JOURNAL OF MATERIALS SCIENCE 30 (1995) 6070–6074

The influence of pyrolysis condition on the partial melting of solution-spun $Y_1Ba_2Cu_3O_x$ superconducting filament

TOMOKO GOTO
Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

The precursor filaments with diameters of 300 and 110 μm were spun through a homogeneous aqueous poly(vinyl alcohol) (PVA) solution containing Y, Ba and Cu acetates. The as-drawn filaments were pyrolysed at a slow heating rate of 30 °C h^{-1} to remove volatile components and partially melted. The effect of pyrolysis condition on the partial melting of the filament was examined to enhance the reproducibility of the high J_C. By controlling the solidifying condition for the filament pyrolysed at 500 and 450 °C, a high J_C of more than 10^4 A cm^{-2} at 77 K and 0 T was attained. A window of heating condition to obtain the high J_C for the thin filament was narrow as compared with the thick filament. The optimum condition for the filament pyrolysed at 450 °C became wider than that for pyrolysing at 500 °C.

1. Introduction

One of the most convenient methods for the fabrication of high T_C superconducting wire nowadays is the Ag-sheathed processing of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ superconductor. However the critical current density, J_C, of the wire falls below 10^2 A cm^{-2} at 77 K when applying a field more than 1 T. This sensitivity to the field at high temperature of 77 K is considered to be intrinsic to the highly anisotropic Bi system material. Thin films of the less anisotropic Y-system superconductor have been produced with J_C of more than 10^4 A cm^{-2} at 77 K by applying a field of 7 T. Therefore the development of a conductor from Y-system superconductor is highly desired.

We have studied the preparation of a long superconducting oxide filament by using a textile fibre spinning technology for the precursor of the oxide and a high J_C value of more than 10^4 A cm^{-2} at 77 K and 0 T was obtained for the solution-spun Y-system filament by controlling the partial-melt growth technique [1, 2]. Nevertheless, the achievements of uniform grain alignment over long length and high yield have been difficult.

It has been reported on the studies of superconducting fibres from organometallic precursors that slow pyrolysis up to 400 °C in air followed by oxygen sintering appeared to give a superior fibre with controlled grain size and phase [3]. The pyrolysis condition followed by partial-melting must enhance the reproducibility of the high J_C.

On the other hand, the optimal ceramic superconducting fibre must be dense, thin and flexible. Commercial ceramic fibres that meet the flexibility criterion are typically less than 20 μm in diameter. Preparation of fine $Y_1Ba_2Cu_3O_x$ (1 2 3) superconducting filament by a solution-spinning method has also been studied. The window of optimum heating conditions for obtaining the high J_C of the fine filament was very narrow [4]. In this paper, the effect of a slow pyrolysis condition on the partial melting of the thick and thin filaments is examined.

2. Experimental details

A long filament was prepared by dry spinning through a starting homogeneous aqueous PVA solution, Y, Ba and Cu acetates and organic acids as reported in a separate paper [5]. The precursor 1 2 3 filaments with diameters of 300 and 110 μm were prepared. The filament was heated at 450 and 500 °C at a heating rate of 30 °C h^{-1} in air to remove volatile components and was partially melted.

The electrical resistivity of the heated filament was measured by a standard four-probe method. Silver paint was used to connect silver sputtered parts of the filament with Ag electrodes of 75 μm in diameter. The transport J_C measurement was performed at 77 K and 0 T using a continuous d.c. current with criterion of 1 μV cm^{-1}.

3. Results and discussion

3.1. Thick filament

The thermal behaviour of the precursor filament was examined by differential thermal analysis and thermogravimetric analysis (DTA–TG). Broad exothermic peaks at 230, 330 and 420 °C and a vigorous exothermic reaction at 465 °C were observed and the weight

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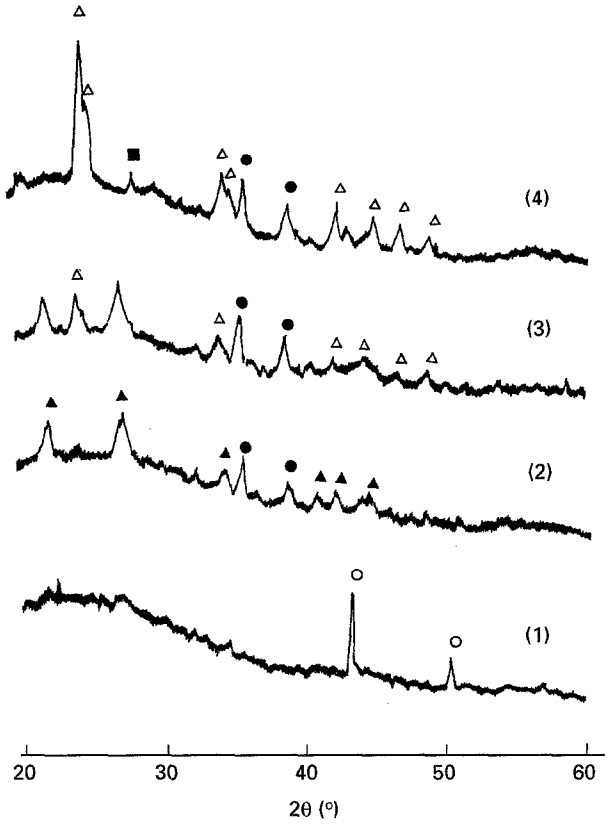

Figure 1 X-ray diffraction pattern of the filament pyrolysed at various conditions. (1) Pyrolysed at 400 °C at a heating rate of 30 °C h^{-1}. (2) Pyrolysed at 450 °C at a heating rate of 30 °C h^{-1}. (3) Pyrolysed at 500 °C at a heating rate of 30 °C h^{-1}. (4) Pyrolysed at 150 °C for 1 h and 500 °C for 1 h.

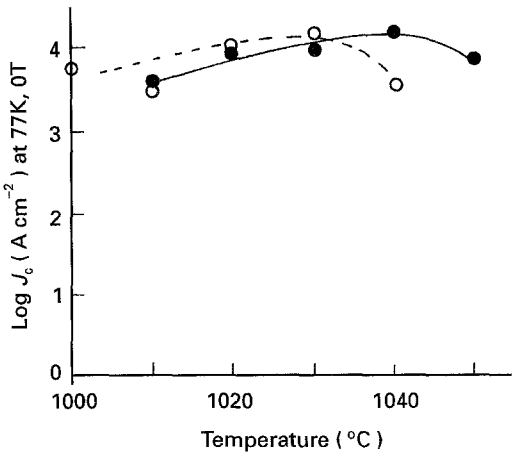

Figure 2 The J_Cs of the thick filament partially melted at various melting temperatures: —●— pyrolysed at 500 °C; —○— pyrolysed at 450 °C.

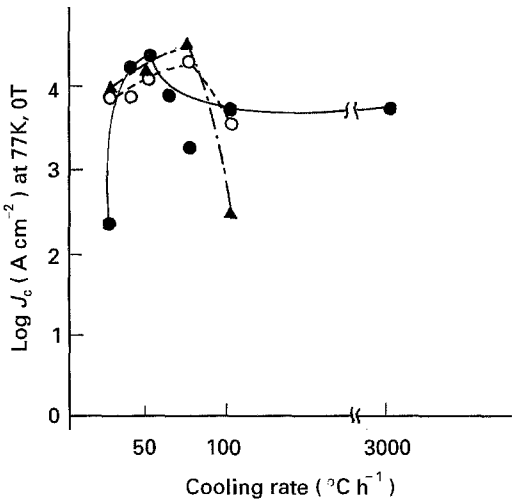

Figure 3 The J_Cs of the thick filament cooled at various cooling rates through the solidus temperatures: —●— pyrolysed at 500 °C and melted at 1020 °C for 60 min; —▲— pyrolysed at 500 °C and melted at 1040 °C for 20 min; —○— pyrolysed at 450 °C and melted at 1030 °C for 20 min.

decreased at 65 wt % from 100 to 500 °C on the DTA–TG curves. These changes are considered to be due to the decomposition of PVA, Y, Ba and Cu acetates [5]. The filaments were heated so far at 150 °C for 1 h and 500 °C for 1 h in air to remove volatile components. In this paper, the filament was pyrolysed up to 500 °C by using a slow heating rate of 30 °C h^{-1} in air.

X-ray diffraction pattern of the filament pyrolysed at various conditions are shown in Fig. 1. The filament pyrolysed up to 400 °C at slow heating had a mixed phase of metallic Cu (FCC $a = 0.3615$ nm) and amorphous phases, whereas the filament pyrolysed at 150 °C for 1 h and 500 °C for 1 h in air consisted of $BaCO_3$, CuO, Y_2O_3. The structure of the filament pyrolysed at 450 °C turns to a mixed phase of CuO and metastable tetragonal phase with $a = 0.520$ nm and $c = 0.806$ nm. Besides, the $BaCO_3$ phase appears on heating at 500 °C. Melt processing of the Y-system superconductor has been found to be effective in increasing J_C value through a combination of the reduction of weak links, grain alignment and the introduction of pinning centres. It was found that the filament pyrolysed up to 400 °C at a heating rate of 30 °C h^{-1} was melted by heating at more than 920 °C and had not undergone a partial-melting process [6]. Partial melting of the filament pyrolysed at 450 and 500 °C can be performed due to the stable CuO surface layer. During the melt growth process of a solution-spun filament, it is essential to control the melting temperature, melting time and the cooling rate of the solidus and peritectic temperature [2]. The filament was partially melted at various temperatures ranging from 1000 to 1050 °C for 20 min. Then temperature was reduced by 120 °C at a cooling rate of 50 °C h^{-1} and slowly cooled by 60 °C at a cooling rate of 40 °C h^{-1}, followed by furnace-cooling in flowing oxygen. The J_C of the filament partially melted at various temperatures for 20 min is shown in Fig. 2. A high J_C, more than 10^4 A cm^{-2}, was obtained at 1030 and 1040 °C for the filament pyrolysed at 450 and 500 °C, respectively. The optimum temperature for the filament pyrolysed at 450 °C is slightly lower than that for the filament pyrolysed at 500 °C. The filament was partially melted for various times. The lower melting temperature needed a longer time to obtain the high J_C. The effect of the J_C on the cooling rate through the solidus temperature was examined and the result is shown in Fig. 3. Maximum J_C is observed at a cooling rate of 75 °C h^{-1} for the filament melted at the optimum melting temperature. The optimum cooling rate

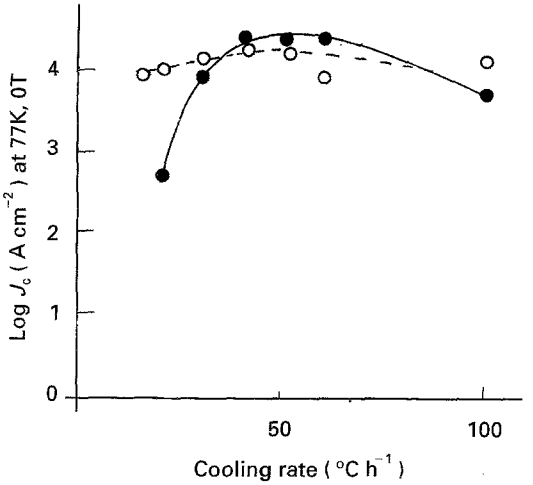

Figure 4 The J_Cs of the thick filament cooled at various cooling rates for 1 2 3 crystal growth: —●— pyrolysed at 500 °C; —○— pyrolysed at 450 °C.

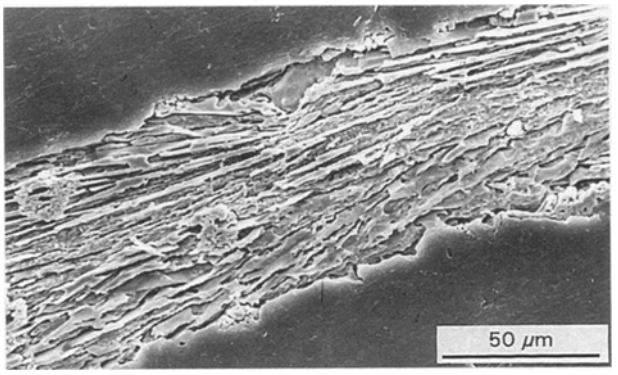

Figure 5 Fracture surface of the thick filament pyrolysed at 450 °C with $J_C = 23\,000$ A cm^{-2} at 77 K and 0 T.

decreases with decreasing melting temperature. It is pointed out on the peritectic reaction from $Y_2Ba_1Cu_1O_5$ (2 1 1) and liquid phase of $BaCuO_2$ and CuO to 1 2 3 phase, when a cooling rate is low enough, the reaction continues to promote grain growth of the existing 1 2 3 crystals rather than to nucleate a new 1 2 3 crystal [7]. It was observed in the filament quenched from 910 °C that the needle-like crystal growth preceded by slow cooling and the shape of the needle-like crystals was also beneficial to the preferred orientation of the following crystal growth [2].

The J_C of the filament is also dependent on a cooling rate for the 1 2 3 crystal growth. The filament was cooled at various cooling rates ranging from 910 to 840 °C. The relation between J_C and the cooling rate is shown in Fig. 4. A window for obtaining the high J_C of more than 10^4 A cm^{-2} for the filament pyrolysed at 450 °C, is wider than that for the filament pyrolysed at 500 °C due to the free $BaCO_3$ present during the pyrolysis. It is well known for the bulk 1 2 3 oxide the crystal growth rate less than 1 °C h^{-1} is needed for good alignment. However one order higher cooling rate is required for crystal grain alignment in the solution-spun filament because of the beneficial filamentary morphology to the crystal alignment. Figs 5 and 6 show the fracture surface and the longitudinal cross-section of the filament with high J_C. The diameter of the filament reduced to 70 μm in spite of the starting diameter of 300 μm. The filament pyrolysed at 450 °C is covered with fine columnar grains, in spite of the plate-like grains aligned perpendicular to the fibre axis which are observed in the core of the filament, as shown in Fig. 5. A well-aligned structure along the fibre axis is also observed as shown in Fig. 6.

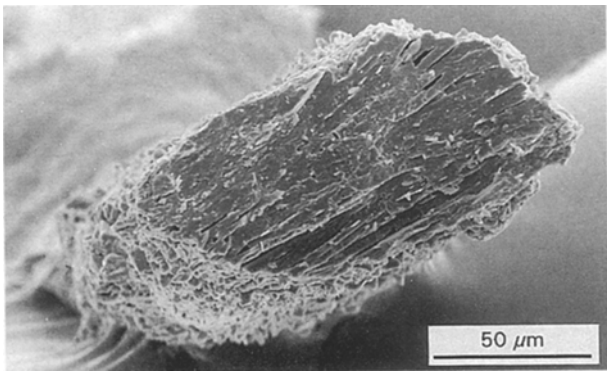

Figure 6 Polished and etched surface on the longitudinal cross-section of the thick filament pyrolysed at 500 °C with $J_C = 34\,000$ A cm^{-2} at 77 K and 0 T.

The current lead for the measurement of J_C is connected on the surface of the filament. Hence the J_C of the filament is dominant on the surface structure of the filament even if the inner grains have a well-aligned texture to both directions parallel and perpendicular to the fibre axis.

3.2. Fine filament

The partial melting of the fine filament pyrolysed at 500 and 450 °C was examined to enhance the J_C and to obtain the textured microstructure. The filament was partially melted at various temperatures and the temperature lowered by 200 °C at a cooling rate of 50 °C h^{-1} followed by furnace-cooling in flowing oxygen. The J_C of the filament partially melted at various temperatures is shown in Fig. 7. The window for the optimum heating condition becomes very narrow when compared with that for the thick filament. The optimum temperature for the filament pyrolysed at 450 °C is lower than that for the filament pyrolysed at 500 °C. The effects of the cooling rate through the solidus temperature were examined and the results are shown in Fig. 8. The optimum cooling rate decreases with increasing melting temperature. A higher J_C is attained for the filament pyrolysed at 450 °C, although the optimum cooling rate is narrow. The cooling rate for the 1 2 3 crystal growth is also dependent on the J_C of the filament as shown in Fig. 9. A higher cooling rate is needed for the thin filament than for the thick filament, due to the finer filamentary morphology. The highest J_C of 27 000 A cm^{-2} is attained for the filament pyrolysed at 450 °C with diameter of 24 μm. The longitudinal cross-section of the filament with high J_C was also examined and a well-aligned texture along the fibre axis, as seen in Fig. 6, was observed.

Some examples of the fracture morphology of the thin filaments pyrolysed at 500 and 450 °C are shown in Figs 10 and 11, respectively. Plate-like grains

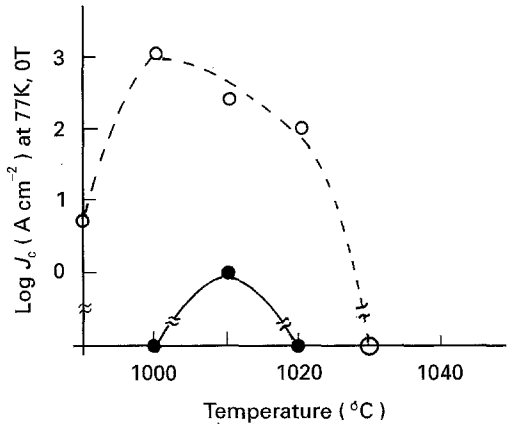

Figure 7 The J_Cs of the thin filament partially melted at various melting temperatures: —●— pyrolysed at 500 °C; —○— pyrolysed at 450 °C.

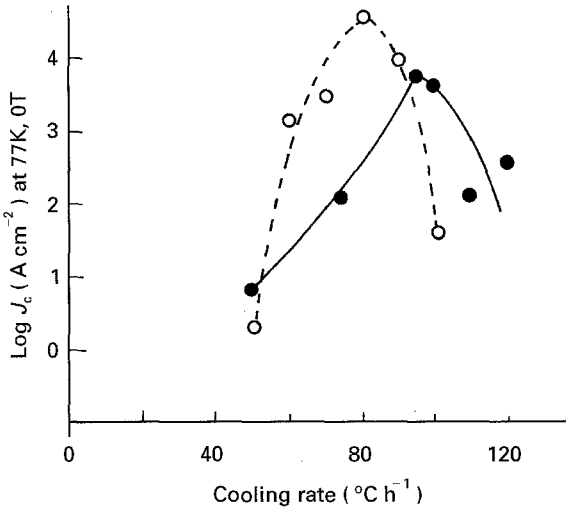

Figure 8 The J_Cs of the thin filament cooled at various cooling rates through the solidus temperatures: —●— pyrolysed at 500 °C and melted at 1010 °C for 15 min; —○— pyrolysed at 450 °C and melted at 1000 °C for 60 min.

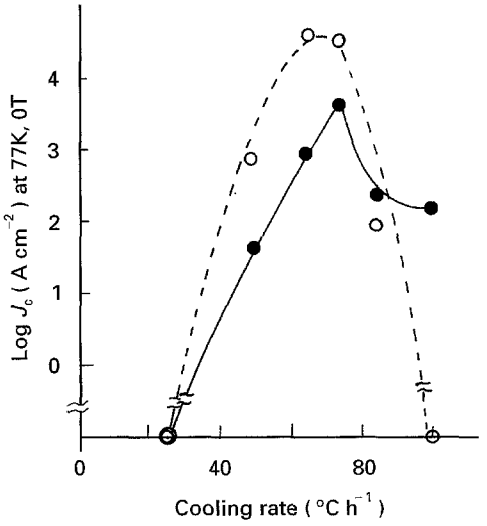

Figure 9 The J_Cs of the thin filament cooled at various cooling rates for 123 crystal growth. —●— pyrolysed at 500 °C; —○— pyrolysed at 450 °C.

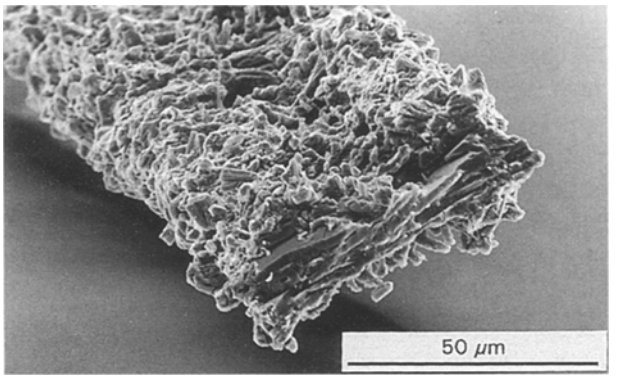

Figure 10 Fracture surface of the thin filament pyrolysed at 500 °C with $J_C = 6800$ A cm^{-2} at 77 K and 0 T.

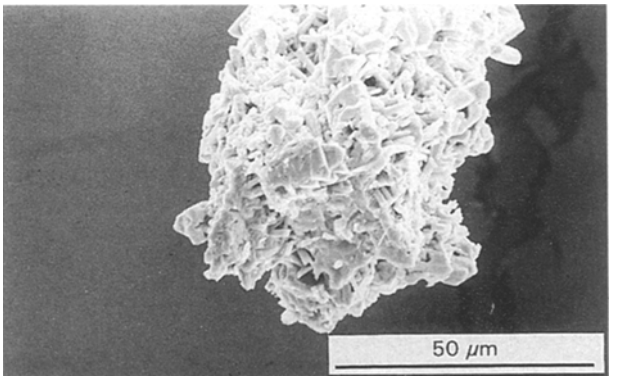

Figure 11 Fracture surface of the thin filament pyrolysed at 450 °C with $J_C = 24000$ A cm^{-2} at 77 K and 0 T.

appeared in the core of the filament pyrolysed at 500 °C. However, the filament is covered with irregular fine grains and hence the J_C is relatively low. In contrast, the surface of the filament pyrolysed at 450 °C consists of a closely packed mixture of plate-like and rod-like grains. Controlling the surface of the filament is a key to obtaining finer filaments with high J_C values.

Thus, the optimum solidifying condition became wider for the filament slowly pyrolysed at 450 °C due to free $BaCO_3$ present during the pyrolysis.

4. Conclusion

The effect of slow pyrolysis condition on partial-melting process of thick and thin filaments produced by solution spinning are examined to enhance the reproducibility of the high J_C. The filament pyrolysed at 400 °C at a heating rate of 30 °C h^{-1} consisted of metallic Cu and amorphous phases and completely melted on heating to more than 920 °C. Hence the partial-melting process was not performed. By controlling the melting growth process, high J_C, more than 10^4 A cm^{-2}, was reproducibly obtained for the thick filament pyrolysed at more than 450 °C. The window of the optimum melting condition became narrow for the fine filament. Achieving the high J_C for the filament pyrolysed at 450 °C was easier than that for the pyrolysis at 500 °C due to the free $BaCO_3$ present during the pyrolysis. A well-aligned texture in

the thin filament needed a higher cooling rate for 1 2 3 crystal growth than that for the thick filament due to the beneficial filamentary morphology to the crystal alignment.

Acknowledgements

This work was partly supported by a grant-in-Aid for Science Research on Priority Areas "Science of High TC Superconductivity" given by the Ministry of Education, Science and Culture, Japan.

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Received 12 October 1994
and accepted 24 May 1995