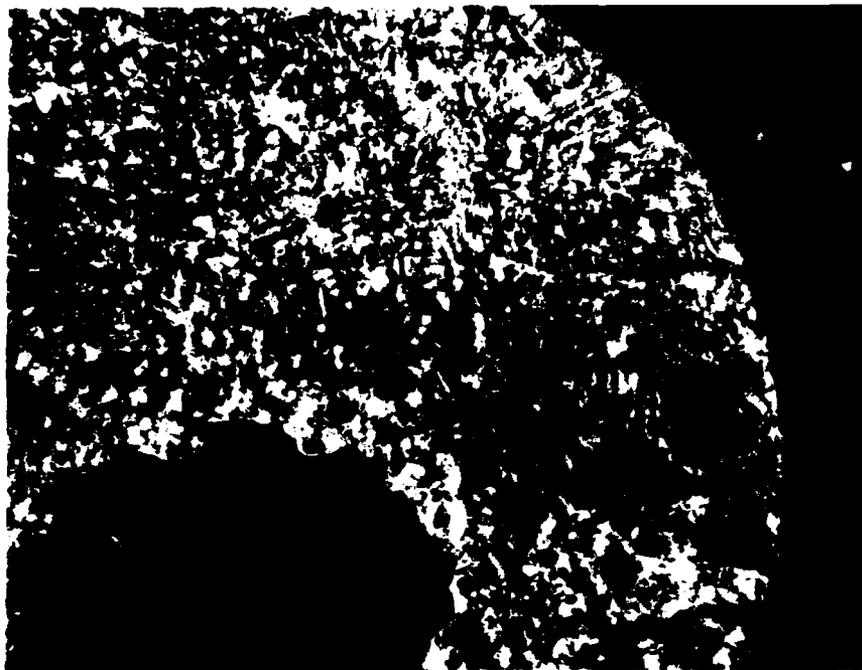
An additional experiment was performed with silver capsules, this time filling one capsule with 2-2-1-2 material and another with leaded 2-2-2-3 material. The furnace time and temperature conditions were the same as the previous experiment. The unleaded sample appeared to react with and bleed out of the silver container. The leaded sample showed no obvious reaction. Both samples were mounted, sectioned, and polished. The unleaded sample appeared to have large amounts of porosity. The leaded sample appeared to sinter rather well, as the low-magnification micrograph (Fig. 25) indicates.

The unleaded sample did not appear to contain either 2-2-1-2 phase or 2-2-3-2 phase material. The bismuth-containing material in general had much less copper and calcium than either of these superconducting phases. In contrast, nearly all bismuth-containing areas of the leaded samples showed x-ray spectra consistent with good 2-2-3-2 material. Both samples, of course, contained the Sr-Ca-Cu oxide phases as well. The appearance of the unleaded sample was similar to that of the bulk samples of unleaded material. It appears that the temperature was just high enough to melt the 2-2-1-2 sample, but not high enough to affect the 2-2-3-2 sample. This result gives enough confidence that if the temperature is lowered slightly, it should be possible to effectively sinter bismuth superconductor of either type inside of silver containers. Consequently, subsequent wire-pulling experiments concentrated on the bismuth materials.



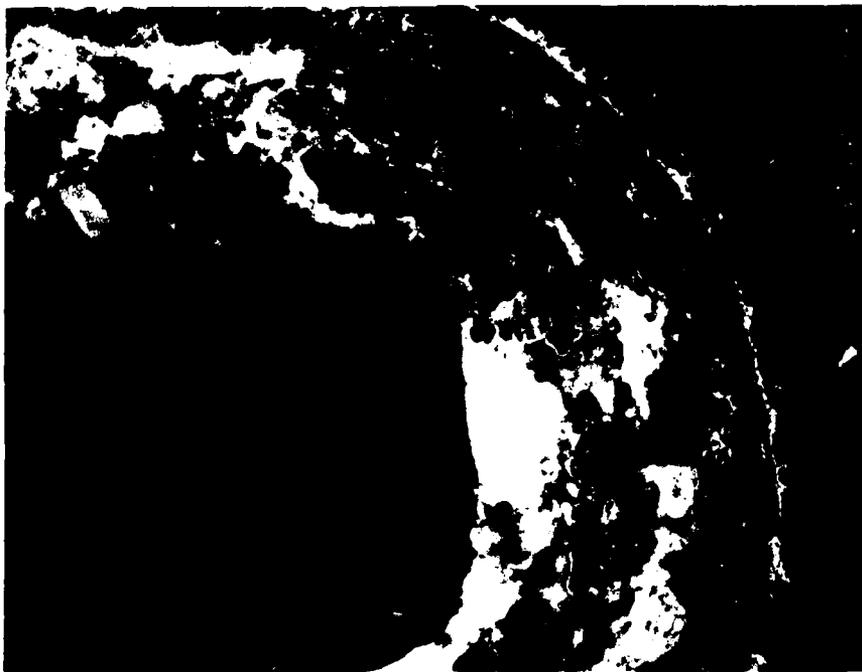
50x

Figure 21. Zirconium container, bismuth 2-2-1-2 material, 4 hours at 850°C.



50x

Figure 22. Copper container, bismuth 2-2-1-2 material, 4 hours at 850°C.



50x

Figure 23. Niobium container, bismuth 2-2-1-2 material, 4 hours at 850°C.



50x

Figure 24. Silver container, bismuth 2-2-1-2 material, 4 hours at 850°C.



20X

Figure 25. Silver container, leaded bismuth 2-2-2-3 material, 4 hours at 850°C.

WIRE DRAWING

Wire drawing is simply the operation of pulling a rod through a tapered hole with an exit size that is smaller than the starting rod size. This plastically reduces the cross section of the rod and increases the length. By making multiple draw passes, long lengths of wire may be made. The simplest equipment required to make wire is a set of wire dies, a device to make a point on the rod for starting, and a device to pull the rod through the die.

An open die swaging device was made up in the machine shop from a punch press die holder. A split die with successively smaller tapered holes was mounted in the punch press tooling. The swaging tool was operated in an Instron test machine which could be set up to cycle up and down. By inserting the tubing in the tapered holes and cycling the die, one could forge a tapered point on the tubing.

A series of carbide draw dies was purchased, ranging from 0.250 inch diameter to 0.030 inch diameter at 12.8% area reduction per pass. A 16-degree included approach angle in the dies was chosen.

A vertical draw bench was made by using the Instron tensile test machine. The load cell was removed from the upper crossmember, and tooling was made to hold the draw dies. The normal tensile test grips were attached to the moving crosshead for pulling the wire through the dies. A series of die holder extensions were made so that a total length of 54 inches could be drawn. Figure 26 shows the Instron setup.



Figure 26. Vertical draw bench for wire production.

Silver tubing to contain the superconducting powders (1/4-inch OD \times 0.040-inch wall) was purchased off the shelf from a laboratory supplier. Bismuth-based 2-2-1-2 superconductor and leaded bismuth 2-2-2-3 superconductor were made up and were supplied for wire-making as powder which had been hand-ground in a mortar and pestle. A mixture of yttrium-based 1-2-3 material produced from barium carbonate starting materials as previously described and 10% of a stoichiometric mixture of barium peroxide containing starting materials was also used as a wire core material.

The end of a piece of silver tubing was swaged down until the central hole was completely shut. The tube was filled from the back with the superconducting powder. The powder was tamped in place each time after about 1 or 2 mm³ were added. When the tubing was almost full, the end was swaged shut to contain the powder. As filled, powder densities of 30% to 40% of theoretical were obtained.

The point of the powder-filled tube was inserted through the first die and attached to the Instron grips. The crosshead was lowered, pulling the composite rod through the die and reducing the diameter. Successive draw passes were made at 12.8% reduction until the powder core reached a constant level of compaction. The composite was then drawn at 24% reduction per pass. When the wire was drawn down to the same diameter as the swaged point, successive points were made by reducing the diameter with a file and abrasive papers. This process was continued until the wire was drawn to at least 0.042 inch in diameter. Some wire was drawn as small as 0.037 inch in diameter, but attempts to draw further broke the wire.

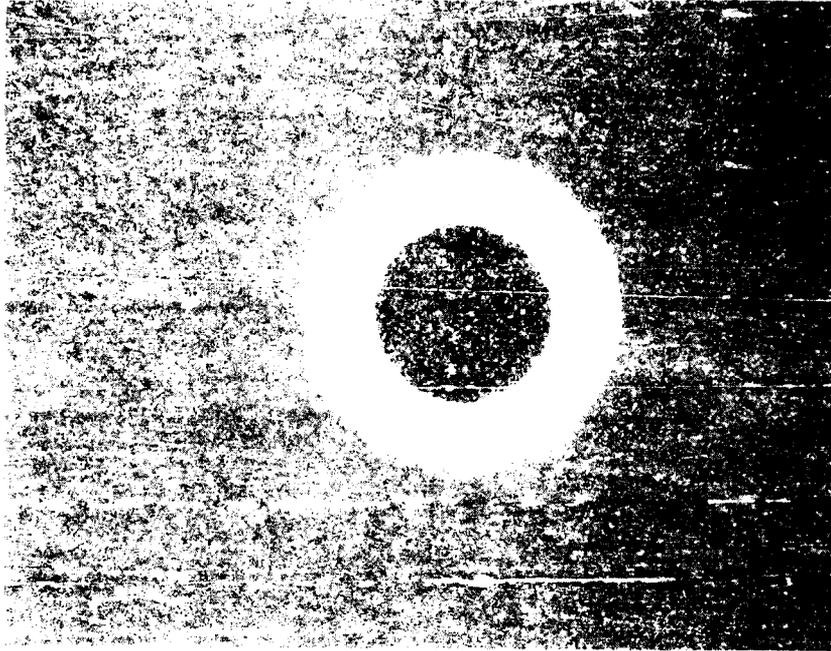
In this demonstration exercise, the maximum length obtainable was 54 inches. When this length was reached, the wire had to be cut. In a wire fabrication operation, when the maximum length of a draw bench is reached, the rod is then drawn on a draw block. A draw block is a machine that pulls the wire through the die and coils it up on a drum.

Measurements of outer diameter, powder-core diameter, length, and weight on drawn-wire samples indicated that the powder cores were compacted to from 70% to 90% of theoretical density. Figure 27 is microphotograph of a cross section of a 0.042-inch-diameter wire.

As a test of formability and ductility, some samples were pressed flat in a platen press to simulate the fabrication of flat wire. A width-to-thickness ratio of over 5 to 1 was easily obtained, indicating that flat wire can be made readily. In a flat-wire fabrication process, round wire is pulled through a rolling mill which shapes it. Square wire can be made by pulling round wire through a "turks head," which rolls the wire flat on four sides. If very close tolerances are desired, the flat or square wire is finished in a shaped wire die. Figure 28 is a microphotograph of a cross section of a 0.013-inch-thick flat wire. It has an aspect ratio of 5.5 to 1.

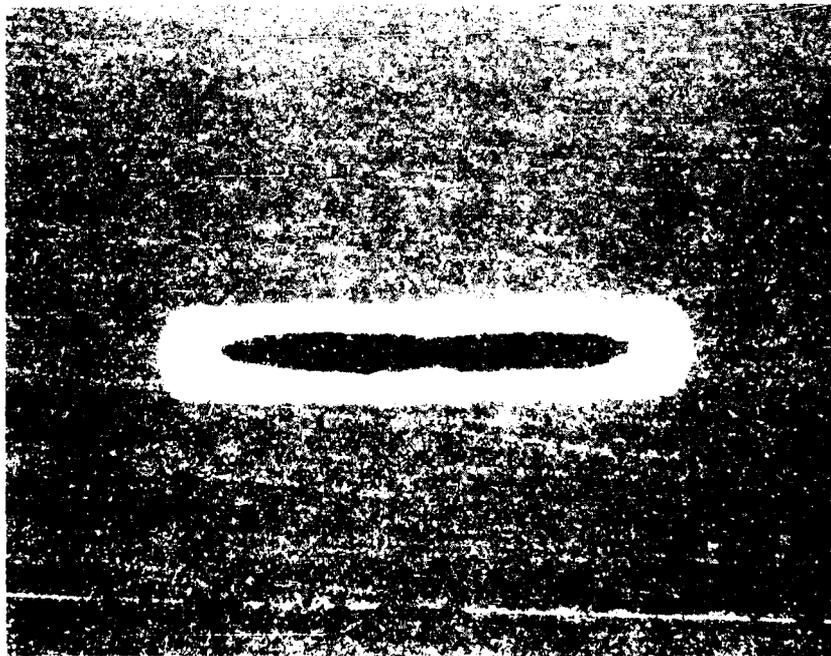
Samples of wire were wound on a cylinder to simulate the winding of a solenoid configuration. This was easily achieved on a fairly tight winding radius, which indicates that the powder-cored composite is easily formed. Figure 29 is a photograph of the coil wound on a quartz tube.

Samples of the various wires were heat-treated in an air-atmosphere tubular furnace and were submitted for the testing of their superconducting properties. The bismuth-based samples were heat-treated in the 840 to 845°C range, and the yttrium 1-2-3 samples were heat-treated at around 890°C.



40x

Figure 27. Cross section of 0.042-inch-diameter wire.



40x

Figure 28. Cross section of 0.013-inch-thick flat wire.

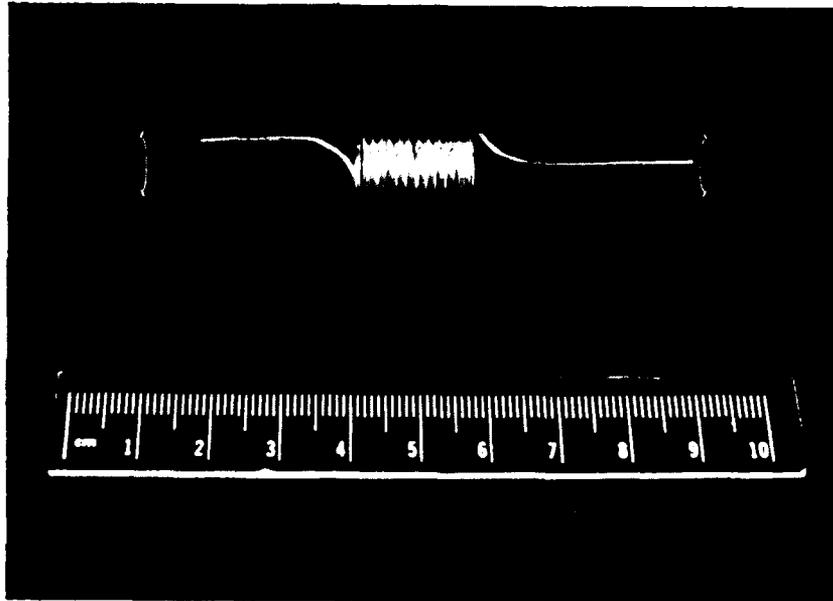


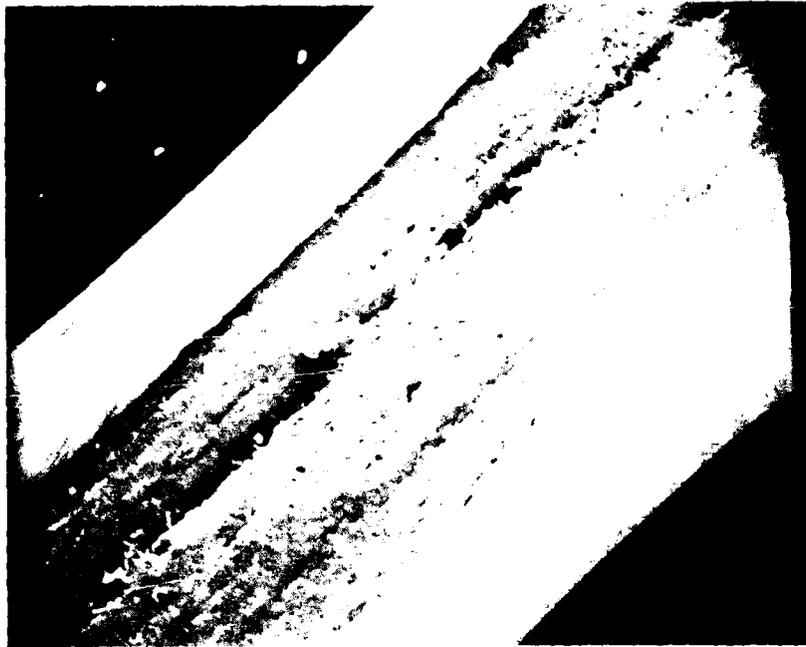
Figure 29. Coil of powder-cored superconducting wire.

CHARACTERIZATION OF WIRE SAMPLES

Some initial resistivity curves were measured for three samples. Two were as drawn yttrium 1-2-3 and 2212 material, and the other was a piece of 2212 sintered at 840°C and removed from the furnace immediately. The resistivity samples consisted of 1-inch-long pieces of the wire with standard four-probe current and voltage leads soldered to the silver cladding. The as-drawn samples did not exhibit superconductivity. The sintered 2212 sample did show a superconducting transition, but zero resistance was not reached until about 45 K. Bulk 2212 material usually begins its transition at 80 K. The critical current may have been exceeded during the test, resulting in the lower apparent T_c . The test current was 250 mA, which is higher than what is usually used. The unusually high current was necessary to produce easily measurable voltage drops across the sample. The voltage drops for a given current were lower than usual because of the highly conductive silver sheath. The test current used implies that the critical current of the sample was only a few A/cm². It was decided that in the future, the silver would be stripped from the samples to allow electrical measurements to be made without the complications introduced by the silver sheath.

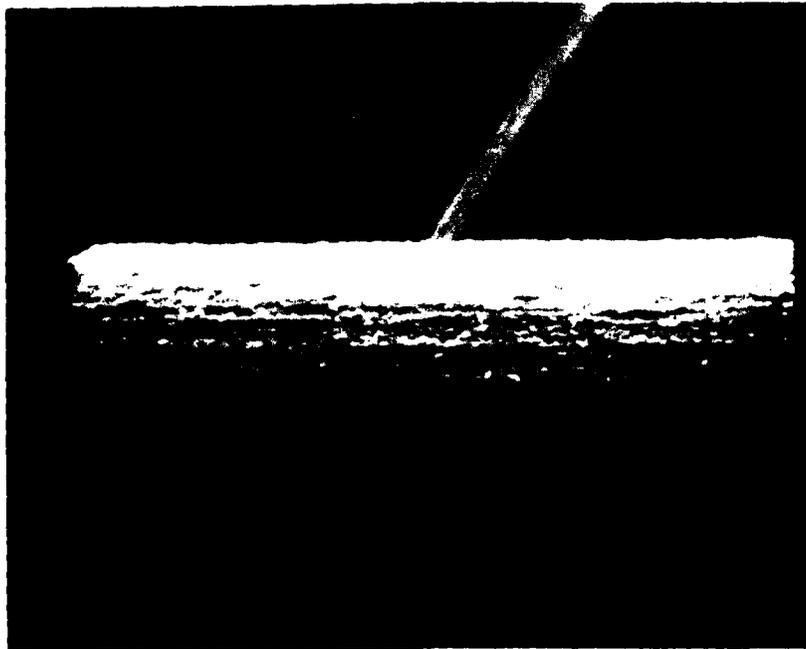
After several techniques were tried (i.e., nitric acid and electrolysis), it was found that the best way to remove the silver sheath from the wire was to use hydrogen peroxide in ammonia. A 1-cm length of silver sheathing could be removed from a piece of wire in less than 5 minutes without any obvious attack on the superconducting ceramic. Stripped pieces were rinsed in isopropyl alcohol and dried in air.

Examination of a section and a portion of the sintered 2212 material with the silver sheath removed (Fig. 30 and 31) showed a fairly well compacted and sintered core, although compaction was somewhat poorer near the center of the core. Low-magnification optical viewing of a piece of yttrium 1-2-3 material with the silver stripped away showed the piece to be in remarkably good condition, with no sign of the microcracks after heat treatment that had been observed by other workers.⁴ Observation of the piece in the SEM at 100 X (Fig. 32) showed the outer surface to be somewhat grooved in the direction of pulling. Higher magnification of the surface (Fig. 33) showed it to be typical of 1-2-3 material except the grains may be slightly smaller than what is normally observed. This may be because the sample was removed from the furnace and allowed to cool in air rather than to cool in the furnace at a slower rate.



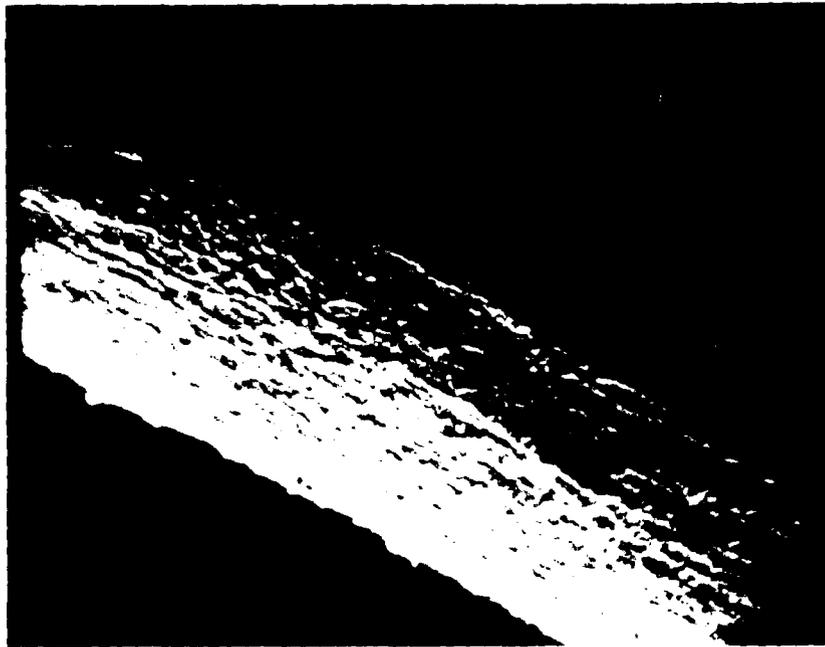
100x

Figure 30. SEM image of sintered bismuth 2-2-1-2 composite wire.



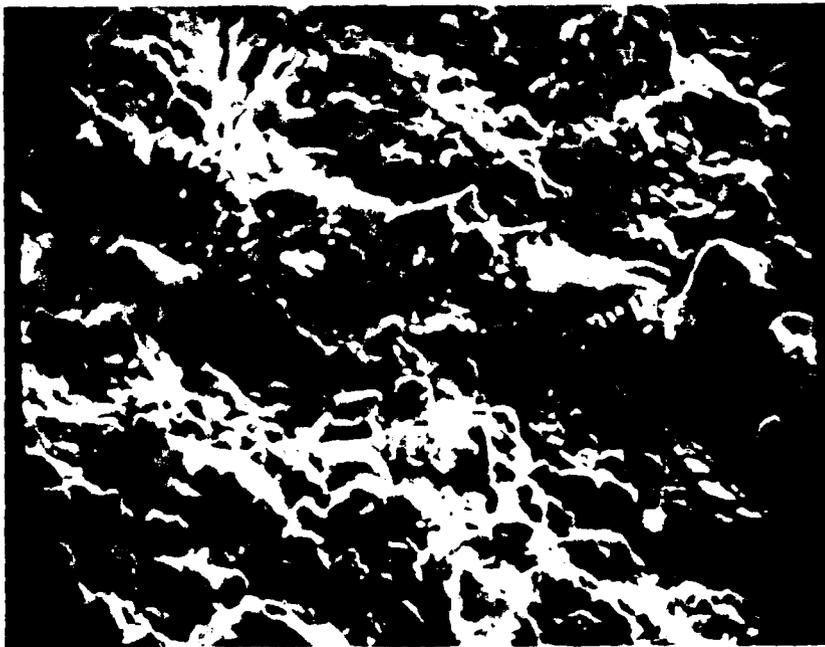
60x

Figure 31. SEM image of bismuth 2-2-1-2 wire with silver sheath removed.



100x

Figure 32. SEM image of heat-treated yttrium 1-2-3 wire with silver sheath removed.



1800x

Figure 33. SEM image of surface of sample in Fig. 31 at higher magnification.

A procedure for preparing samples for electrical tests was developed. Approximately 0.5 cm of each end of a 1-inch wire sample was first coated with solder. The appropriate current and voltage probe connections were made to this soldered area. The sample was then attached to the substrate (a 1-inch-square piece of anodized aluminum) with varnish. Enough varnish was used to cover the wire connections so that bending the connecting wires did not strain the bond between the leads and the superconducting wire, and so that the superconducting wire remained immobile on the substrate. After the desired number of samples were attached to the substrate, the whole assembly was immersed in the ammonia peroxide mixture to strip silver away from the middle of the wire sample. The solder and varnish provided protection for the ends of the sample. One of the samples prepared in this manner is shown in Fig. 34.

Current and resistance measurements of samples were made. Figure 35 is a resistance curve for a piece of leaded bismuth-based 2-2-2-3 flat wire. The results of the critical current measurements are summarized in Table 1.



Figure 34. Superconductor wire samples prepared for J_c measurement.

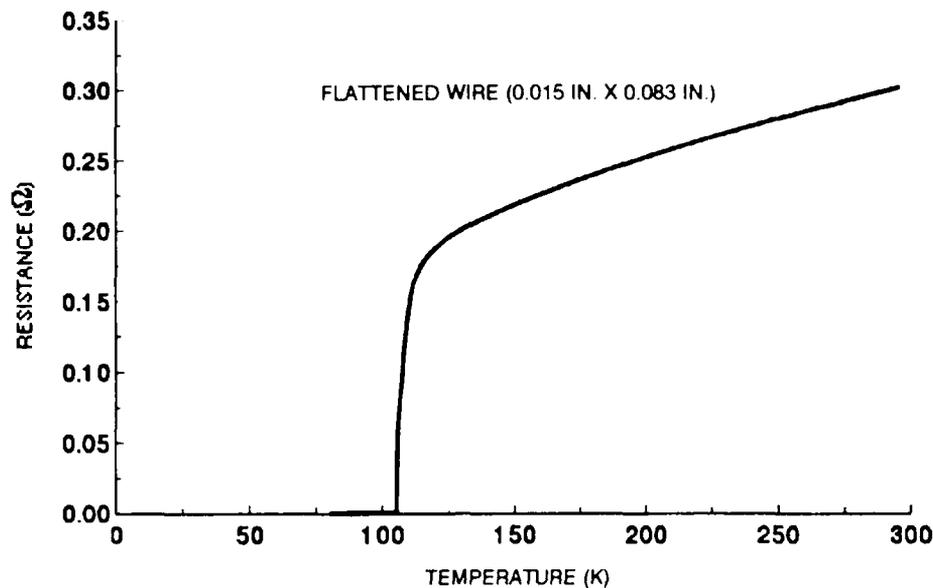


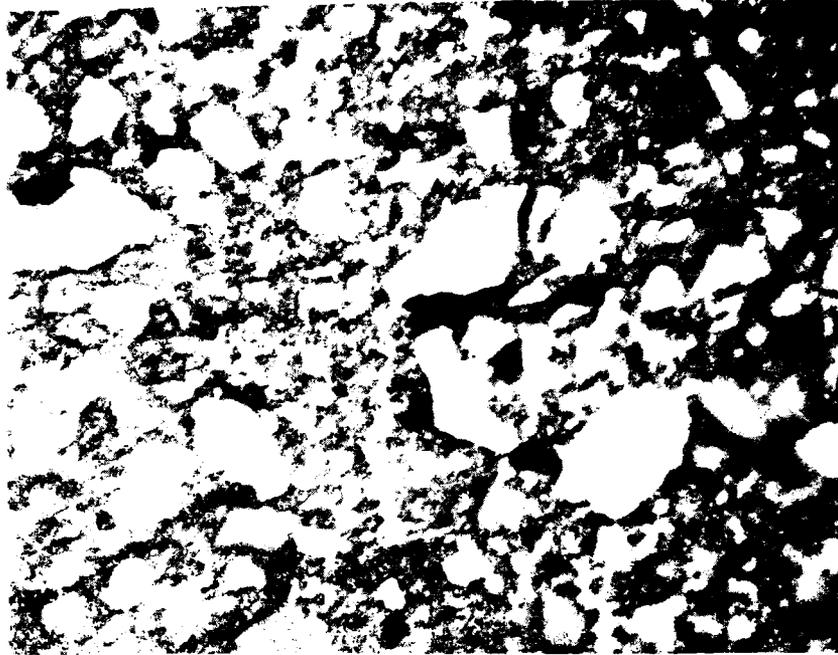
Figure 35. Resistance curve for leaded bismuth 2-2-2-3 flat wire.

Table 1. Critical current measurements.

Material	Heat Treatment	J_c (A/cm ²)		
		30 K	45 K	77 K
Bi 2212	15 hr @ 845°C	0.28	-	-
Bi 2223	15 hr @ 845°C	-	-	74
Bi 2212	3 hr @ 845°C	0.87	0.44	-
Bi 2223	26 hr @ 845°C	-	-	2.7
Bi 2223	26 hr @ 845°C (Flat wire, sheath removed)	-	-	450
Bi 2223	26 hr @ 845°C (Flat wire, sheath not removed)	-	-	660

The yttrium 1-2-3 wire did not superconduct. This is not too surprising, since no oxygen anneal was performed on this sample. An optical micrograph of the sample (Fig. 36) showed some very small grains of well-twinned material in a matrix of somewhat more amorphous material. Elemental dot mapping in the SEM showed that the matrix material had essentially the same composition as the twinned grains. Most likely the matrix material is the under-oxygenated tetragonal phase, which does not superconduct, while the twinned grains are good superconductor.

The critical currents of the bismuth 2-2-2-3 material were markedly better than those of the bismuth 2-2-1-2 material. This is somewhat surprising, since the 2-2-1-2 material showed the best compaction. Also the 2-2-1-2 material appeared to be mostly single phase (Fig. 37), while the 2-2-2-3 material contained significant amounts of extraneous nonsuperconducting phase material (Fig. 38). Note that wire that had been pressed flat had significantly better critical currents than cylindrical wire subjected to the same heat treatment. Flat-pressing probably increased the compaction and perhaps caused some alignment of the superconducting grains. Unfortunately, enough samples were not measured to either characterize the effect of heat-treatment time on critical currents or statistically show the benefits of flat-pressing the wire.



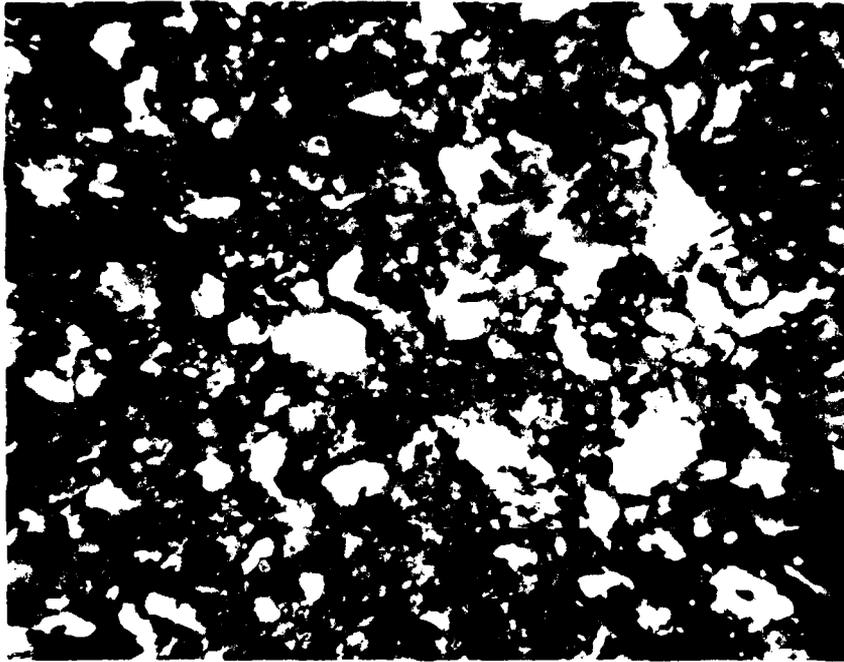
800x

Figure 36. Optical micrograph from yttrium 1-2-3 wire, longitudinal section.



400x

Figure 37. Optical micrograph of bismuth 2-2-1-2 wire, longitudinal section.



400x

Figure 38. Optical micrograph of bismuth 2-2-2-3 wire, longitudinal section.

CONCLUSIONS

This work shows that composite wires made of cores of high-temperature superconducting ceramic with silver cladding can be drawn and heat-treated to produce wire segments that do superconduct. The as-drawn wires have sufficient ductility to be wound into solenoids, although the ability of a heat-treated solenoid to conduct a supercurrent has not been tested.

The single attempt at the *in situ* oxygenation of yttrium 1-2-3 superconducting wire by the addition of barium peroxide to the powder core was not successful. Additional experiments would be necessary to explore the effect of higher oxygen additions and heat-treatment variations on the production of superconducting orthorhombic phase material.

The critical currents observed in even the best wire samples were not particularly good. However, the wires tested here probably did not have an optimum heat treatment. Other workers⁷ have observed critical currents in excess of 10^3 A/cm² in leaded bismuth 2-2-2-2 wires. Their critical currents were found to increase as the wire was pressed flat to smaller thicknesses. This is similar to our result that wire that had been pressed flat had better critical current performance than the cylindrical wire from which it had been pressed.

The methods used here to produce composite superconducting wire are very effective at producing small samples of wire for test purposes. The 54-inch lengths that can be produced yield a large number of smaller samples that can be subjected to additional processing (e. g., heat treatment or pressing). Wire production and testing in this manner could easily be run concurrently with a program to improve the superconducting current-carrying capacity of bulk materials. Efforts of this sort are bound to increase the performance of high T_c conductors.

REFERENCES

1. Van Wees, A. C. A., Hoogendam, P., and Veringa, H., "Development of High Current Nb₃Sn Multifilament Superconducting Material Following the ECN Powder Method," *IEEE Transactions* vol. 19, no. 3, pp. 556-559, May 1983.
2. Jin, S., Sherwood, R. C., Van Dover, R. B., Tiefel, T. H., and Johnson, D. W., Jr., *Appl. Phys. Lett.*, **51**, 203 (1987).
3. Flukiger, R., Muller, T., Goldacker, W., Wolf, T., Seibt, E., Apfelstedt, I., Kupfer, H., and Shauer, W., *Physica C*, pp. 153-155, 1574 (1988).
4. Kohno, O., Ikeno, Y., Sadakata, N., and Goto, K., *Jap. Jour. of Appl. Physics*, **27**, L77-79 (1988).
5. Kao, M., *Materials Letters*, **6**, 53 (1987).
6. Salama, K., Selvamanickam, V., Gao L., and Sun, K., *Appl. Phys. Lett.*, **54**, 2352-54 (1989).
7. Kawashima, M., Nagata, M., Hosoda, Y., Takano, S., Shibuta, N., Mukai, H., and Hikata, T., *IEEE Trans. on Magnetics*, **25**, 2168-70 (1989).

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