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Preparation and characterization of high-T_c superconducting $YBa_2Cu_3O_{7-x}$ filaments

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High-T_c superconducting filaments of the Y–Ba–Cu–O system were prepared using a low-cost suspension spinning method, where the solvent was removed by a phase inversion technique. The Y–Ba–Cu oxide precursor, containing polysulphone (PSF), was spun as a filament into a precipitating medium, removing the solvent by phase inversion and using water as a non-solvent. The "green product" filament was washed, dried and subjected to a heat treatment to remove the binding material and generate the oxide in the appropriate superconducting phase. Stoichiometry, porosity and grain size were investigated by scanning electron microscopy, energy-dispersive X-ray analysis and electron probe micro analysis, while crystal structure was checked by X-ray diffraction analysis. Resistivity measurements as a function of temperature were performed by the four-point method and typical T_c values of 88 K were observed, while J_c was in the range of 125 A cm^{-2} at 77 K and zero field.

1. Introduction

Following the discovery of high-temperature superconductivity in the Y–Ba–Cu–O system [1], research activities in many laboratories have concentrated on the development of manufacturing high-T_c superconducting tape and wire with adequate mechanical and electromagnetic properties, as required for large-scale technological applications. The ceramic $YBa_2Cu_3O_{7-x}$ material is not easily shaped into the desired fibre geometry and many problems need still to be overcome.

Various methods have been proposed to prepare high-T_c fibres with high chemical and phase purity, in order to obtain good superconducting properties. The powder-in-binder [2, 3], powder-in-sol [4], sol–gel and metallo-organic [5–7] methods adopt the spinning process, which has been established for ceramic fibre production.

This paper describes a low-cost preparation method for superconducting $YBa_2Cu_3O_{7-x}$ filaments using a suspension spinning method with a polysulphone binder. The solvent was removed by a phase inversion step using water as a non-solvent.

2. Experimental procedure

The aim of this study is to investigate the production of superconducting wires starting from commercially available material. Therefore a purchased powder (Hoechst High Chem) with an average grain size of about 10 μm was used as a starting material. This "pre-sintered" powder needs a high-temperature heat treatment to become superconductive. The powder was characterized in a scanning electron microscope equipped with energy-dispersive X-ray analysis (SEM-/EDX), electron probe microanalysis (EPMA) and X-ray diffraction (XRD) to check the stoichiometry and crystal structure. No impurities or contaminating phases could be detected.

The spinning suspension is prepared by dissolving the polysulphone (PSF) binder in N-methyl-2-pyrrolidone (NMP) and adding the Y–Ba–Cu–O powder to this solution. The suspension has a viscosity of about 5000 centipoise and a weight ratio of 90% of Y–Ba–Cu–O powder to 10% of PSF is used in the experiments.

The suspension is filtered to remove all particles larger than 90 μm. The fibres are prepared using a phase inversion technique [8]. In this procedure, the filaments are formed by crystallization of the polymer (PSF) from the casting suspension, by extraction of the solvent with a non-solvent. The suspension is forced through a cylindrical hole (ϕ 1 mm). An adapted compressed-air-driven PTFE cylinder head provides the pressure (600 kPa) required to force the suspension through the spinning hole. With 50 ml of suspension a wire of about 10 m can be made. The quality and diameter of the "green product" filament depends on the distance between the spinning head and the precipitation bath, the spinning speed, the diameter of the spinning hole, the non-solvent and the rheology of the suspension. Table I gives a list of the spinning parameters and Fig. 1 shows a schematic drawing of the spinning apparatus.

Thermogravimetric analyses of pure PSF (Fig. 2) indicate that the sample starts to react at about 380 °C and that the decomposition of the polymer is complete at 500 °C, i.e. well below the sinter temperature of the superconducting material. In an oxidizing atmosphere, the remaining ash content is smaller than

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TABLE I Spinning parameters

Powder	Y–Ba–Cu–O (Hoechst High Chem), 90 wt %
	Average grain size = 10 μm
	Specific surface = 2–4 $m^2 g^{-1}$
Binder	Polysulphone (PSF) (UDEL P-1700), 10 wt %
Solvent	N-methyl-2-pyrrolidone (NMP)
Suspension viscosity	± 5000 centipoise
Non-solvent	Water
Spinning	Hole diameter 1 mm
	Air gap (max.) 5 mm
	Speed 2 m min^{-1}

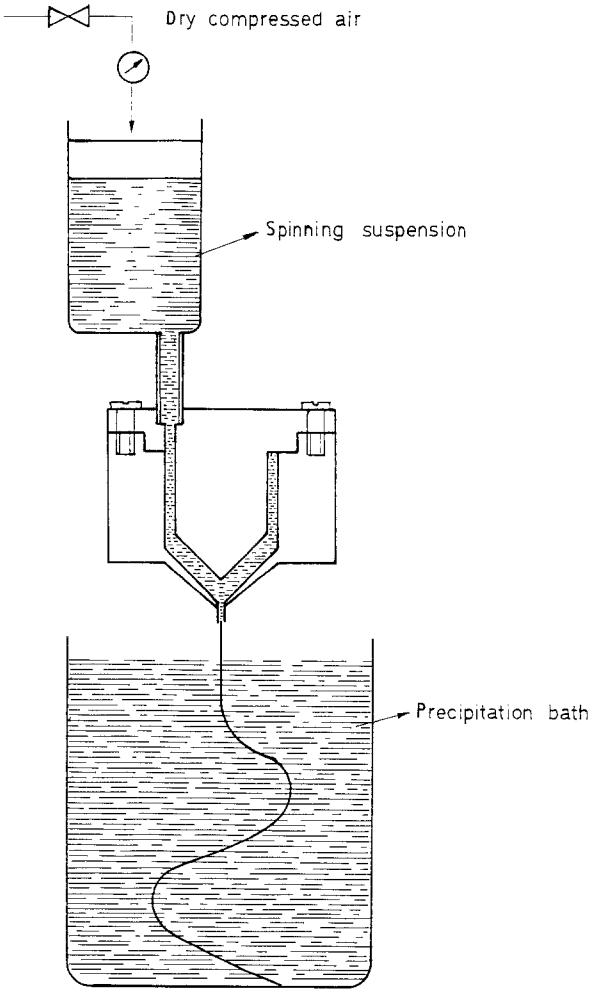

Figure 1 Schematic drawing of the suspension spinning equipment.

0.08 wt % and no remaining sulphur can be detected. A further advantage of using PSF is that the addition of a plasticizer is not required. However, more experiments are needed to confirm this aspect.

Because of its good film-forming properties, water has been chosen as the non-solvent. In order to minimize the influence of water on the Y–Ba–Cu–O material, the residence time of the green filament in the non-solvent has been limited to about 10 min, which was found to be sufficient to extract the solvent. Subsequently the wire is washed and stored in isopropanol until the heat treatment is applied. After drying, the green filament has a tensile strength between 1.1 and 2.2 MPa and the good mechanical properties allow the filament to be shaped into a coil (Fig. 3).

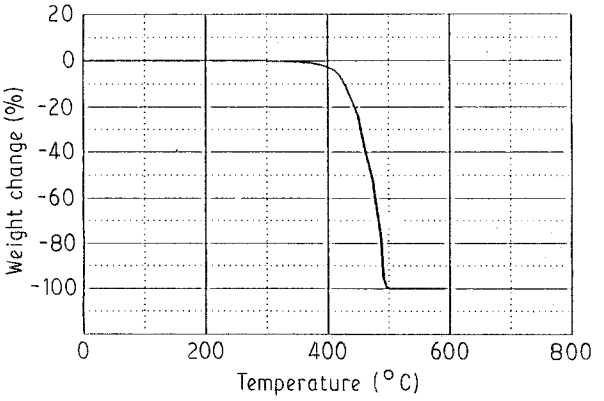

Figure 2 Thermogravimetric analysis of polysulphone (PSF) heated at the rate of 10 °C min^{-1} in oxygen.

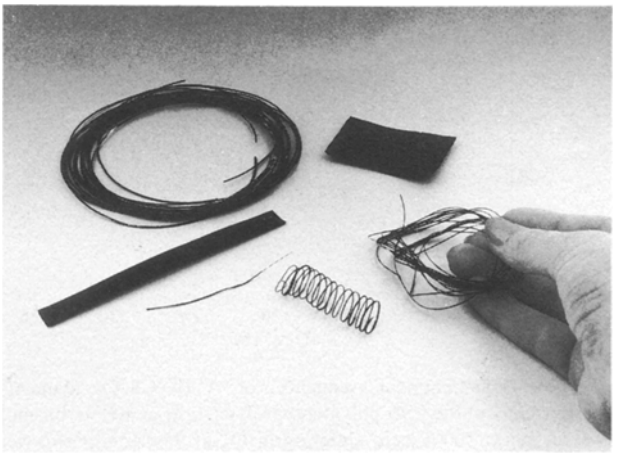

Figure 3 Wire and tape produced with Y–Ba–Cu–O powder using a suspension technique.

The filaments have a diameter of about 0.75 mm and have a very smooth surface. SEM pictures of the cross-section (Fig. 4) reveal some porosity which accounts for the relative low density of the material, about 60% of the theoretical value. The spinning conditions will be optimized to reach higher densities of the green fibre. The SEM pictures also show that the surface of the wire is slightly brighter, probably caused by the interaction of water with the material. Filaments spun in another non-solvent, e.g. isopropanol, do not show this effect but the quality of these fibres deteriorates when subjected to the heat treatment.

2.1. Thermal treatment

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) of the Y–Ba–Cu–O powder, the pure PSF-binder and the green filament were performed in different atmospheres. Although the pure PSF is completely decomposed at 500 °C (Fig. 2), i.e. well below the sinter temperature of the Y–Ba–Cu–O material, special care has to be taken when submitting the green filament to the heat treatment. In order to produce $YBa_2Cu_3O_{7-x}$ superconducting wire, interaction of the binder with the Y–Ba–Cu–O powder has to be avoided as much as possible and the remaining ash content must be minimal. In the heat treatment, three stages are important:

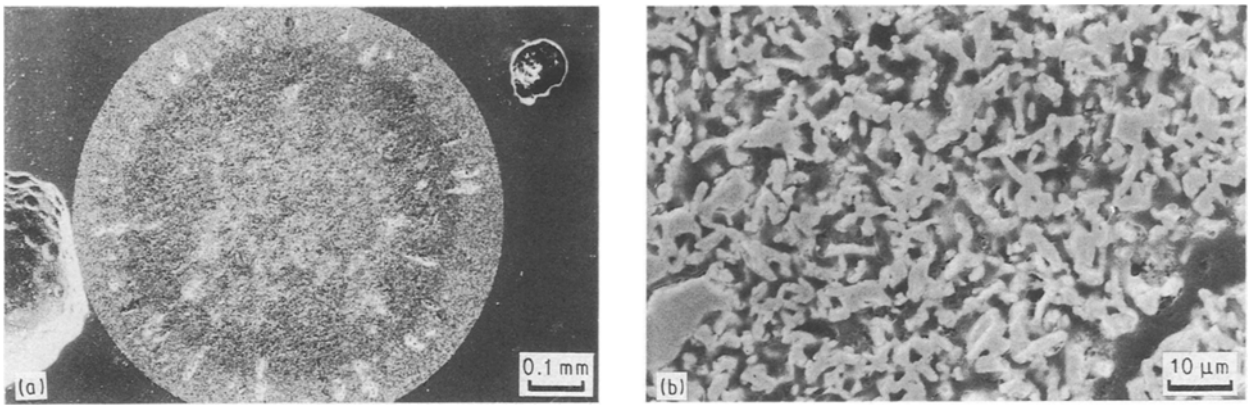

Figure 4 (a, b) SEM micrographs at different magnifications of a cross-section of a Y–Ba–Cu–O "green product" filament.

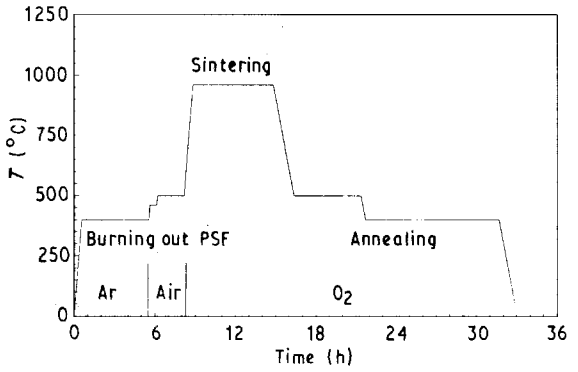

Figure 5 Heat-treatment sequence of Y–Ba–Cu–O filaments: (i) burning out the PSF-polymer (pyrolysis in Ar at 400 °C, burning out in air at 500 °C); (ii) sintering in O_2 at 950 °C; (iii) two-step annealing in O_2 at 500 and 450 °C (heating rate + 12 °C min^{-1}, cooling rate − 5 °C min^{-1}).

(i) burning out the PSF polymer without destroying the shape of the filament; (ii) sintering the filament to form a high-density ceramic; (iii) annealing the ceramic in an oxygen atmosphere to produce the superconducting 1:2:3 phase. Removal of the PSF binder is accomplished by pyrolysis of the polymer in a vacuum or in an inert atmosphere at 400 °C and subsequently burning it out in air at 500 °C. After this stage, the fibres are quite fragile, suggesting little or no sintering. SEM analysis confirmed that little or no intergranular connections had formed at this stage. After sintering and annealing in an oxygen atmosphere, a polycrystalline high-T_c superconductive filament is obtained. The superconductive properties of the filament are strongly affected by the precise heat treatment conditions and further optimization is currently being studied. A typical thermal treatment sequence is shown in Fig. 5.

3. Results and discussion

The sintered and annealed filaments are superconductive above liquid nitrogen temperature. The material, however, loses its flexibility and behaves as a true ceramic: hard and brittle but sufficiently firm to be handled without breaking. Stoichiometry measurements by EPMA and EDX confirmed the 1:2:3 composition. Close examination of the EDX spectra revealed the presence of small amounts of sulphur in the samples, indicating that the ash of the pyrolysed PSF binder was not completely removed during the thermal treatment. A typical X-ray diffraction pattern of the $YBa_2Cu_3O_{7-x}$ filament is shown in Fig. 6. Some small peaks of the Y_2BaCuO_5 phase can be observed but no evidence of a sulphur-or carbon-containing phase could be detected.

SEM analyses (Fig. 7) reveal the relatively porous nature of the microstructure of the superconducting filaments. In Fig. 7a large, radially oriented cracks can be observed, probably caused by the fast extraction of the solvent by the phase inversion technique.

The superconducting transition temperature (T_c) and the critical current density (J_c) have been measured by the four-probe d.c. technique, in which thin copper wires were fixed on the sample with a silver–epoxy paint. The resistivity as a function of temperature (Fig. 8) clearly shows metallic behaviour from room temperature to a T_c (onset) of above 90 K and zero resistivity can be observed at about 88 K. Transport critical current density measurements were carried out at liquid nitrogen temperature and zero field. Despite the porous structure of the filament, values of about 125 A cm^{-2} were obtained.

4. Summary and conclusions

A preparation technique for high-temperature $YBa_2Cu_3O_{7-x}$ superconducting filaments was developed based on a suspension spinning method and the extraction of the solvent by phase inversion. Polysulphone was used as a binder in a weight ratio of 10% to 90% of Y–Ba–Cu– O powder. The spinning suspension, with a viscosity of about 5000 centipoise, was obtained by dissolving the polymer in N-methyl-2-pyrrolidone and adding the Y–Ba–Cu–O powder to this solution. Because of its good film-forming properties water was chosen as the non-solvent. To minimize the influence of water on the Y–Ba–Cu–O material, the filament was washed in isopropanol after spinning. After a three-stage heat treatment, a polycrystalline superconductive wire could be formed.

Resistivity measurements indicated a superconducting transition temperature of about 88 K. A critical current density of 125 A cm^{-2} was measured at 77 K and zero field, using a transport current technique. A relatively high porosity of the filament is thought to be

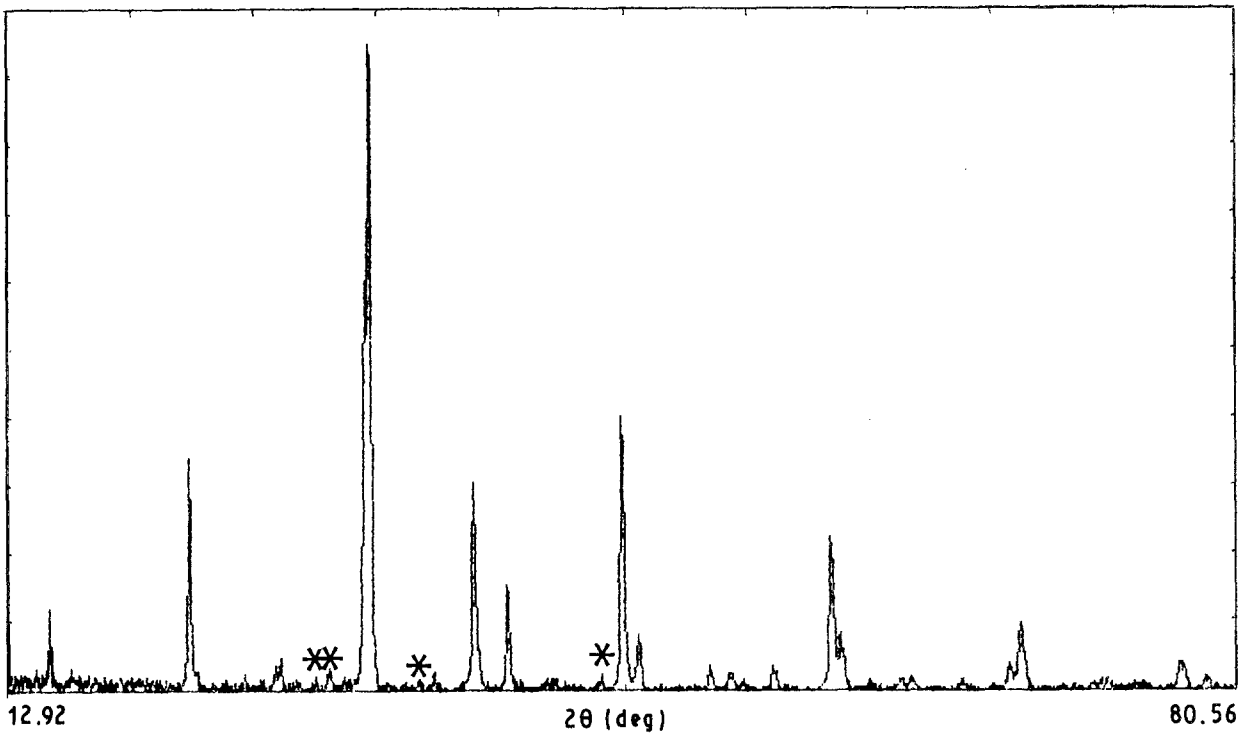

Figure 6 X-ray diffraction pattern of the $YBa_2Cu_3O_{7-x}$ superconducting filament: (*) peaks associated with the Y_2BaCuO_5 phase.

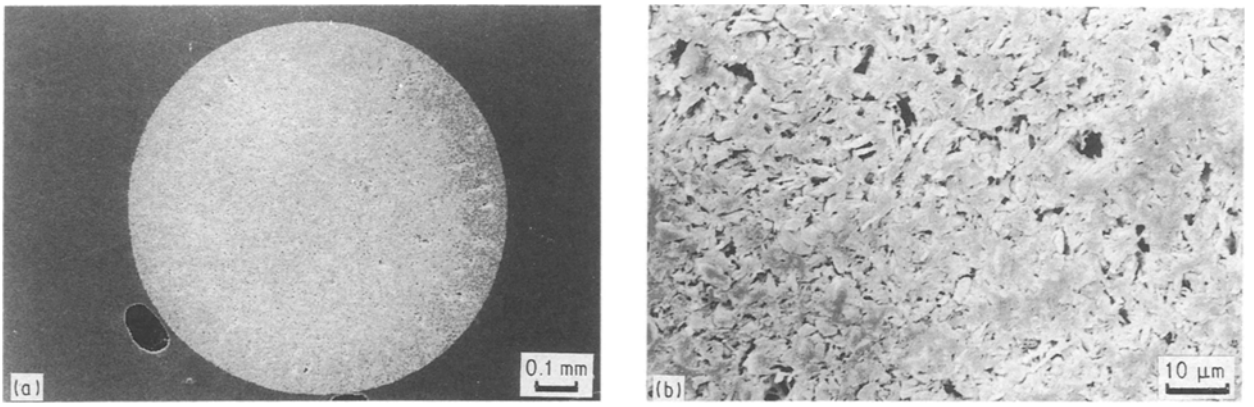

Figure 7 (a, b) SEM micrographs at different magnifications of a cross-section of a $YBa_2Cu_3O_{7-x}$ superconducting filament.

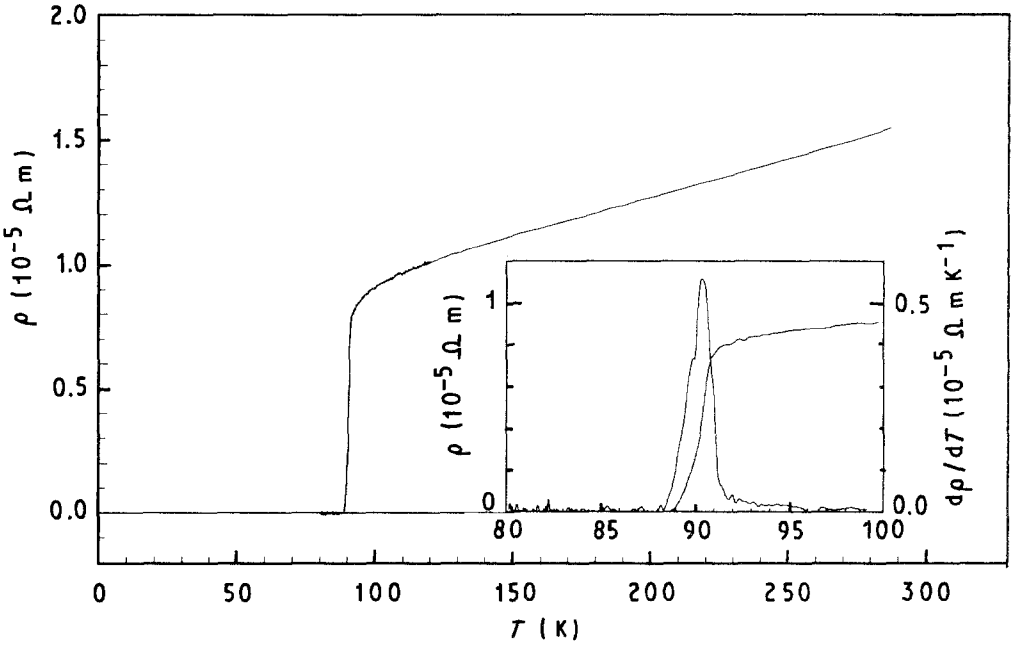

Figure 8 Resistivity as a function of temperature for the $YBa_2Cu_3O_{7-x}$ superconducting wires.

responsible for the rather low critical current density presently obtained. The spinning conditions and thermal treatment will be optimized to obtain denser material and improved superconducting properties. A systematic study of the influence of these parameters on T_c and J_c is generally accepted to be very important [3, 9, 10] and is being carried out.

Acknowledgements

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