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ABSTRACT

Silver was added to $YBa_2Cu_3O_x$ (123) powder by a melt technique using $AgNO_3$ and heated to ~600°C to decompose the nitrate. This process yields 123 powder that is uniformly coated with Ag, as indicated by optical and scanning electron microscopy (SEM). The composite powder is formed into rods (~4 mm diameter) via drawing and swaging through conical converging dies. Wires of finer diameter (~1 mm) and substantially greater linear uniformity have been produced by slurry extrusion of the composite powder in a polymeric vehicle. Transport critical current density, J_c, of these wires at present is about 750 A/cm^2. This value may be expected to rise due to further reduction of second phase impurities localized at grain boundaries and better understanding of the Ag/superconductor interface. This paper describes the wire fabrication in some detail and discusses the results of microscopic analyses by scanning electron microscopy (SEM), X-ray photoemission spectroscopy (XPS), and X-ray diffraction (XRD).

INTRODUCTION

The most useful shape of an electrical conductor is wire, with a round or a rectangular cross section or a ribbon, which can be conveniently made into a coil. It is, therefore, necessary to develop procedure(s) to convert the recently discovered high temperature superconductors into coilable forms. Since these materials are oxides, they are inherently brittle and present a challenge as far as conversion to wire form is concerned. During the past year, many efforts [1-3] have focused attention on this aspect with varying degree of success. The most logical approach appears to be one in which a very ductile metallic matrix is utilized to impart formability to the oxide [4]. Silver is a preferred matrix because it does not react with the superconductor even above its melting point (960°C) [5].

Obviously, for good fabricability and electrical properties, the distribution of the Ag matrix and the $YBa_2Cu_3O_7$ ceramic must be very homogeneous. The powder mixing procedures applicable for metal matrix composites are inadequate. Very high concentration (>75 volume %) of the oxide is mandatory to maintain superconduction in the composite. It was discovered that the unique physical properties of silver nitrate allow the attainment of a very homogeneous coating of Ag on the superconductor particles. Various wiremaking methods can be applied to this composite powder for processing into a coilable superconducting wire of high quality. Equally important, the approach is generic and may be applicable to all present oxide superconductors and those yet to be invented.

EXPERIMENTAL PROCEDURES

Silver nitrate is a white crystalline solid with a melting point to a liquid phase at 222°C. The liquid decomposes as its temperature is raised to 444° evolving nitrogen oxides and leaving only a high purity Ag deposit. Appropriate amounts of $AgNO_3$ and superconductor oxide powder were weighed and mixed in a mortar and pestle. The mixture then was heated on a hotplate in a glass beaker to melt the nitrate (>222°C) and wet the

powder completely by stirring. After cooling, the mixture was ground to break up the aggregates into a fine powder. The mixture was transferred to an alumina crucible and heated to ~600°C to decompose the nitrate. This "composite" powder was used for all experiments described.

The composite powder was formed into a wire by swaging. Typically, the powder was packed into a copper or silver tube as shown schematically in Figure 1. Tube size and drawing die size sequence are shown in Table 1. The copper tubes, which required intermediate annealing during the swaging process, proved reactive towards 123 even at the relatively low annealing temperature (e.g., ~400°C). This mandated the use of silver tubes to avoid degradation of the123 powder.

Transition temperature and current carrying capacity were measured by the standard, 4-point method. Silver paste was utilized for connecting copper wire leads to the superconductor. In some later work, $AgNO_3$ itself was used for this purpose. It was observed that the very low resistance sheath both prevented proper O_2 anneal after swaging and rendered T_c and J_c measurements difficult because of current requirements and instrumental sensitivity. The silver sheath, therefore, was removed by machining to facilitate measurements on the wire core, composed entirely of the Ag/123 composite superconductor.

RESULTS AND DISCUSSION

Decomposition of silver nitrate may be represented by:

$$AgNO_3 \text{ ---------> } AgNO_3 \text{ (liquid)} \quad @\ 222°C$$

(Brown Fumes)

$$2AgNO_3 \text{ -------> } 2Ag + 2NO_2 + O_2 \quad @\ 444°C$$

The $AgNO_3$ liquid formed at >222°C is observed to have very low viscosity. As a consequence, it spontaneously flows, wets, and encapsulates the 123 powder. After further heating to above its melting point, the nitrate decomposes leaving a uniform and adherent deposit of Ag on the 123

powder. The optical microstructure of an agglomerate of $YBa_2Cu_3O_x$ (123) particles (dark areas) in a silver matrix is presented Figure 2. The silver coating is continuous with no readily observable porosity. Under high magnification SEM examination, a typical 123 particle in the as-received state is characterized by high surface area (Figure 3 at left). A similar particle after treatment with silver nitrate (Figure 3 at right) is devoid of all the surface asperities and morphological features, indicating that the process is capable of depositing Ag on large as well as fine particles. This feature of the process is very important because the coating is necessary to permit Cooper pairs to travel from one superconducting grain to the next. This phenomenon is commonly referred to as the "proximity" effect [6] and is necessary to enhance the coupling between the grain boundaries of the 123 particles.

It is pertinent to note here that the composite powder at this stage is only weakly superconducting. X-ray diffraction analysis was used to detect if there are any compositional changes occurring during the fabrication process. After decomposition of the $AgNO_3$, the XRD pattern consists mainly of Bragg diffraction lines corresponding to the combination of 123 phase and metallic silver. After the swaging and final annealing steps, the XRD pattern is qualitatively similar to that taken after the $AgNO_3$ decomposition with no alteration in composition except for a reduction in the amount of metallic Ag present. The percent ratio of intensity for the most intense Bragg line of Ag to that of 123 has decreased from 30 (value after the AgNO3 decomposition) to 17 after swaging and to 13 after final annealing. A reduction, and quite possibly agglomeration, of the Ag content is expected after annealing due to the high vapor pressure of Ag at the 900°C annealing temperature which is close to the Ag melting point of 960 °C. Furthermore, analysis of the XRD data presented in Table 2 indicates that significant change in the full-width-at-half-maximum (FWHM) and peak positions of the Bragg diffraction lines are taking place after the $AgNO_3$ decomposition, swaging, and final anneal steps. The origin of these changes is not yet understood, but it may be related to a change in the oxygen content of the sample or stresses introduced during processing. More work must be undertaken to correlate the physical state of the 123 material (with respect to strain,

degree of shear, etc.) during mechanical processing with its degree of retention of superconducting properties and, in turn, with the XRD spectra.

Table 2. Analysis of XRD Data

PROCESSING STEP	PEAK POSITION, 2θ	FWHM
As Received	32.550	0.272
	32.865	0.312
$AgNO_3$ Melt	32.550	0.255
(mixture)	32.865	0.328
$AgNO_3$ Decomposition	32.538	0.203
	32.844	0.243
Swaging	32.486	0.260
	32.817	0.296
Final Anneal	32.522	0.254
	32.834	0.305

X-ray photoemission spectroscopy (XPS) analysis of the near surface region of a 15 wt% Ag/123 pellet after swaging and final annealing have indicated a 20% reduction in the Ag content. XPS analysis also shows that the near surface region composition contains, in addition to the 123 phase, significant amounts of Ba and Y carbonate species. After removal of approximately an 0.5 micron thick layer from the surface by argon ion sputtering, the Ag content was 22% of its nominal value. This indicates a significant variation in the Ag content with depth from the top surface of the sample. These observations are consistent with those of XRD.

Initial swaging experiments were very ambitious. The preform was reduced from the starting outside diameter of 0.250" (6.35 mm) to as low as 0.030" (0.762 mm) without intermediate annealing. As mentioned previously, the high conductivity of Ag interfered with T_c and J_c measurements. The Ag/123 powder had suffered deformation beyond its formability limits, and "sausaging" familiar in the low temperature superconductor processing was encountered [7]. Swaging, therefore, was terminated at a convenient stage where the removal of the Ag sheath was possible by machining and the core material 0.155" (3.93 mm) was free from sausaging effects.

The effort thus far has been concentrated on material containing 15 wt% Ag based primarily on the knowledge that "percolation" effect is operative up to ~35 wt% Ag [8]. Furthermore, at about 15 wt% Ag, depending upon particle size, the volume of AgNO3 liquid is sufficient to adequately encapsulate the 123 powder mass. At lower concentrations, it is necessary to dilute the $AgNO_3$ with a nonreactive liquid, such as ethylene glycol, to provide adequate wetting volume. The powder was prepared in small batches and put through the swaging process (Figure 1). Typical curve of resistance and magnetic susceptibility vs. temperature for such rods after oxygen anneal are shown in Figure 4. The relatively high density (~90-95%) of the material in the swaged rod probably contributes to the sharpness of the transition. The J_c values, however, did not exceed 200 A/cm^2. Increasing the annealing temperature to >950°C and the annealing time from 18 hours to 72 hours did not improve J_c. (Figure 4.)

The sensitivity of 123 and other compositions to environmental degradation is well documented [5,9]. To determine the protection provided by the coating, one sample exposed to laboratory air was tested several times in a period of 3 months. The measured Jc value remained constant (~150 A/cm^2). Such is not the case with pure 123 samples. A decrease in J_c of 40% or more was common with the latter after several weeks atmospheric exposure. This indicates that the silver coating is responsible for the stability of the sample.

WIRE EXTRUSION AT ARGONNE NATIONAL LABORATORY

The demonstrated expertise of Argonne National Laboratory (ANL), Argonne, IL, in the preparation and extrusion of high temperature superconductor compounds into wires and coils led to a cooperative effort in which ANL's 123 superconductor powder was treated with Ag by Naval Surface Warfare Center (NSWC) using the $AgNO_3$ process. The superconducting 123 powders are prepared by calcining the precursor mixture at about 800°C for 4 h in flowing oxygen at a total pressure of about 2 mm Hg [10]. Silver is added to this powder by the melt technique using $AgNO_3$. To prepare for extrusion, the composite powders are mixed with several additives to make a formulation that has enough fluidity to be easily formed into various shapes, but still has satisfactory strength in the green state. This formulation, known as a slip, consists in general of a solvent, a dispersant, a binder, a plasticizer, and superconductor powder [11]. This formulation is vibratory milled for 16 h. After milling, some solvent is allowed to evaporate from the above formulation. This yields a plastic mass that is forced through a die at high pressure to give a superconducting wire. Superconductor wires have been extruded at ANL with diameters between 0.1 and 3.0 mm and lengths up to 12 m. In the green state (i.e., before firing), extruded wires exhibit flexibility and can be easily formed into the shape of a coil.

The extruded wires and coils are fired in flowing oxygen at a reduced total pressure (about 2 mm Hg). This facilitates the removal of gaseous species formed during decomposition of the organic additives and prevents their reaction with the superconductor. After sintering coils are annealed in oxygen for 24 h. Transport critical current density of approximately 750 A/cm^2 in wires and about 300 A/cm^2 in a 15 turn coil are measured at 77 K.

SUMMARY AND CONCLUSION

A novel, yet simple process, has been developed to produce Ag coated 123 high temperature superconductor powder precursor for the preparation of wires and rods via swaging, extrusion, or other wiremaking

path. The swaging of silver coated 123 powder filled in silver tubes has been carried out successfully. Atmospherically stable rods and wires of 0.1-0.25" (2.5-6.4 mm) outside diameter have been produced. Measurements on short wire segments indicate a Tc of 92 K with relatively sharp transition region. The maximum J_c measured was about 200 A/cm^2. The rods were found to maintain their superconducting properties in laboratory ambient conditions for at least several months. A series of microscopic studies on the composite powder by XRD, XPS, and SEM revealed a reduction in the Ag content from its nominal value and also some unanticipated Ag non-uniformity in the annealed samples.

The collaborative effort with Argonne National Laboratory has led to the production of straight and coiled lengths of high temperature superconductor wire by an extrusion method using HTSC powders coated by the $AgNO_3$ process. These wires have a relatively fine diameter of 0.050" (1.27 mm). Jc measurements performed at 77 K on the wires indicate typically 750 A/cm^2 in straight sections and about 300 A/cm^2 in the coiled form.

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Ag TUBE = 0.290" O.D. 6" LONG
0.245" I.D.

CU TUBE = 0.365" O.D. 6" LONG
0.300" I.D.

POWDER WT: 12gms
DIE SEQUENCE FOR
Ag TUBE PREFORMS
1. 0.250" D
2. 0.234"
3. 0.203"
4. 0.187"
AFTER Ag JACKET REMOVAL: 0.155" D

POWDER WT: 15gms
DIE SEQUENCE FOR CU TUBE
PREFORMS
1. 0.335"D
2. 0.299"
3. 0.250"
4. 0.234"
5. 0.203"
6. 0.187"
AFTER CU JACKET REMOVAL: 0.155" DIA

TABLE: 1 DETAILS OF 1,2,3/Ag PREFORM PREPARATION

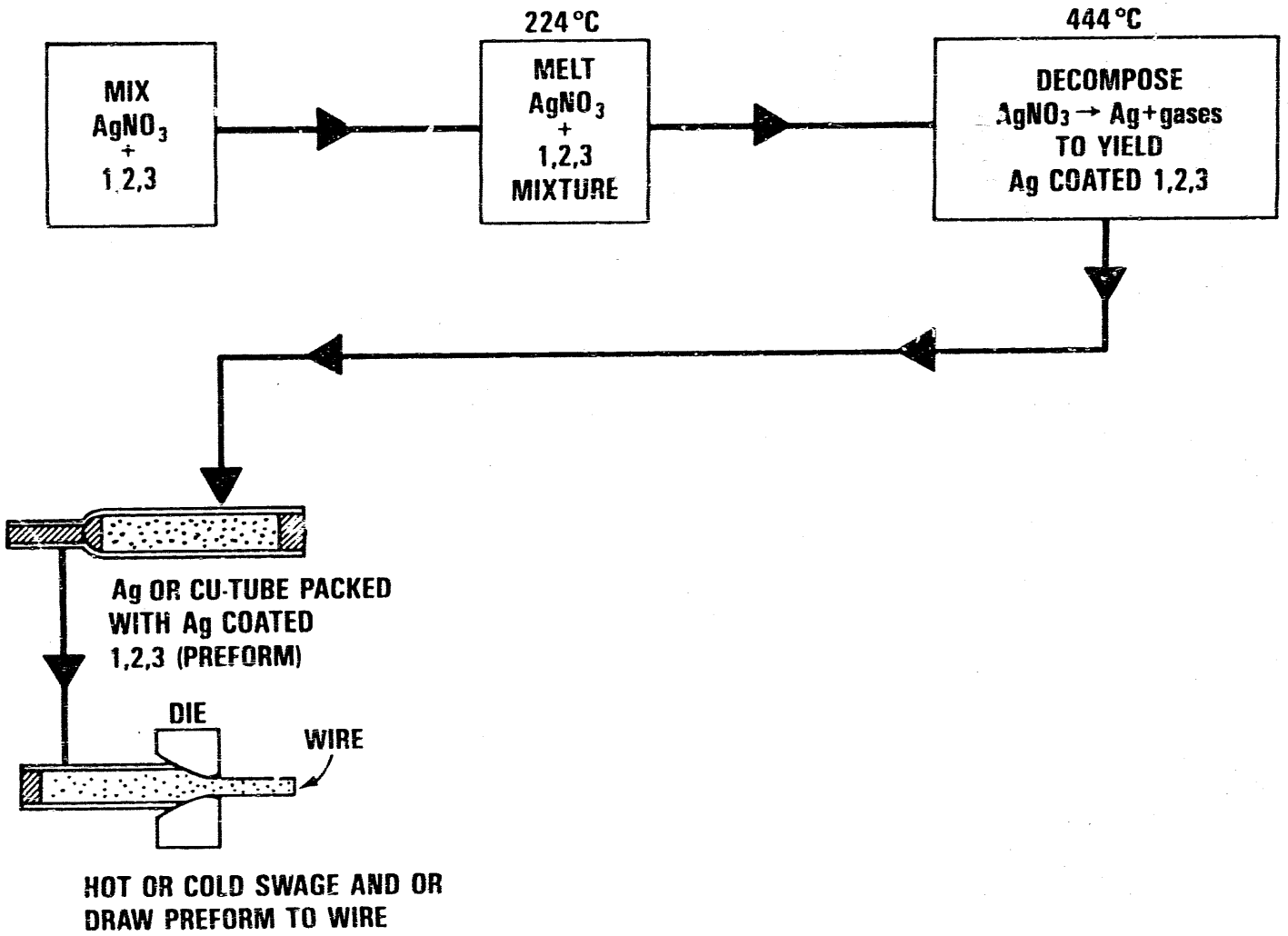


FIGURE 1. HTS WIRE PROCESSING FLOW CHART

FIGURE 2. **Microstructure of YBCO Powder Mass Infiltrated with Ag from $AgNO_3$**

AS RECEIVED

Ag COATED

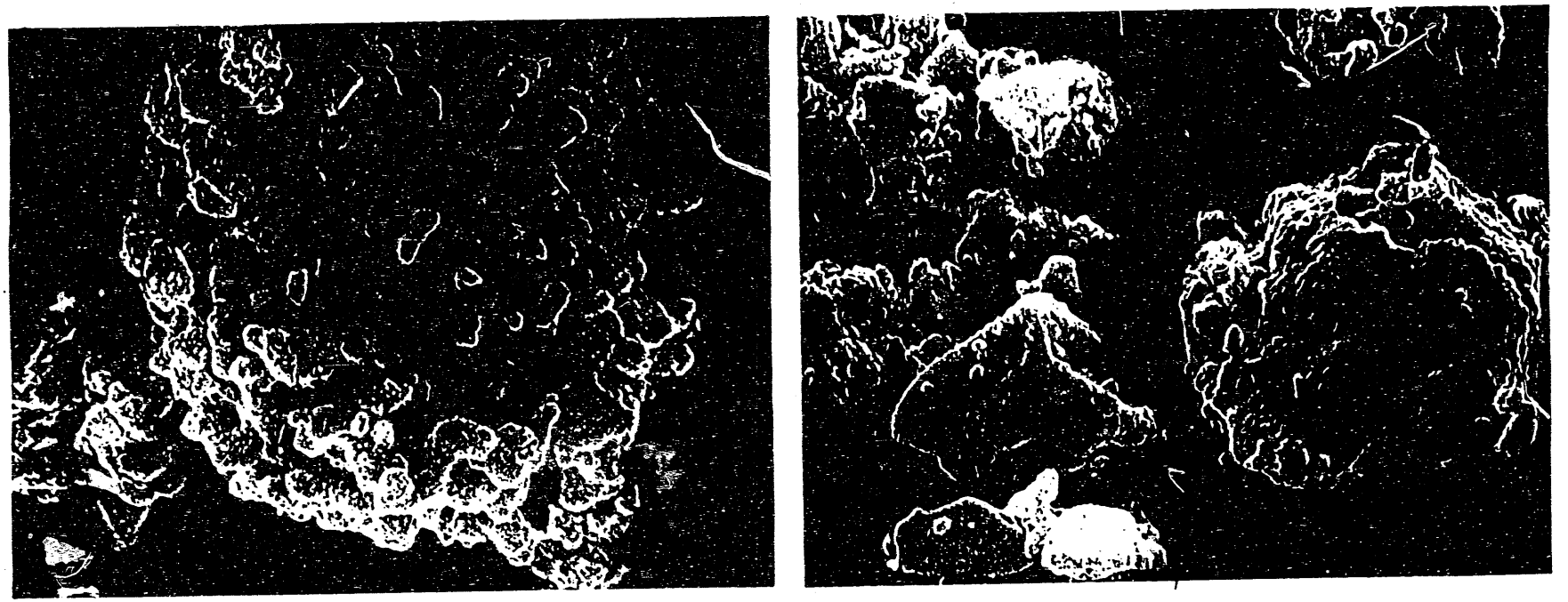
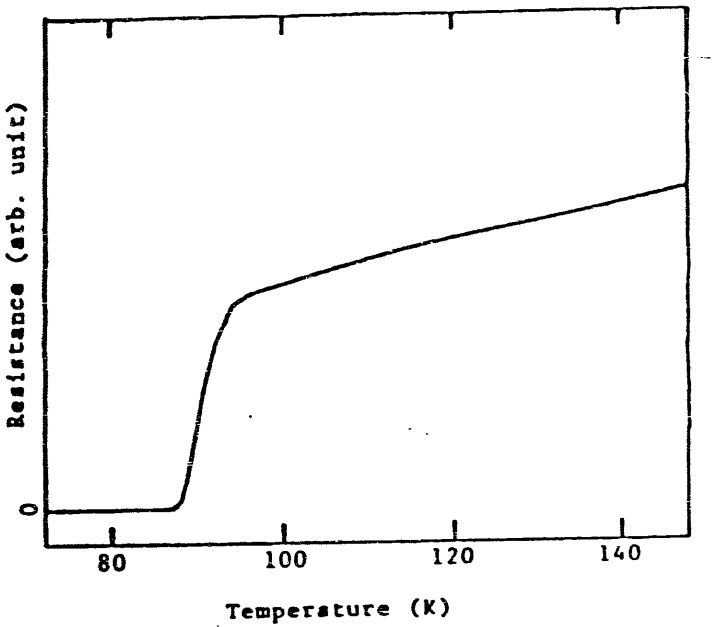
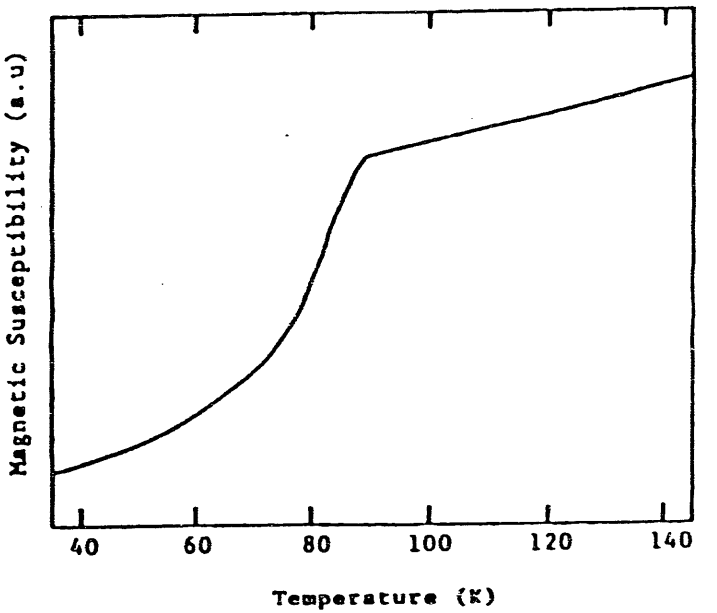


FIGURE 3. SEM Photo of YBCO (123) Powder





RESISTANCE MEASUREMENT

AC SUSCEPTIBILITY

FIGURE 4. SUPERCONDUCTING TRANSITION OF Yb1Ba2Cu3Ox - 20 w/o COMPOSITE.

END

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