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A melt process to superconductive fibres of $Bi_2Sr_2CaCu_2$ oxide

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A particulate precursor of superconductive $Bi_2Sr_2CaCu_2$ oxide dispersed in an aqueous poly(vinyl alcohol) solution, was shaped into fibres. The fibres fired at a T_{max} of 850 °C were very porous. Although they exhibited a Meissner on-set transition at 85 K, electrical resistance at 0.02 $A\,cm^{-2}$ at 77 K was still not zero. Exposing the porous fibres to a temperature slightly above their melting point densified them. The treated fibres had a sharp Meissner transition and could carry critical current (J_c) as high as 331 $A\,cm^{-2}$ at 77 K. They were also more resistant to the effect of a magnetic field than the fibre fired at 850 °C. Eighty percent of the treated fibre was found to be the superconductive 2 2 1 2 phase.

1. Introduction

Since the discovery of $Bi_2Sr_2CaCu_2$ oxide (Bi2212) superconductors in 1988 by Maeda [1], immense efforts have been directed towards shaping of the oxides into useful articles [2–4]. Extrusion or spinning are commonly employed to shape superconductive YBa_2Cu_3 oxide into fibres [5–6], but these have not been as fully explored for Bi2212. The first step in the process involves dispersing superconductive oxide or a particulate precursor in an organic polymer solution. The resulting dispersion must be fluid and extensible for further steps in the shaping process. The extruded or spun polymer/superconductive-oxide or polymer/precursor fibre is dried and then fired at high temperatures to burn off carbonaceous species and sinter the preform into a superconductive fibre. The process often yields fibres having high porosity and poor superconductivity properties. One could resort to melting to densify the fibres, but it is known that Bi2212 undergoes incongruent melting, resulting in multiple phases [7]. In addition, melting could cause fibres to lose physical integrity. This may be the reason why this simple process is not exploited for making dense, superconductive Bi2212 fibres. In this paper, we discuss superconductive Bi2212 fibres made from a dispersion of a Bi2212 particulate precursor in an aqueous poly(vinyl alcohol) (PVA) solution and the improvement in superconductive properties of the fibres after subjecting them to a brief melting at a temperature slightly above the melting point (875 °C) of Bi2212. A portion of this work was disclosed in a US patent [8].

2. Experimental procedure

2.1. Synthesis of Bi2212 particulate precursor

A particulate precursor was first made by mixing bismuth nitrate pentahydrate, strontium nitrate, calcium acetate monohydrate, and cupric acetate monohydrate in the Bi:Sr:Ca:Cu ratio of 2:2:1:2. Each of the ingredients was ground in a mortar prior to weighing and then ground together in a mortar. The blended mixture was placed in an alumina crucible and heated in a furnace from room temperature to 300 °C and held at 300 °C for 30 min; the temperature was raised to 400 °C and held at 400 °C for 60 min. The mixture was reground after cooling and reheated in the furnace at 500 °C for 2 h. The powder was not superconductive and exhibited several major X-ray (CuK_α) reflection peaks at 2θ of 12.4, 25.2, 28.1, 29.3, 30.7, 38.4, 38.8, 44.2 and 46.8, which could not be attributed to Bi_2O_3, SrO, CaO, or CuO.

2.2. Preparation of PVA/Bi2212-particulate-precursor dispersion and fibre spinning

Twenty grams of the particulate precursor made in Section 2.1 was mixed with 20 g water containing 0.1 g of Dowfax® 382, a deflocculating/wetting agent. The mixture was then blended in an oscillating ball mill for 1 h. The precursor/water slurry was mixed with an aqueous PVA solution prepared by mixing 2.3 g of Elvanol® 5042, 20 g water, 0.23 g glycerol and 0.5 g glutaric acid. The mixture was stirred and concentrated under vacuum. The resulting thick dispersion was loaded into a 5 ml plastic syringe fitted with a 22 gauge stainless steel needle, and fibres were extruded onto a polytetrafluoroethylene sheet using a syringe pump.

2.3. Firing of the PVA/Bi2212-particulate-precursor fibre at a T_{max} of 850 °C

Six pieces (each 10 cm long) of the fibre made in Section 2.2 were suspended on silver tubing supported horizontally on a 9-cm high metal rack. The whole

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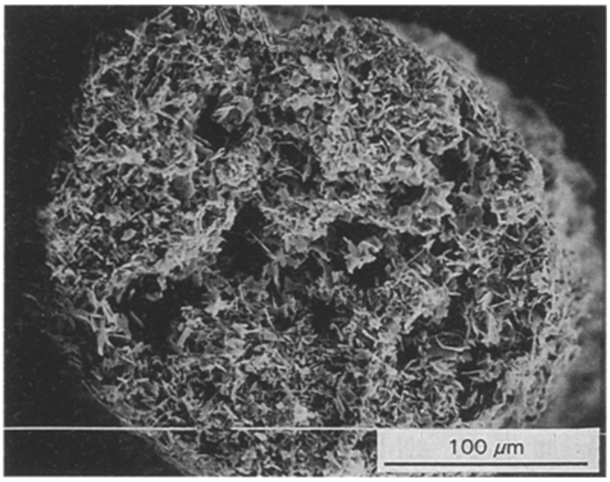

Figure 1 Cross-section of the fired fibre prepared from the cycle with a T_{max} of 850 °C.

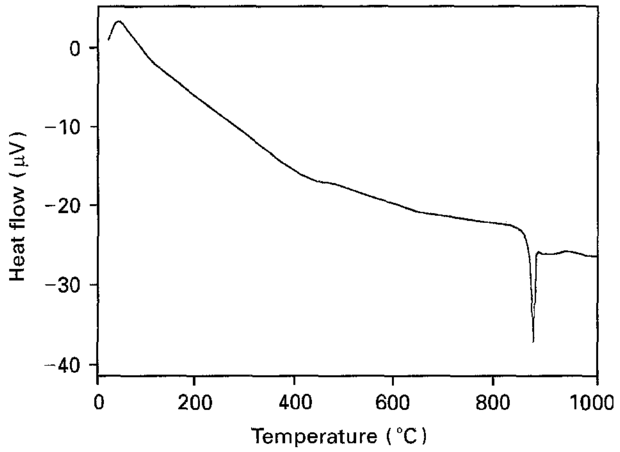

Figure 2 Differential thermal analysis of the fired fibre prepared at 850 °C.

assembly was placed in a Fisher #497 furnace for firing in air according to the following cycle: room temperature to 160 °C at 2 °C min^{-1}, 10 min at 160 °C, 2 °C min^{-1} to 830 °C, 6 h at 830 °C, 2 °C min^{-1} to 850 °C, 5 min at 850 °C, 20 °C min^{-1} to 600 °C, 1 min at 600 °C, 20 °C min^{-1} to 300 °C, 1 min at 300 °C, 10 °C min^{-1} to room temperature. The cross-section of a fired fibre is shown in Fig. 1. Differential thermal analysis in Fig. 2 shows that the fired fibres melt at 875 °C.

2.4. Firing of the PVA/Bi2212-particulate-precursor fibre at a T_{max} of 880 °C

Since Bi2212 melts at 875 °C, it was decided to expose the fibres to 880 °C for a short time. Six pieces (each 10 cm long) of the fibre made in Section 2.2 were suspended on alumina tubing supported horizontally by a 9-cm high metal rack. The whole assembly was placed in a Fisher #497 furnace. The following cycle was used for firing in air: room temperature to 160 °C at 2 °C min^{-1}, 30 min at 160 °C, 2 °C min^{-1} to 830 °C, 60 min at 830 °C, 5 °C min^{-1} to 880 °C, 5 min at 880 °C, 20 °C min^{-1} to 600 °C, 1 min at 600 °C, 20 °C min^{-1} to 300 °C, 1 min at 300 °C, 10 °C min^{-1} to 35 °C. Four of the six fibres survived through the entire cycle without breaking. The cross-section and surface of a fired fibre are shown in Fig. 3.

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 Ω. 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 flows at a voltage of 1 μV is defined as the threshold current. The threshold current normalized by the cross section of the fibre sample is defined as J_c(A cm^{-2}).

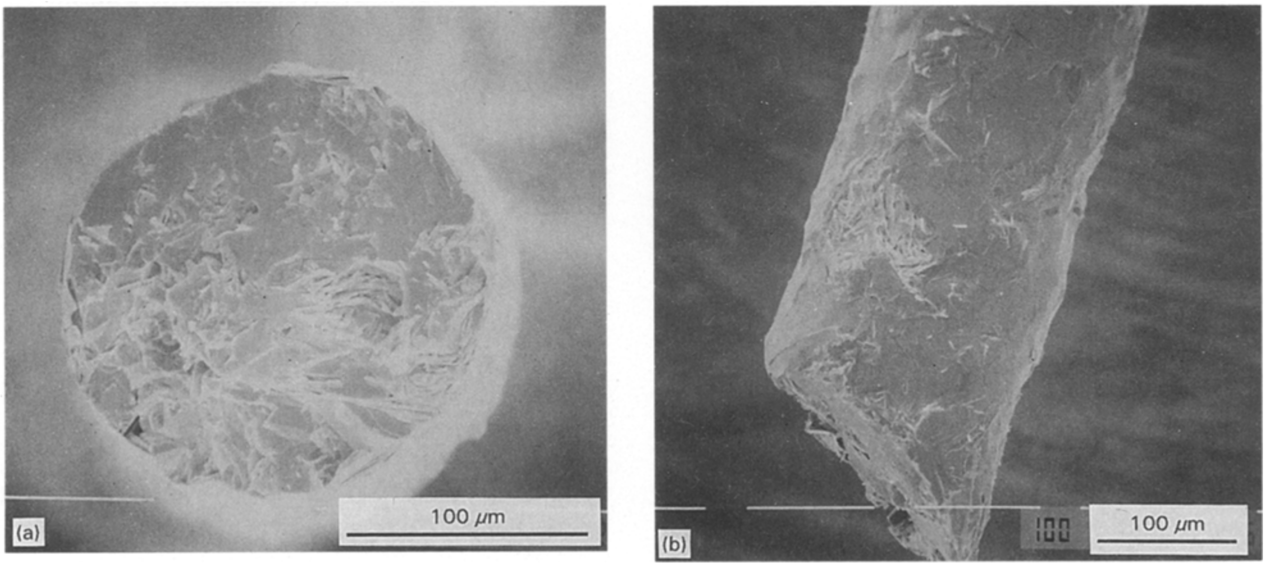

Figure 3 Scanning electron microscopy (SEM) photographs of a fused fibre; (a) cross-section (b) fibre surface.

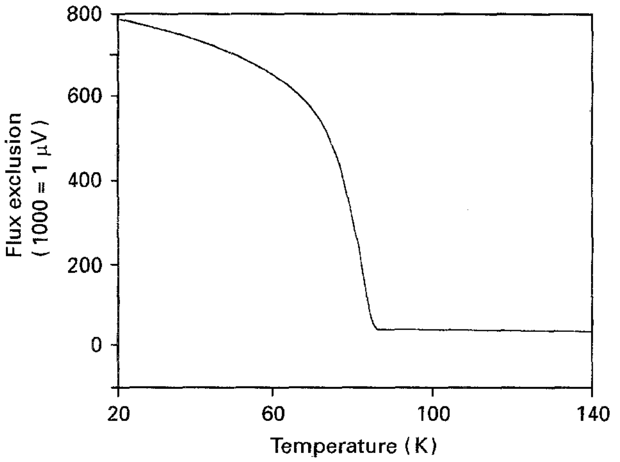

Figure 4 Magnetic flux exclusion versus temperature of the fired fibre prepared at 850 °C.

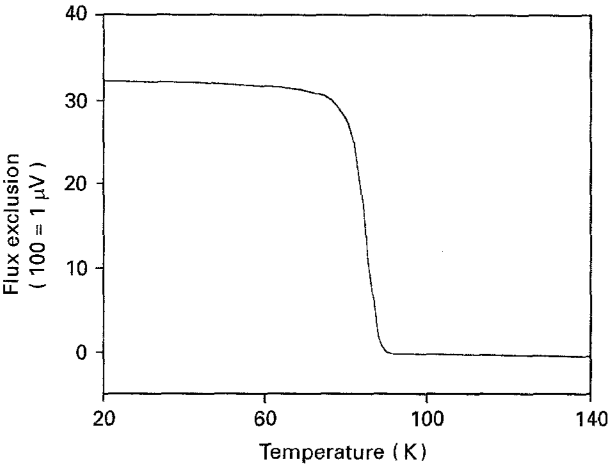

Figure 6 Magnetic flux exclusion versus temperature of the fused fibre made at 880 °C.

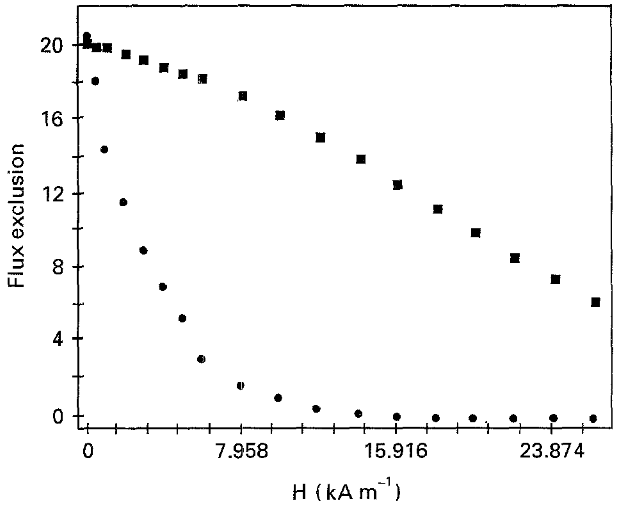

Figure 5 Magnetic flux exclusion versus applied d.c. magnetic field at 77 K. ● Fired fibre made at 850 °C; ■ fused fibre made at 880 °C.

2.6. Flux exclusion (Meissner effect) 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 measurements over a range of temperatures, the temperature dependence of the flux exclusion and the critical temperature of the sample could be obtained. The Bi2212 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 zero to 26.257 kA m^{-1} to determine the degree of coupling between superconducting grains.

3. Results and discussion

Fig. 1 shows a cross-section of one of the fired fibres prepared from the cycle with a T_{max} of 850 °C. The fibre is porous and has a diameter of 240 μm. Fig. 4 shows that these fired fibres have a Meissner on-set transition toward superconductivity at 85 K, typical for superconductive Bi2212. The transition is not sharp, and the flux is not completely excluded even at 20 K, indicating that superconducting grains are very small in size. In addition, flux exclusion of the fired fibres drops very rapidly in the presence of magnetic field and is reduced by 95% in an applied field of 7.956 kA m^{-1} and almost 100% in an applied field of 23.870 kA m^{-1} as shown in Fig. 5. The rapid reduction of magnetic flux exclusion is not surprising since the superconducting grains are small and grain boundaries are not well connected, as shown in Fig. 1. The fibres do not have zero resistance at an applied current density of 0.02 A cm^{-2} at 77 K. The electrical resistance does not drop significantly from room temperature to 77 K. Electrical conductivity of one of the fired fibres at room temperature is 14 S cm^{-1}. The electrical resistance data further confirm that superconducting grains are not well connected.

Fig. 3 shows a cross-section and fibre surface of a fibre prepared with the cycle 880 °C T_{max} cycle. It is only slightly porous and has fairly smooth, apparently fused surface indicating melting has occurred. The fibre diameter has been reduced to 170 μm. The fibres shown in Figs 1 and 3 have a diameter ratio of 1.4, indicating a reduction in porosity of about 50% on fusion. These fibres show a sharp Meissner transition when cooled from room temperature to 20 K, as shown in Fig. 6. Magnetic flux exclusion begins at 90 K and is almost complete at 75 K, which is expected since melting tends to result in an increase in grain size. The flux exclusion, as shown in Fig. 5, is reduced only by 17% in an applied magnetic field of 7.956 A m^{-1}. The reduction is much smaller compared with 95% reduction for the non-melted fibres, indicating that superconducting grains are more strongly coupled due to fusion. J_C of the fired fibres at 77 K was 331 A cm^{-2}. Electrical conductivity at room temperature is 210 S cm^{-1}. The fused fibre has superior superconductive properties compared to the non-melted fibre; J_C (77 K) is higher, flux exclusion is more complete and resistance to a magnetic flux is superior.

One of the fused fibres was analysed with energy dispersive X-ray to determine the composition. Based on a calculation of relative areas of the different phases observed in the micrograph, about 80% of the fibre was superconductive Bi2212. Three other oxide phases are also present: (1) A copper-free phase with the metal ratios $Bi_2(Sr_{0.69}Ca_{0.31})_{1.24}$, (2) $Ca_xSr_{1-x}Cu$ and (3) $Bi_2(Sr_{0.58}Ca_{0.42})_{1.39}Cu_{0.88}$. It is surprising that melting at 880 °C for 5 min does not totally destroy the Bi2212 phase. It is tempting to believe that decomposition is relatively slow at this temperature which is only slightly above the melting point.

4. Summary and conclusion

A particulate precursor of superconductive $Bi_2Sr_2CaCu_2$ oxide dispersed in an aqueous poly(vinyl alcohol) solution was shaped into fibres. The fibres fired at a T_{max} of 850 °C were very porous. They exhibited a Meissner on-set transition at 85 K, but electrical resistance at 77 K with a current density of 0.02 A cm^{-2} was still not zero. Fusing the porous fibres at a temperature of 880 °C densified them. The fused fibres had a sharp Meissner transition and carried a current (J_c) up to 331 A cm^{-2} at 77 K. They were more resistant to the effect of a magnetic field up to 7.956 A m^{-1} than the fibres fired at 850 °C. About 80% of the fused fibre was the superconductive Bi2212 phase.

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