

N 93 - 27575

DEVELOPMENT OF SUPERCONDUCTING $\text{YBa}_2\text{Cu}_3\text{O}_x$ WIRES WITH
LOW RESISTANCE ELECTRICAL CONTACTS

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p. 15

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SUMMARY

Materials exhibiting superconductivity above liquid nitrogen temperatures (77 K) will enable new applications of this phenomena. One of the first commercial applications of this technology will be superconducting magnets for medical imaging. However, a large number of aerospace applications of the high temperature superconducting materials have also been identified. These include magnetic suspension and balance of models in wind tunnels and resistanceless leads to anemometers. The development of superconducting wires fabricated from the ceramic materials is critical for these applications. The progress in application of a patented fiber process developed by Clemson University for the fabrication of superconducting wires is reviewed. The effect of particle size and heat treatment on the quality of materials will be discussed. Recent advances made at Christopher Newport College in the development of micro-ohm resistance electrical contacts which are capable of carrying the highest reported direct current to this novel material is presented.

*Supported by NASA Grant NAG 1-796

**Supported by NASA Grant NAG 1-820

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INTRODUCTION

The high temperature superconductivity research program at Langley Research Center is focused on developing technology required for the early application of the new high temperature superconducting materials to aerospace systems. The near term effort addresses the fabrication of superconducting wires utilizing a process proven successful for making wires from ceramic materials. Superconducting wires will find use in airborne and spacecraft platforms as interconnects between electronic devices and to ground planes at 77 K (liquid nitrogen temperatures). Important to the exploitation of the effort to develop electronic devices (detectors, etc.) is the development of low resistance contacts which are compatible with existing electronic technology. The long term objective will merge these efforts into the development of a Superconducting-Insulating-Superconducting (SIS) thin film detector for 100 micron radiation for atmospheric remote sensing.

The following report summarizes the results of the research efforts on sample preparation techniques, the development of low-resistance contacts to the new superconducting material and the progress in forming superconducting wires using c-shaped carbon forms.

SAMPLE PREPARATION TECHNIQUE

This section focuses on the procedure for preparing $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) superconducting samples using the sintering (solid-state reaction) method. The starting materials for our samples are oxide and carbonate powders. The purities of the starting materials are as follows: BaCO_3 - 99.997%; Y_2O_3 - 99.999%; CuO - 99.999%. The sintering method involves several steps of mixing, grinding and heat treatment (ref. 1). Systematic studies for producing better quality samples (capable of carrying relatively larger current densities) resulted in the following procedure:

- 1) Mixing powders of BaCO_3 , Y_2O_3 and CuO using a mixer/mill machine.
- 2) Pressing pellets of 1/2" diameter using a 10 ton hydraulic press, and treating these pellets in a split tube furnace at 950 C for 8-12 hrs in air.
- 3) Regrinding the material in alcohol slurry using the mixer/mill machine; heating the slurry to remove alcohol, and repeating step 2.
- 4) Regrinding the material in alcohol slurry using the mixer/mill machine, heating the slurry to remove alcohol, and pressing the resulting powder to form 1/2" pellets for the final O_2 treatment.

- 5) Retreating the pellets in oxygen flow (0.2 lpm in a 1" diameter quartz tube) at 950 C for 24 hrs, cooling down the pellets to 700 C and treating for 16 hrs, then cooling to 400 C and treating for 5 more hours.

The resulting samples are hard, black and brittle. Resistance measurements indicate a sharp superconducting transition with an onset temperature of 93 K and a transition width of 1 K.

Figure 1 shows the resistance of two samples after air treatment. One sample was pressed into a pellet before the air treatment while the other was treated as compacted powder. They were subsequently given an additional air treatment as pellets. It is clear that we get better results by pressing the samples before the air treatment.

Figure 2 shows the effect of duration of the air treatment. All samples were given the initial air treatment indicated on the graph followed by a 24 hour air treatment and oxygen treatment. The resistance results suggest that treating samples for periods of 8 to 12 hrs is sufficient to produce a transition temperature of 92 K and little improvement for samples treated for longer periods. Similar results were obtained for the time of the second air treatment.

Figure 3 shows the effect of hand grinding (HG) where the sample was ground by hand using a mortar and pestle, machine grinding (MG) using a mixer/mill machine, and machine grinding in alcohol (AG). All samples underwent two air treatment and a final oxygen treatment. Alcohol ground sample has a higher transition temperature.

We have found that using the results in figures 1-3 to develop the sample preparation procedure described earlier results in dense samples with mass density of 5.7 g/cm^3 (90% of the theoretical value) and a relatively larger current density that is limited only by grain effects present in polycrystalline bulk superconductors (ref. 2). Using this procedure we obtained critical current density J_C of 200 A/cm^2 at 77 K and J_C of 480 A/cm^2 at 20 K.

LOW-RESISTANCE CONTACTS

Since the new high T_C superconductors are ceramics, electrical contact to these novel materials presents a challenge. While silver paste and pressure

contacts can be used to measure the resistive transition, their inability to carry large currents without burning out make them unsuitable for determining large critical currents directly or for use in high current carrying applications (refs. 3 and 4).

Following previous work on gold contacts to sapphire (ref. 5), we form the contacts by placing small squares of gold foil on the surface of a shaped resistivity sample that has been cut from a fully oxygen treated pellet. The gold squares are ≈ 1 mm on a side (or less) and 0.1 to 0.3 mm thick (the thicker pieces for current contacts and thinner for voltage contacts). We then bring the sample to ≈ 1065 °C in air in from one half to one hour. The gold melts and diffuses into the sample pores. The sample is removed from the oven once it has cooled to ≈ 900 °C. At this point the gold bead that is formed is slightly oxidized and firmly connected to the sample; however, the contact resistance is high (\approx kohms). Since some of the oxygen is lost from the sample during this process, retreatment in oxygen is necessary.

Restoration of the superconducting properties and good electrical contact are achieved by the following: expose to flowing oxygen (≈ 0.2 lpm) at 900 °C for 24 hr, 700 °C for 16 hr, and 400 °C for 8 hr. The slight oxide coating remaining on the gold bead after retreatment is abraded off before soldering wires to the bead for measurement. It is easy to solder external leads to the beads making good electrical contact. Lead-tin solder can be used if the temperature of the soldering iron is kept to a minimum. This relatively simple technique promises to be of practical use in many applications of high T_C superconductors.

Figure 4 shows a macroscopic scanning electron microscope (SEM) picture of a typical bead of diameter ≈ 1 mm with a copper wire soldered in place. All measurements of resistance were made in a closed cycle refrigerator capable of covering the temperature range of 15 to 300 K. The samples were mounted on a copper block with GE varnish for thermal contact and lens paper soaked in GE varnish for electrical insulation. A calibrated platinum thermometer (good to 0.1 K) mounted in a well directly below the sample was used to measure the temperature. A four probe dc method was used to measure the resistance of the sample and the contact resistance (see inset of figure 5). Each data point represents an average of twenty readings with the current reversed each time to eliminate thermal offsets (with a precision of $\approx 0.1\%$). Figures 5 and 6 show typical resistance vs temperature runs using gold bead contacts and silver epoxied leads bonded to sputtered gold films. Each figure

displays the resistance of the sample only (curve a) and the resistance of the sample plus two current contacts (curve b) after adjusting for the different length of sample between the current and voltage leads. Our best sample contacts show resistances of $< 50 \mu\Omega$ below the superconducting transition and $< 18 \text{ m}\Omega$ at room temperature. We can only report an upper limit since the resistance we measure includes the solder and gold bead. Since the area of the beads is typically 0.01 cm^2 the surface resistivities are $< 0.5 \mu\Omega\text{cm}^2$ and $180 \mu\Omega\text{cm}^2$ respectively. Figure 6 shows that the contact resistances for epoxied leads bonded to sputtered gold films is considerably higher: $\approx 0.2 \Omega$ per contact at 77 K. The gold bead contacts are clearly superior.

Poor contact hampers direct measurement of critical current densities. With silver paint contacts we were typically obtaining critical current densities up to 30 A/cm^2 which did not vary much with temperature. Feeling that these were spurious due to the local heating effects of the high resistance of the silver paste contacts (especially once they burn out), we made measurements on similar samples with the gold bead contacts. We obtained 200 A/cm^2 at 77 K and $> 480 \text{ A/cm}^2$ at 20 K. A current of 7.5 ampere was passed through the sample while making the critical current measurement at 20 K in vacuum with the sample bonded to a copper block. If the contacts can perform that well in vacuum, they should present no problem in high current carrying applications where the devices will most likely be immersed in liquid nitrogen.

The strength of the contact was determined by measuring the force necessary to cause shear failure of a contact of given area. The results varied among the samples so we report the range, the average value, and the standard deviation of the shear strength. The gold beads ranged from 5 to 23 MPa with an average of $13 \pm 6 \text{ MPa}$; the epoxy ranged from 4 to 11 MPa with an average of $8 \pm 3 \text{ MPa}$; and the silver paste ranged from 0.6 to 1.7 MPa with an average of $1.2 \pm .8 \text{ MPa}$. The gold bead contacts were the strongest, having a shear strength about 1/20 that of iron while that of the silver paste was about the same as concrete. In some cases the sample failed before the gold bead contact.

The contacts have the clear advantage of being reasonably robust making it possible for the leads attached to the contacts to withstand mechanical stress without need for support.

DEVELOPMENT OF SUPERCONDUCTING WIRE

Clemson University has recently demonstrated a technique to produce ceramic fibers using its C-shape carbon fibers (reference 6). In this technique, ceramic fibers are formed by filling c-troughs of the carbon fibers (CF) (fig. 7) with a ceramic precursor sol or a fine slurry followed by pyrolyzing the CF. This technique was thought to be equally applicable in fabricating superconducting fibers from the new ceramic oxide superconductor.

Since the discovery of the new ceramic high T_c superconductor, Clemson University has also developed a simple way (refs. 7 and 8) to produce high quality YBCO powder. Moreover, it has developed a method to produce a YBCO material by way of a homogeneous solution called a sol-gel technique. Thus, it is the objective of this study to develop methods to obtain strong and flexible fibers or wires which are superconducting above the temperature of the boiling point of liquid nitrogen.

The C-shape of CF were produced by the procedure described in reference 6. Two kinds of C-shape CF were used. One is heat treated at 240 C for crosslinking and the other one is carbonized at 1500 C. YBCO sol was prepared by dissolving alkoxides of yttrium and barium and copper cyclohexanebutyrate in an organic solvent in a nitrogen atmosphere under refluxing conditions: A YBCO powder dispersion (b) was prepared in the following steps. The carbonized CF were pretreated to improve wetting by YBCO A or B. The pretreatments included soaking the CF in concentrated HNO_3 , heating in air @400 C, or soaking in ethanolic 3-aminopropyltriethoxysilane. Bundles of the uncarbonized CF and the surface treated carbonized CF were dipped into YBCO A or B. The wet fibers were dried in air followed by heat treatments in air, oxygen or nitrogen at 500 C, 600 C or 900 C. To prevent CF from oxidizing, the YBCO coated fibers were heat treated in nitrogen gas at 900 C followed by oxygen annealing at 400 C. In some cases, silver oxide powder (10-50 V/O) was added to YBCO B to furnish oxygen in situ for firing in nitrogen gas and the resulting silver to increase ductility of the fibers. Cotton threads in various lengths were impregnated with YBCO A or B followed by direct heat treatments at 910 C in air, or the impregnated threads were coated with silver paint prior to heat treatments. Resistance vs temperature curves were obtained by using AC four-point probe and silver paste and indium pads.

Figure 8 shows an SEM micrograph of the YBCO powder used in the slurry B. It shows submicron size of particles after 8 hrs. ball-milling in ethanol.

Figure 9 shows the superconducting transition temperature of 94 K where the resistance is zero. As shown in figure 10, a wafer derived from YBCO sol A after firing in air has no transition above 77 K. This is thought to be the incorrect stoichiometry of the sol. The composition of the sol is currently being determined. Figure 11 shows the CF after coated with YCO A or B with or without silver oxide followed by heat treatments in nitrogen at 940 C for 2 hours and oxygen annealing at 400 C for 8 hours. The YBCO containing CF were too brittle and showed little strength. These poor mechanical properties should be caused by the reactions between carbon and YBCO during nitrogen firing and/or the oxygen annealing at 400 C. It is conceivable that carbon provides a reducing condition during the firing in nitrogen gas. In that case, oxygen annealing should have no effect in restoration of the superconductivity of the fibers.

Figure 12 shows wires produced by impregnating a cotton thread and coated with silver paint followed by firing in air for 6 hours at 910 C. The wires are flexible and mechanically moderately strong. However, the surface is not so uniform resulting from the all manual process. Figure 13 shows a resistance versus temperature curve indicating the wires are superconducting above 77 K. The low resistance throughout the temperature region is due to the silver conductivity. It clearly shows the superconducting transition above the liquid nitrogen temperature. The wire showed good ductility originating from the silver. Refinement of the technique to produce more uniform surface of the wire is underway.

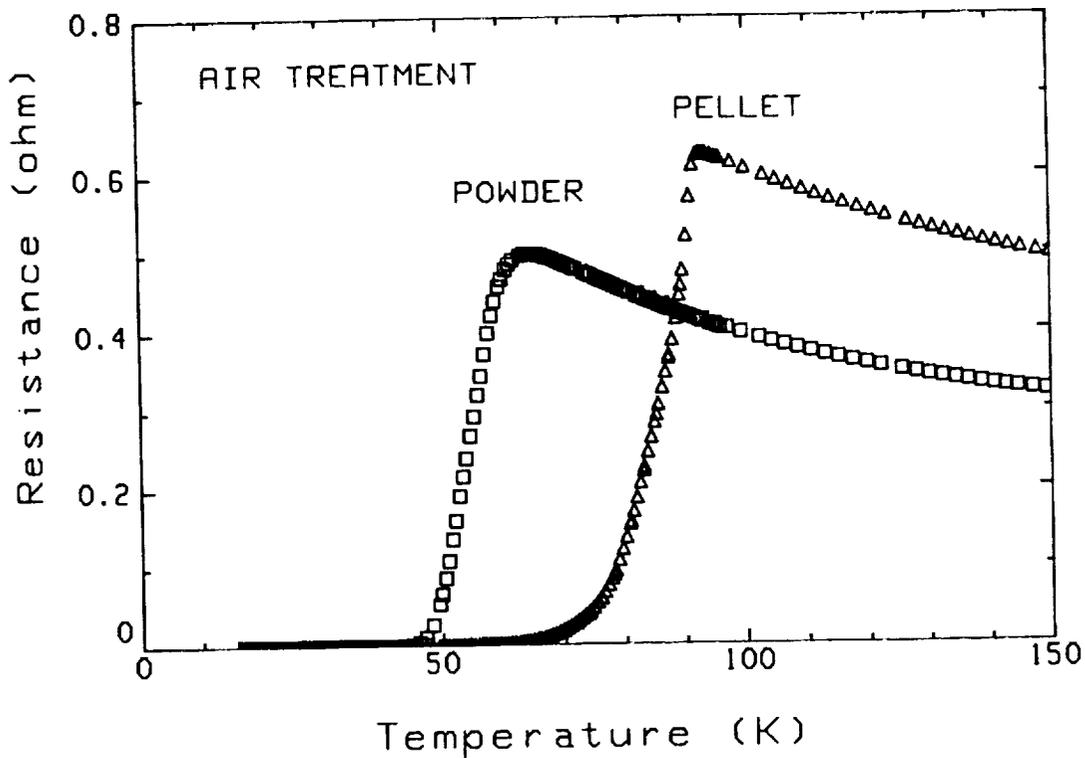
ACKNOWLEDGMENTS

We wish to acknowledge the efforts of Raquel Caton and Robert Harvey for preparing samples.

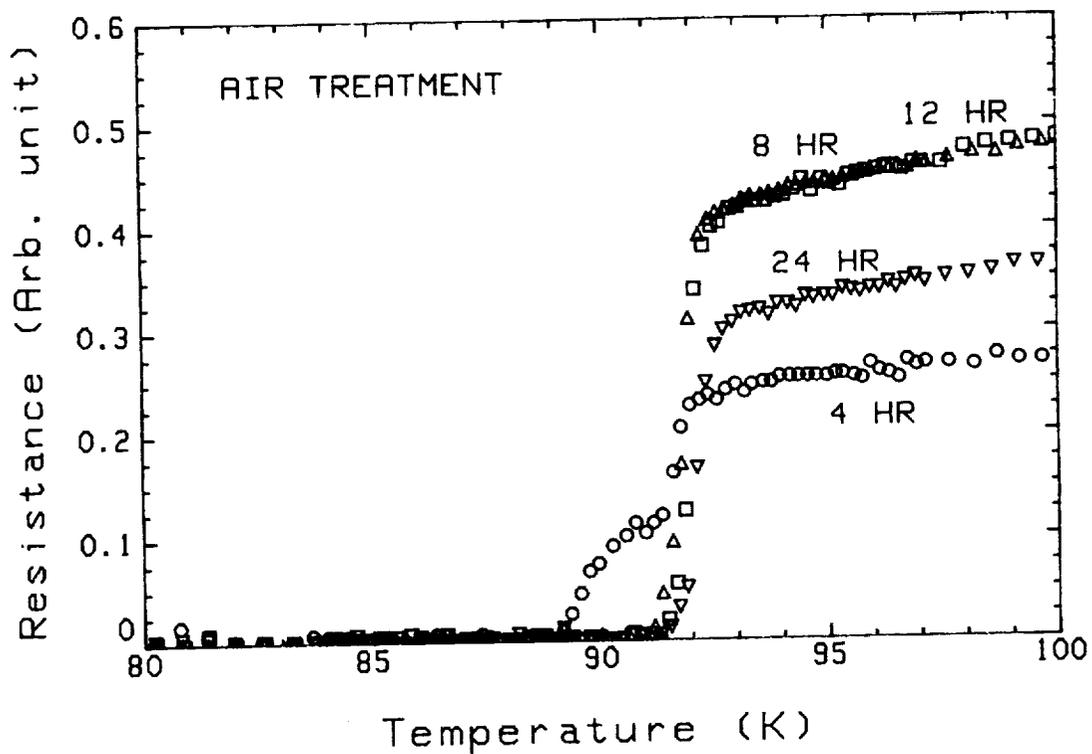
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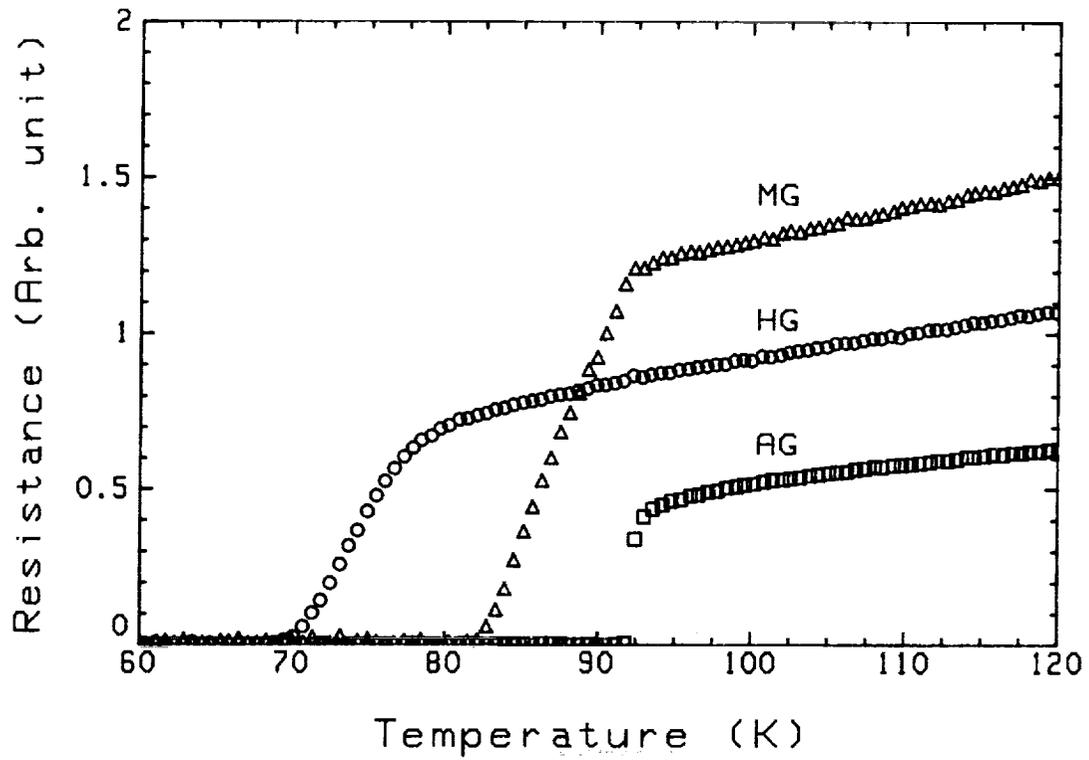
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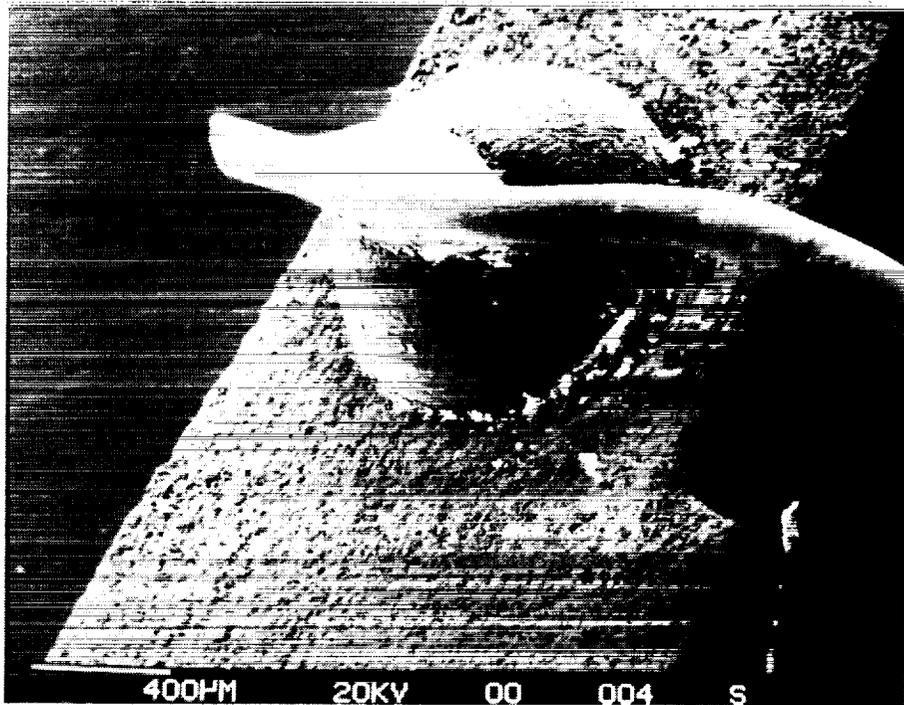
1. Resistance vs temperature for a pressed pellet and a compacted powder sample.



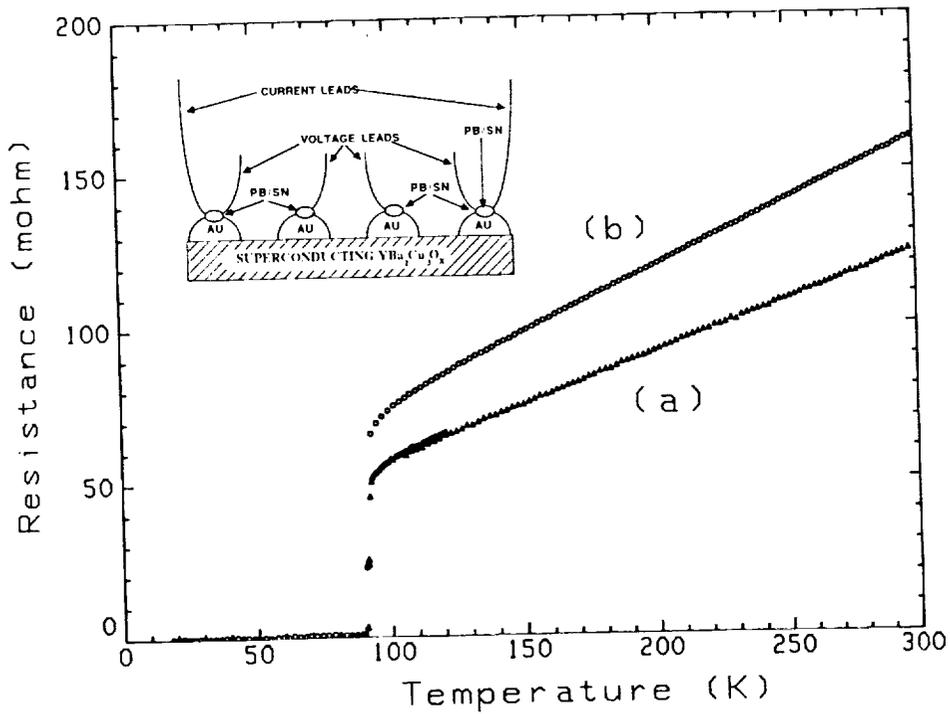
2. Resistance vs temperature for 4 samples showing the effect of air treatment for 4, 8, 12 and 24 hours.



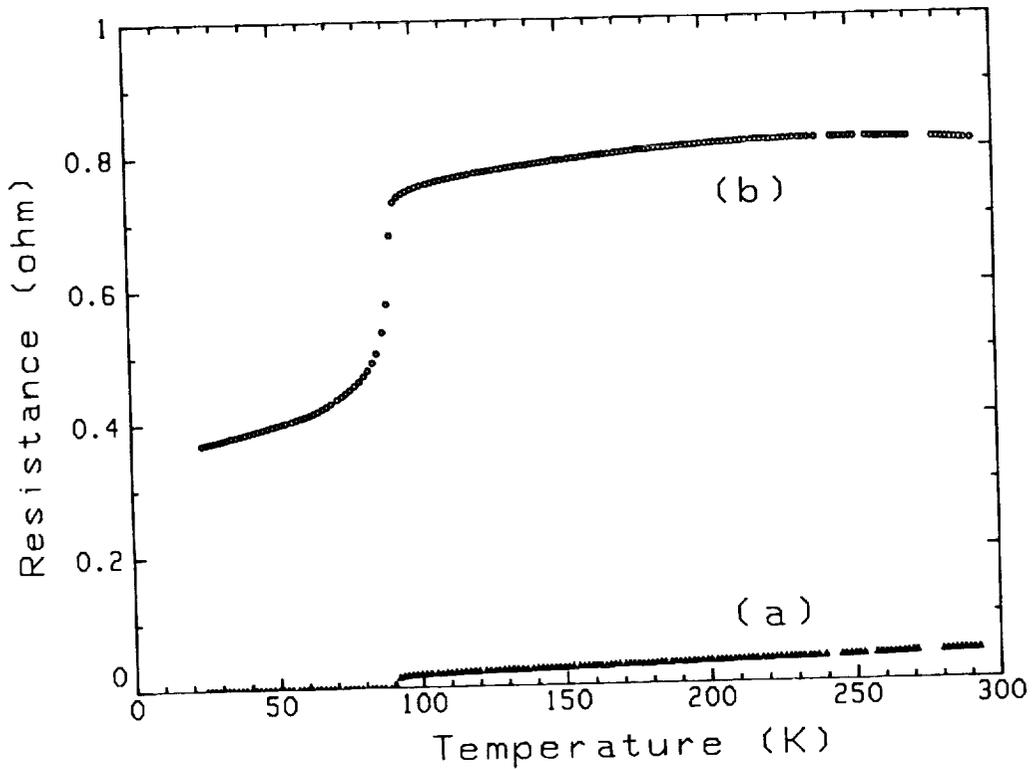
3. Resistance vs temperature for 3 samples showing the effect of hand grinding (HG), machine grinding (MG) and grinding in alcohol slurry (AG).



4. Macroscopic SEM picture of a gold bead contact with a soldered copper lead.



5. Resistance vs temperature for the gold bead contacts. Curve a is the resistance of the sample only. Curve b includes the resistance of two contacts. The inset is a schematic diagram of the contacts made to the sample for resistance measurement.



6. Resistance vs temperature for the epoxy to metal film contacts. Curve a is the resistance of the sample only. Curve b includes the resistance of two contacts.

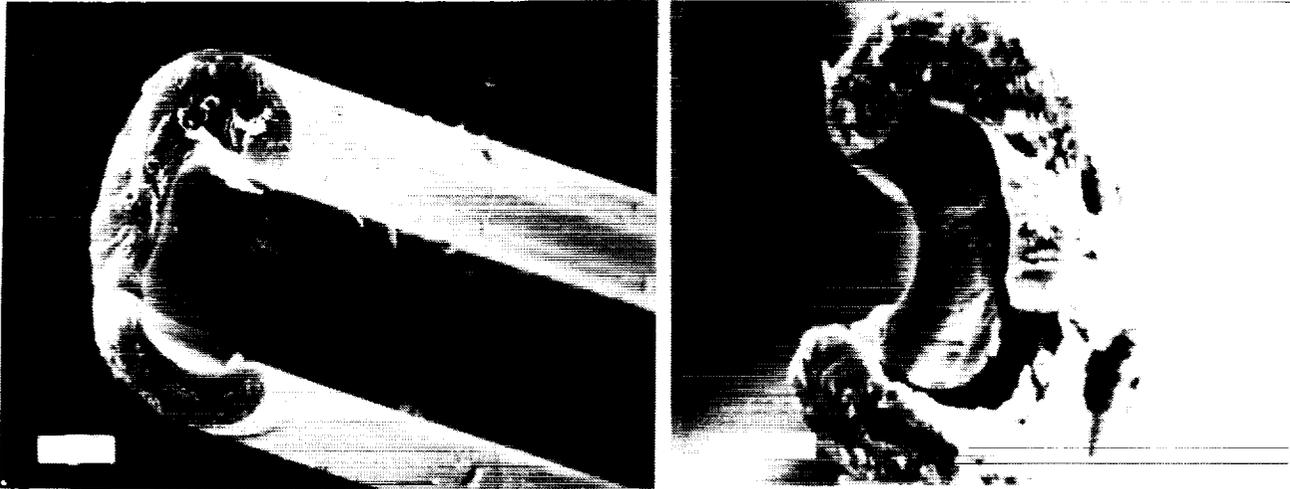


Figure 7. A C-shape carbon fiber derived from a petroleum pitch (left), the C-trough filled by a silica precursor sol (right).

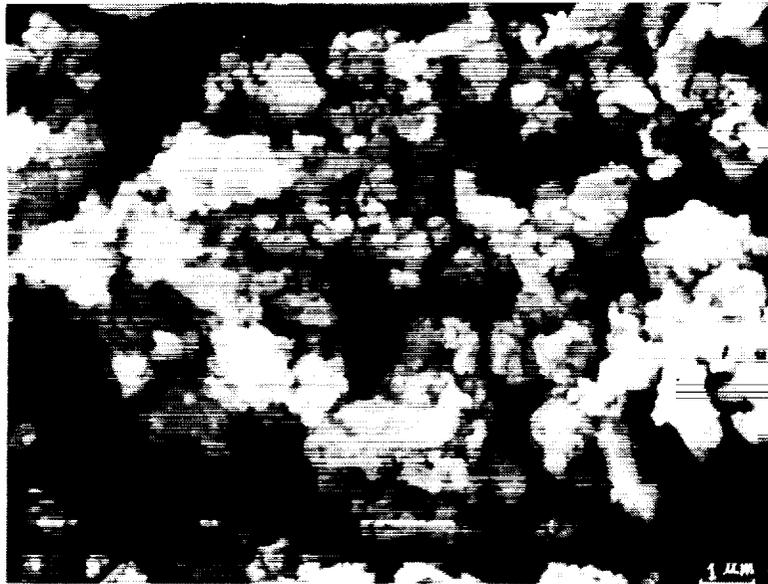


Figure 8. A scanning electron micrograph of YBCO powder after ball milling.

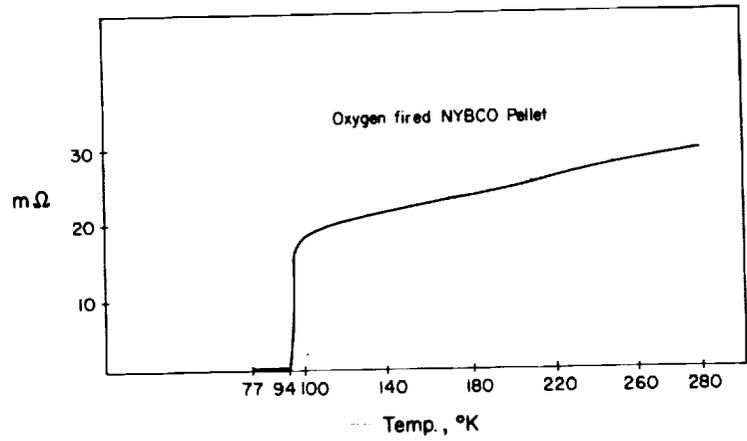


Figure 9. Resistance as a function of temperature for YBCO powder derived directly from nitrates of yttrium, barium and copper.

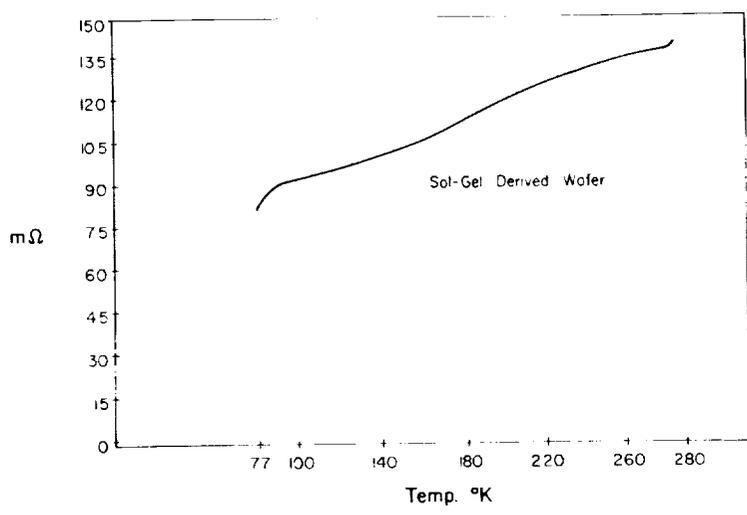


Figure 10. Resistance as a function of temperature for Sol A.



Figure 11. CF before dipping in YBCO Sol (left) and after dipping and firing (right).

Figure 12. Superconducting wires produced by impregnation of cotton threads.

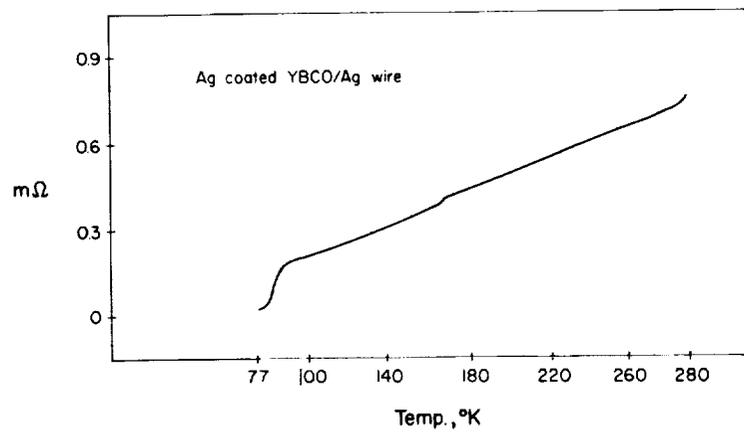


Figure 13. Resistance as a function of temperature for wires in figure 12.

