

# Superconductive $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ fibres from an extrudable dispersion of a particulate precursor

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A particulate precursor of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  was dispersed in a concentrated acetic/formic acid solution of yttrium, barium and copper acetates to form an extensible, viscous mixture. This dispersion was stable, unlike one prepared from superconductive  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  itself. Fibres extruded from the viscous dispersion were fired at 935 °C in the presence of oxygen. Although the fired fibres were not fully densified, they had a sharp Meissner transition temperature at 90 K and an apparent critical current density ( $J_c$ ) of 900 A cm<sup>-2</sup> (1800 A cm<sup>-2</sup> corrected for porosity) at 77 K. The superconducting fibre was sensitive to magnetic field, which is evidence of weak coupling between the superconducting grains.

## 1. Introduction

Since the discovery of high-Tc oxide superconductors, immense efforts have been directed towards shaping of the oxides into useful articles [1]. Extrusion or spinning are processes commonly employed to shape the oxide into fibres, wires and coils. Usually, the process involves dispersing superconductive  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (SC-123) or a particulate precursor in an organic polymer solution [2-6]. The resulting dispersion must be viscous and extensible for use in the shaping process. The polymer/SC-123 or polymer/SC-123-precursor fibre, after drying to remove most of the solvent, is then fired at high temperatures to burn off carbonaceous species and sinter the preform into a stronger, denser form. Though organic polymer solutions are commonly used as carriers for the particulates, organometallic solutions [7] or solutions of metal acetates [8, 9] should be in principle useful for the same application, with the potential for forming fewer volatile products during firing and a less porous fibre. In this paper, we discuss dispersibility of SC-123 particulate and a precursor particulate in an acetic/formic acid solution of yttrium, barium, copper acetates, extrusion of the dispersion to form fibres, and the superconductivity properties of the fired fibres.

## 2. Experimental procedure

### 2.1. SC-123 precursor powder synthesis

Copper acetate monohydrate, yttrium acetate hydrate, and barium hydroxide were mixed at a stoichiometric ratio of 1:2:3 Y:Ba:Cu in water at 75 °C. The resulting brownish mixture was spray dried and then calcined in air at 500 °C for one hour. The calcined powder was dark brown in colour. X-ray analysis of the calcined powder showed the presence of

barium carbonate and cupric oxide. Yttrium evidently exists as a non-crystalline species.

### 2.2. SC-123 powder synthesis

Yttrium oxide, barium nitrate, and cupric oxide were mixed in the stoichiometric 1:2:3 Y:Ba:Cu ratio. The mixture was ground in a mortar and then calcined for 3 h at 970 °C in an oxygen atmosphere. The temperature was lowered to 500 °C and held for 1 h before cooling to room temperature. The calcined powder was first ground in a stainless steel blender and then milled in an alumina jar with zirconia beads. The major phase in the powder as determined by X-ray analysis was SC-123 with only trace amounts of other phases present.

### 2.3. Preparation of acetic/formic acid solution of yttrium, barium and copper acetates and powder dispersion in the solution

A concentrated acetic/formic acid solution of yttrium, barium and copper acetate was prepared as follows: 3.42 g yttrium acetate hydrate (equivalent to 1.194 g  $\text{Y}_2\text{O}_3$ ), 5.36 g barium acetate, 6.28 g cupric acetate monohydrate, and 20 ml glacial acetic acid were placed in a 250 ml beaker. The stoichiometric Y:Ba:Cu ratio is 1:2:3. The beaker was covered with a watch glass and heated to about 60 °C with constant stirring. To the warm mixture was added 6.5 ml formic acid. As soon as the formic acid was added, the mixture of acetates dissolved and the resulting solution turned dark green. The solution was heated to 75 °C and held there while about 13 ml of acetic/formic acid evaporated. The concentrated solution was very viscous and highly extensible. Fibres with diameters less

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than 100  $\mu\text{m}$  could be pulled from the concentrated solution with a spatula. Eight grams of either SC-123 powder or the precursor powder were mixed with the 75°C solution to determine whether they formed stable, extrudable dispersions for shaping into preforms for conversion into SC-123 fibres.

#### 2.4. Extrusion and conversion of the fibres into SC-123

A viscous dispersion of the SC-123 precursor particulate made in Section 2.3 was loaded into a 5 ml plastic syringe fitted with a 22 gauge stainless steel syringe needle. This was placed in a syringe pump for extrusion. The fibres were collected on a polytetrafluoroethylene sheet and dried at room temperature. The dried fibres were fired in an oxygen atmosphere according to the following cycle: RT to 220°C at 1°C min<sup>-1</sup>, 1 h at 220°C, 1°C min<sup>-1</sup> to 500°C, 2 h at 500°C, 1°C min<sup>-1</sup> to 935°C, 2 h at 935°C, cooled to 600°C at 5°C min<sup>-1</sup>, 2 h at 600°C, 5°C min<sup>-1</sup> to 300°C, 1 min at 300°C, 5°C min<sup>-1</sup> to 35°C. The diameter of the fired fibres is in the range of 200  $\mu\text{m}$ . The fired fibre was very hard and tough, indicating that grains were well consolidated.

The superconductive SC-123 powder made in Section 2.2 could not be uniformly dispersed in the concentrated acetic/formic acid solution of the metal acetates. The mixture remained lumpy even with constant stirring. When the mixture was loaded into a 20 ml plastic syringe with a 20 ml diameter nozzle and extruded, the syringe nozzle repeatedly clogged and the collected extrudate pieces were uneven and short in length. Upon drying in air at room temperature the pieces turned blue, the colour of cupric acetate.

#### 2.5. $J_c$ measurement

This measurement was done using a four-probe method. Silver paste was used as electrode material to reduce contact resistance to about 5  $\Omega$ . The two inner electrodes were about 6 mm apart. While the fibre was immersed in liquid nitrogen, current was applied through the two outer electrodes. The voltage corresponding to the current applied through the outer electrodes was measured between the two inner electrodes with an electrometer. As current was increased, at a certain point the fibre sample was driven to the normal state. The current which flowed at a voltage of 1  $\mu\text{V}$  is defined as the threshold current. The threshold current normalized by the cross-section of the fibre sample is defined as  $J_c$  ( $\text{A cm}^{-2}$ ).

#### 2.6. Flux exclusion measurement

This measurement was made by using an a.c. technique in which the change in inductance of a coil caused by flux exclusion from a sample inside the coil was measured. A voltage signal was obtained which, after subtraction of a background empty coil voltage, could be related to the amount of superconducting material in the sample volume. By making measure-

ments over a range of temperatures, the temperature dependence of the flux exclusion and the critical temperature of the sample could be obtained. The SC-123 fibre samples were placed in 0.13-cm diameter glass capillaries, which were then placed in the coil. The inductance change was also measured at 77 K as a function of an external d.c. magnetic field from 0–26.257  $\text{kA m}^{-1}$  to determine the strength of the linkage between superconducting grains.

### 3. Results and discussion

The concentrated acetic/formic acid solution of the metal acetates is viscous and extensible, indicating that the metal acetates form a polymeric structure. It is believed that the metal ions are co-ordinated through acetate oxygens to form metal–oxygen chains. Firing of the non-particulate containing dried fibres made with the solution gave an extremely fragile product which was difficult to handle. Addition of superconductive SC-123 particulate to the acetate solution in an effort to increase the integrity of the fired fibres did not yield a usable dispersion. The oxide, as one might expect from literature descriptions, is reactive with acids and this reaction is probably responsible for the coagulated state of the mixtures and their poor processability.

The precursor particulate made in Section 2.1 behaved quite differently, however. The dark brown powder and the acetate solution formed a homogeneous almost black dispersion which remained highly extensible. The dispersion kept at 65°C could be extruded easily through the syringe nozzle. The extrudates collected on a polytetrafluoroethylene sheet remained very dark in colour after being dried in air at room temperature for more than one day. This is taken as evidence that the precursor particulate, unlike SC-123 particulate, was not substantially altered chemically by the acids. This is especially remarkable because the only phases identifiable were  $\text{BaCO}_3$  and  $\text{CuO}$  both of which would be expected to be reactive with the acetic/formic acid.

X-ray powder diffraction pattern of a fired fibre obtained from the SC-123 precursor particulate dispersion is shown in Fig. 1. The peaks in the pattern are all accounted for as being derived from the superconductive phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  [6]. Fig. 2 shows a portion of a cross-section of a SC-123 fibre with a diameter of 200  $\mu\text{m}$ . The fibre is porous and individual grains are fairly large in the range 3–10  $\mu\text{m}$ . The fibre is hard and tough, indicating that the grains are strongly connected.

A plot of flux exclusion versus temperature, shown in Fig. 3, for the SC-123 fibres, reveals an onset transition of superconductivity at 90 K. The transition is very sharp, which can be explained by the size of the SC-123 grains. The effect of an applied d.c. magnetic field, in the range of 0–26.257  $\text{kA m}^{-1}$ , on the magnetic flux exclusion for the SC-123 fibres is shown in Fig. 4. Flux exclusion at the applied field is normalized versus the exclusion in zero field. The flux exclusion decreases as the field is increased to 6.365  $\text{kA m}^{-1}$  and then it almost plateaus though

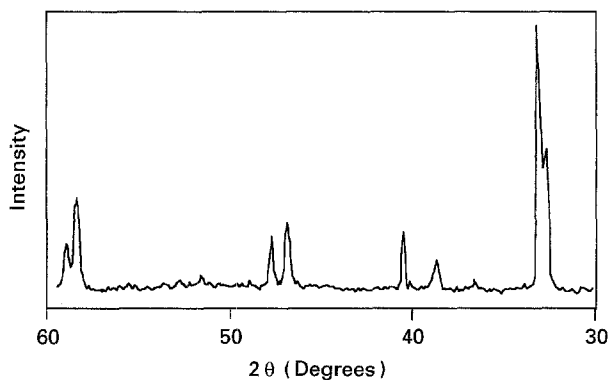


Figure 1 X-ray diffraction of the fired fibre obtained from the SC-123 precursor particulate dispersion.

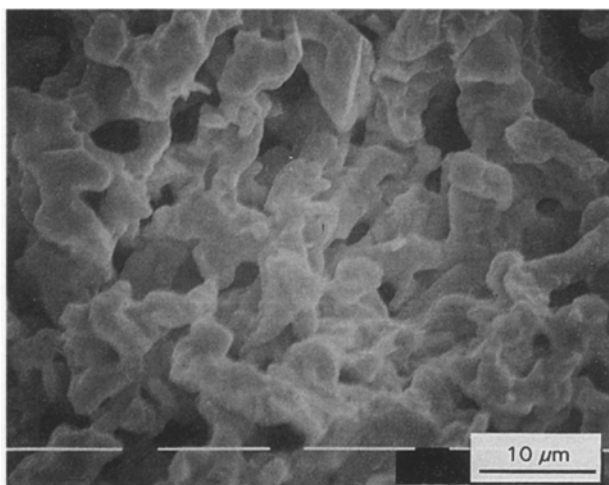


Figure 2 Cross-section of a fired fibre obtained from the SC-123 precursor particulate dispersion.

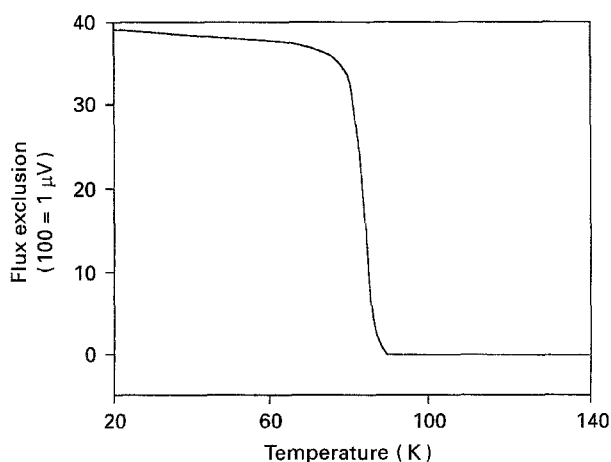


Figure 3 Magnetic flux exclusion versus temperature of the SC-123 fibre.

there is a slight decrease as the field continues to increase. The initial drop is attributed to weakly superconductive links between grains, which can be easily penetrated by a weak magnetic field. The slow decrease after the initial drop is due to magnetic field penetration into the individual superconducting grains which are less field-dependent. The SC-123 has

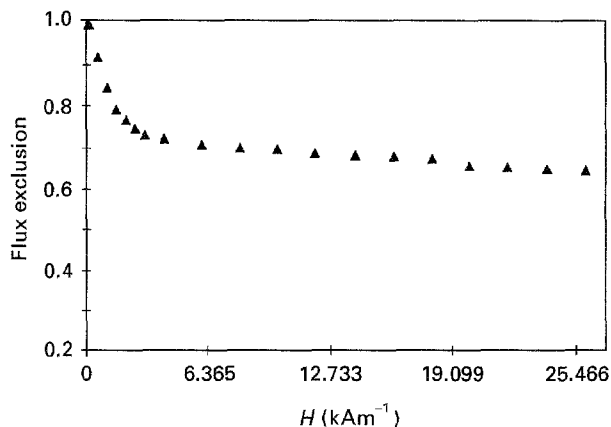


Figure 4 Flux exclusion versus applied d.c. magnetic field of the SC-123 fibre at 77 K.

an apparent room temperature electrical resistivity of  $7.5 \times 10^{-4} \Omega \text{cm}$  and an apparent  $J_c$  (77 K) of  $900 \text{ A cm}^{-2}$ . It is interesting to point out that the apparent electrical resistivity and apparent  $J_c$  fall on the curve established in Reference 2 for SC-123 fibres having 95% of the theoretical density. Based on the cross-section shown in Fig. 2, it is estimated that the fibre is about 50% of the theoretical density. If the  $J_c$  is corrected for the porosity, it would be  $1800 \text{ A cm}^{-2}$ .

#### 4. Summary and conclusions

A particulate precursor of superconductive  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  can be dispersed in a concentrated acetic/formic acid solution of yttrium, barium and copper acetates. The viscous dispersion is stable, unlike one prepared with superconductive  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  itself. Fibres extruded from the dispersion were fired at  $935^\circ\text{C}$  in presence of oxygen. Although the fired fibres were not fully densified, they had a sharp Meissner transition temperature at 90 K and apparent  $J_c$  of  $900 \text{ A cm}^{-2}$  at 77 K. The  $J_c$  would have been  $1800 \text{ A cm}^{-2}$  if the fibres were fully densified. The SC-123 fibre was still sensitive to magnetic field, which is evidence of weak coupling between superconducting grains.

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