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Solution spinning of high-T_c oxide superconducting filament

Part VIII *The effect of degree of saponification of poly(vinyl alcohol) on the critical current density of $YBa_2Cu_3O_x$ superconducting filament*

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The precursor $YBa_2Cu_3O_x$ (Y-123) filaments were prepared by solution spinning through aqueous poly(vinyl alcohol) (PVA) solution containing mixed Y, Ba and Cu acetates. The as-drawn filaments were heated to remove volatile components and to generate a superconducting phase. The effect of degree of saponification (DS) of PVA in the precursor filament on the critical current density, J_c, for the heated filaments was studied. The precursor filaments were successfully prepared using PVA with DSs ranging from 65 to 81 mol%. The liquid-phase sintering throughout the filament occurred for the filament spun from PVA solution with a DS of 71 mol% and sintered at 920 °C for 15 min. The filaments were partially melted to enhance J_c. The minimum J_c was observed for the filament with a DS of 67 mol%, and the highest J_c of 3.5×10^4 A cm^{-2} at 77 K and 0 T was achieved for the filament with a DS of 81 mol%. A configuration of PVA in the precursor filament affects the superconductivity of the heated filament.

1. Introduction

Processing of Y-system superconducting wires with a high critical current density, J_c, more than 10^5 A cm^{-2} at 77 K is required for practical applications as superconducting magnets and transmission lines. J_c is dependent on its microstructure, and hence the processing technique. Various melt texture techniques for the Y-system superconductor are well known for fabricating a microstructure with a non-weak link, strong flux pinning and good grain alignment and to enhance J_c for the bulk Y-system oxide [1, 2].

We have studied the preparation of high-T_c oxide superconducting filaments using textile fibre spinning technology for the precursor of the filament. The precursor filaments were prepared by dry spinning from a starting homogeneous aqueous solution containing Y, Ba and Cu acetates and poly(vinyl alcohol) (PVA). The superconducting properties of the heated filaments depend on the spinning conditions as well as on the heating treatment [3, 4].

In particular, it is found that J_c for the heated filament was strongly dependent on the degree of the polymerization (DP) of PVA and the content of acetates in the precursor filaments [5–7]. In this paper, the effect of the degree of saponification (DS) of PVA in the precursor filament on J_c for the filament heated is examined.

2. Experimental procedure

PVA with various DSs were prepared by alkaline hydrolysis of poly(vinyl acetate) (PVAc) in methyl alcohol. PVAc with a DP of 1500 was dissolved in methyl alcohol, and sodium hydroxide aqueous solution was added to the solution. The obtained PVA was purified by a reprecipitation method. The DS of the PVA was determined by infrared (IR) spectroscopy measurement.

Precursor filaments were produced by dry spinning with a starting homogeneous aqueous solution of Y, Ba and Cu acetates as reported in a separate paper [3]. An aqueous solution was prepared by dissolving the PVA, propionic acid and 2-hydroxy isobutyric acid. A mixture of the acetates with an atomic ratio of Y:Ba:Cu = 1:2:3 were dissolved in the aqueous solution. The weight ratio of the mixed acetates to PVA was 2.8. The resultant solution was concentrated to obtain a stable homogeneous spinning dopant. The dopant was deaerated at 80 °C for 20 h and then extruded as a filament into a hot air zone and coiled on a winding drum.

The as-drawn filaments with diameter of 250 μm were heated up to 450 °C at a heating rate of 30 °C h^{-1} in air to remove volatile components. The pyrolysed filaments were sintered in the temperature range from 880 to 940 °C for 15 min in flowing oxygen. The

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pyrolysed filaments were partially melted at various conditions in flowing oxygen in order to enhance J_c.

The electrical resistivity of the heated filaments was measured by a standard four-probe method. Silver paint was used to connect silver sputtered parts of the filaments with Ag electrodes of 75 μm diameter. The transport J_c measurement was performed at 77 K and 0 T with a voltage of 1 $\mu V\, cm^{-1}$.

3. Results

3.1. Preparation of the precursor filament

The DS of PVA was determined by IR spectroscopy measurement. The IR spectrum of PVA film with a DS of 85 mol% is shown in Fig. 1. Absorptions observed at 3300, 1700 and 1400 cm^{-1} are characteristic bands of hydroxy groups, carboxylate groups and methylene groups, respectively. The DS of the present PVA was estimated from the average value of a relative absorbance decrease at 3300 cm^{-1} and a relative absorbance increase at 1700 cm^{-1} to that at 1400 cm^{-1}. Calibration curves were made using commercial PVA with various DSs and PVAc.

The dry spinning of the precursor oxide was examined using the PVA solutions with DSs ranging from 65 to 92 mol% were obtained. A stable jet of the dopant was not obtained using the PVA solution with a DS of more than 90 mol%. The solution spinning was successfully performed using PVA with DSs ranging from 65 to 81 mol%.

3.2. Sintering of the filaments

The as-drawn filaments were pyrolysed up to 450 °C at a heating rate of 30 °C h^{-1} in air to remove volatile components. The structure of the pyrolysed filaments is a mixed phase of CuO and metastable tetragonal phase with $a = 0.520$ nm and $c = 0.806$ nm. The pyrolysed filaments were sintered at various temperatures ranging from 880 to 940 °C for 15 min in flowing oxygen. A single $YBa_2Cu_3O_x$ (Y-123) phase was observed for all the sintered filaments by means of the X-ray diffraction method. The relationship between J_c and sintering temperature for the filaments spun from PVA solutions with DSs of 65, 71 and 81 mol% is shown in Fig. 2. J_c for the filaments from PVA with DSs of 65 and 81 mol% were comparatively high at temperatures ranging from 880 to 940 °C. A very low J_c was observed for the filament with a DS of 71 mol% sintered at 920 °C, in spite of the fact that the filament consisted of Y-123 single phase. The microstructure of the filaments was examined with scanning electron microscopy. The fracture surfaces of the filaments with DSs of 71 and 65 mol% sintered at 920 °C are shown in Fig. 3. The filament with a DS of 65 mol% and with a high J_c consists of a porous structure. The filament

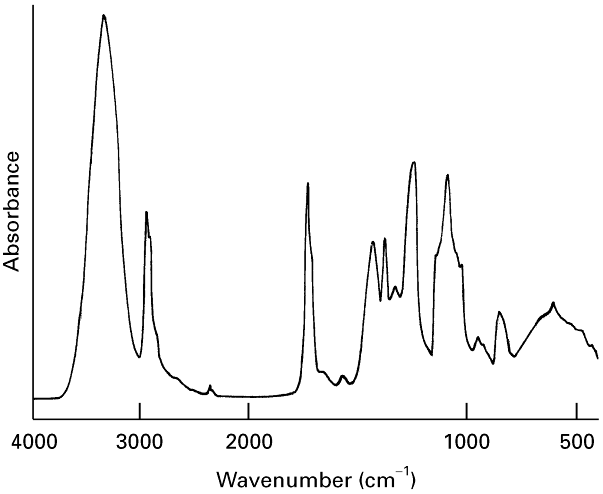

Figure 1 IR spectrum of the PVA with a DS of 85 mol%.

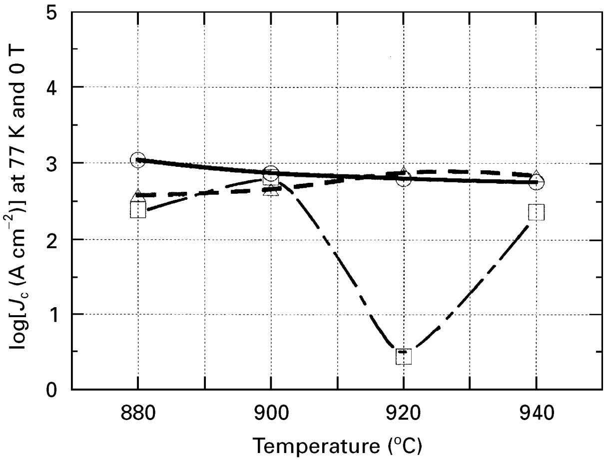

Figure 2 The J_c values of the filaments sintered at various temperatures for 15 min. (—⊖—), filament spun from the PVA solution with a DS of 81 mol%; (—-⊟-—), filament spun from the PVA solution with a DS of 71 mol%; (--△--), filament spun from the PVA solution with a DS of 65 mol%.

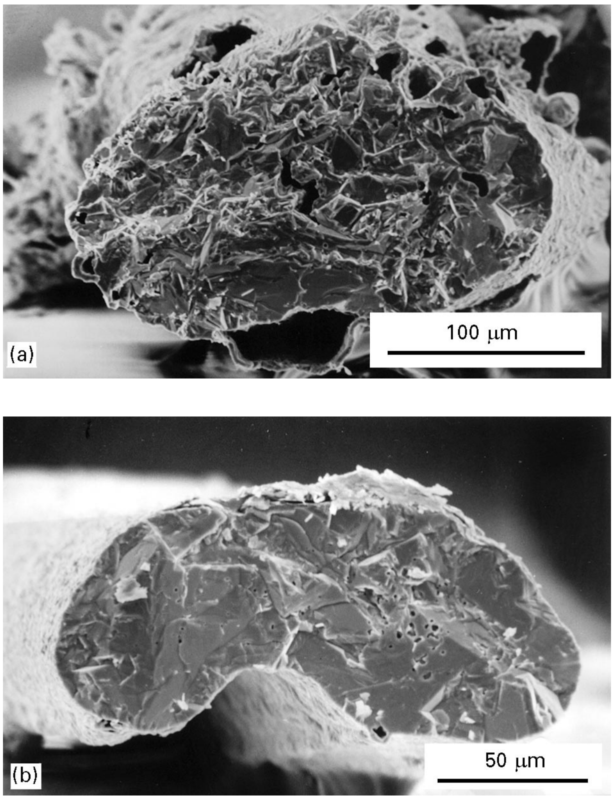

Figure 3 Fracture surface of the filament sintered at 920 °C: (a) filament spun from PVA solution with a DS of 65 mol%; (b) filament spun from PVA solution with a DS of 71 mol%.

with a DS of 71 mol% and the lowest J_c shows a densely packed structure throughout the filament. It is pointed out that the liquid-phase sintering results in improved density and increased grain size, but it also results in an insulating phase along the grain boundaries and a decrease in J_c [8]. The dense structure of the present filament was similar to that obtained by liquid-phase sintering.

3.3. Partial melting of the filaments

A partial melting process of the precursor filaments was examined to enhance J_c. For the melt growth process of the filaments, it was important to control the melting temperature, the melting time and the cooling rate through the solidus and the peritectic temperatures [4]. The filament spun from the PVA solution with a DS of 81 mol% was partially melted at various temperatures ranging from 1010 to 1045 °C for 20 min and cooled by 120 °C at a cooling rate of 75 °C h^{-1}. Then the temperature was reduced by 60 °C at a cooling rate of 40 °C h^{-1}, followed by furnace cooling in flowing oxygen. Fig. 4 shows the relationship between J_c and the partial melting temperature. The filaments with DSs of 65 and 71 mol% were also partially melted and the J_c values are shown in Fig. 4. A maximum J_c of more than 10^4 A cm^{-2} was obtained for the filament from PVA with a DS of 81 mol% melted at 1040 °C. For the filament with a DS of 65 mol% the highest J_c of 8.9×10^3 A cm^{-2} was observed at 1040 °C. On the contrary, the filament with a DS of 71 mol% exhibited low J_c values and the highest J_c of 1.9×10^3 A cm^{-2} was observed at a high temperature of 1060 °C.

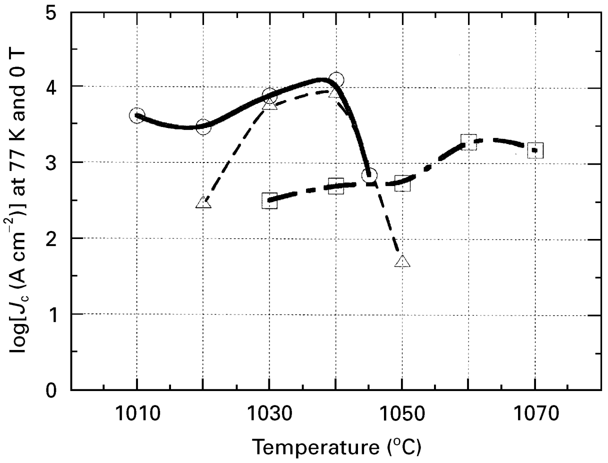

Figure 4 The J_c values of the filaments partially melted at various melting temperatures. (—○—), filament spun from the PVA solution with a DS of 81 mol%; (—-□-—), filament spun from the PVA solution with a DS of 71 mol%; (--△--), filament spun from the PVA solution with a DS of 65 mol%.

The filaments were partially melted at optimum temperatures for various melting times, followed by the above heating schedule. J_c for the filaments is shown in Fig. 5. High J_c values of more than 10^4 A cm^{-2} were observed for the filament with a DS of 81 mol% for melting times ranging from 20 to 40 min, although the maximum J_c for the filaments with DSs of 71 and 65 mol% was obtained for 20 min. J_c for the filament with a DS of 71 mol% is very low.

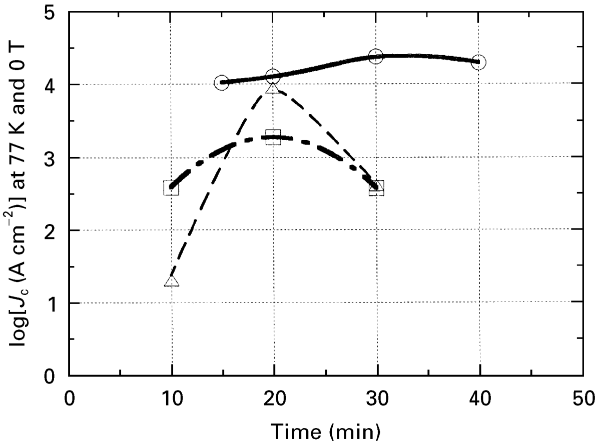

Figure 5 The J_c values of the filaments partially melted for various melting times. (—○—), filament spun from the PVA solution with a DS of 81 mol%; (—-□-—), filament spun from the PVA solution with a DS of 71 mol%; (--△--), filament spun from the PVA solution with a DS of 65 mol%.

The effect of the cooling rate through the solidus temperature was examined. The filaments were partially melted and cooled through the solidus temperature at various cooling rates. The results are shown in Fig. 6. The window for obtaining the high J_c of the filament with the highest DS is wider than that of the filaments with a lower DS. The highest J_c of 3.5×10^4 A cm^{-2} was attained for the filament with a DS of 81 mol% cooled at 50 °C h^{-1}.

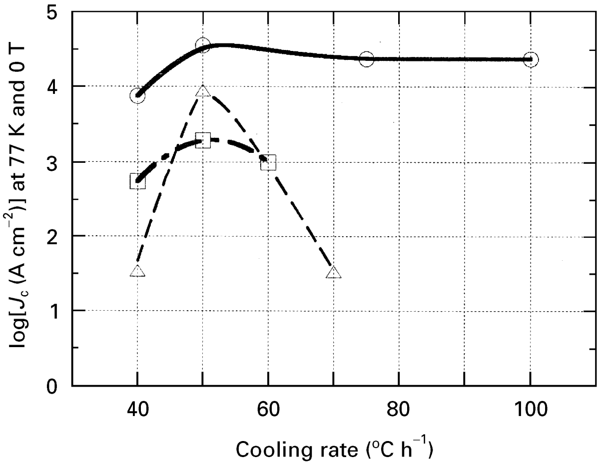

Figure 6 The J_c values of the filaments cooled at various cooling rates through the solidus temperatures. (—○—), filament spun from the PVA solution with a DS of 81 mol%; (—-□-—), filament spun from the PVA solution with a DS of 71 mol%; (--△--), filament spun from the PVA solution with a DS of 65 mol%.

As J_c for the filaments is also dependent on the cooling rate for the Y-123 crystal growth, the filaments were cooled at around 900 °C at various cooling rates. J_c for the filaments is shown in Fig. 7. High J_c values of more than 10^4 A cm^{-2} were observed for the filament with the highest DS by cooling at rates ranging from 20 to 60 °C h^{-1}. The maximum J_c for the filament with a DS of 71 mol% was lower than that for the filament with the lowest DS.

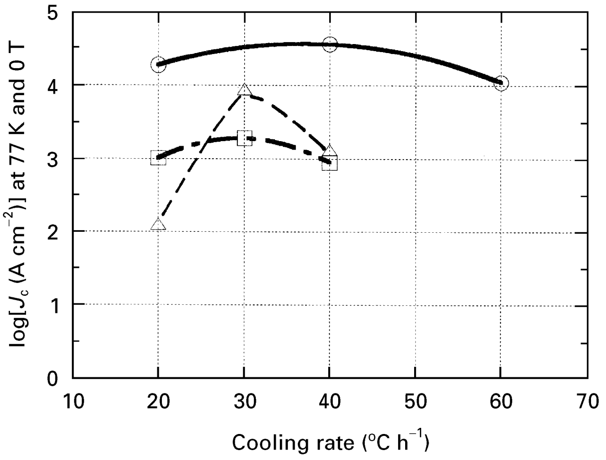

Figure 7 The J_c values of the filaments cooled at various cooling rates for Y-123 crystal growth. (—⊖—), filament spun from the PVA solution with a DS of 81 mol%; (— - ⊟- —), filament spun from the PVA solution with a DS of 71 mol%; (– –△– –), filament spun from the PVA solution with a DS of 65 mol%.

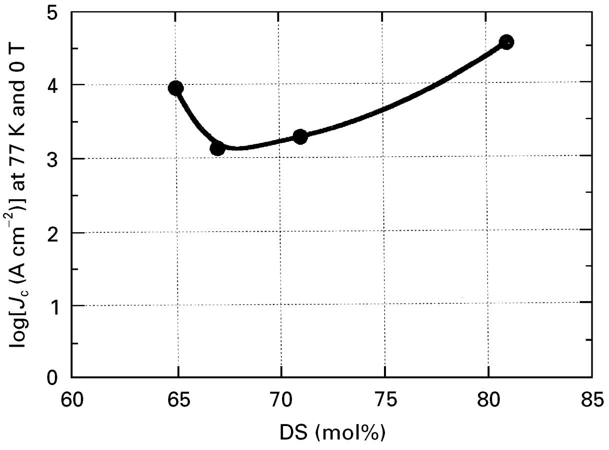

Figure 8 The relationship between the maximum J_c of the partially melted filament and the DS in the precursor filament.

Thus, the window of optimum heating conditions for the filament spun from PVA with a low DS is very narrow.

The relationship between the maximum J_c of the partially melted filament and the DS of the PVA in the precursor filament is summarized in Fig. 8. J_c is dependent on the DS. Although the highest J_c value of 3.5×10^4 A cm^{-1} was obtained for the filament with the highest DS of 81 mol%, the minimum J_c was observed for the filament with a DS of 67 mol%. A relatively high J_c was obtained for the filament with the lowest DS of 65 mol%.

The fracture surface and the polished and etched surface on the longitudinal cross-section of the filaments with DSs of 81, 71 and 65 mol% are shown in Figs 9, 10 and 11, respectively. The filaments are covered with irregular grains, and plate-like grains are aligned in the core. The grains are densely packed and well aligned along the fibre axis throughout the filament with the highest DS, as shown in Fig. 9. The filaments with low DSs of 71 and 65 mol% consist of a porous structure, and the grains are roughly packed and loosely aligned compared with the filament with the highest DS.

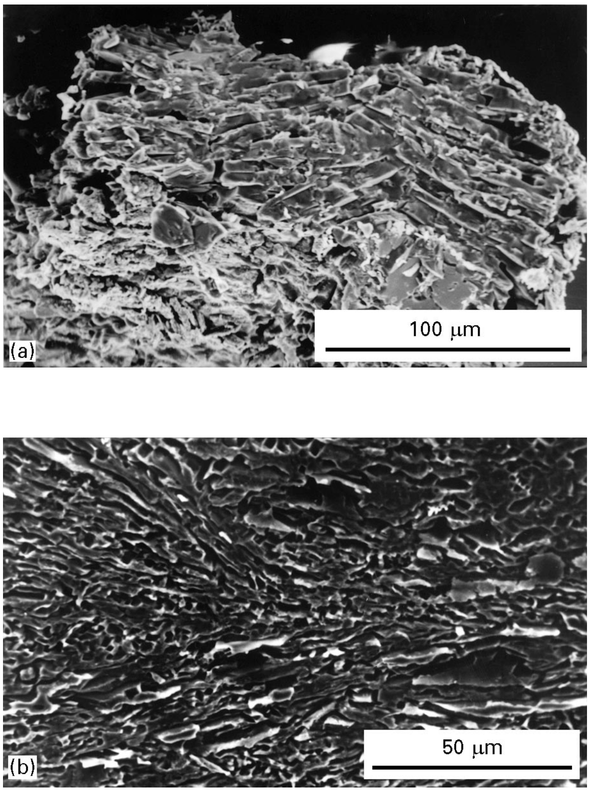

Figure 9 Scanning electron micrographs of the filament with $J_c = 3.5 \times 10^4$ A cm^{-2} at 77 K and 0 T, where the filament was spun from the PVA solution with a DS of 81 mol% and partially melted: (a) fracture surface; (b) the polished and etched surface on the longitudinal cross-section.

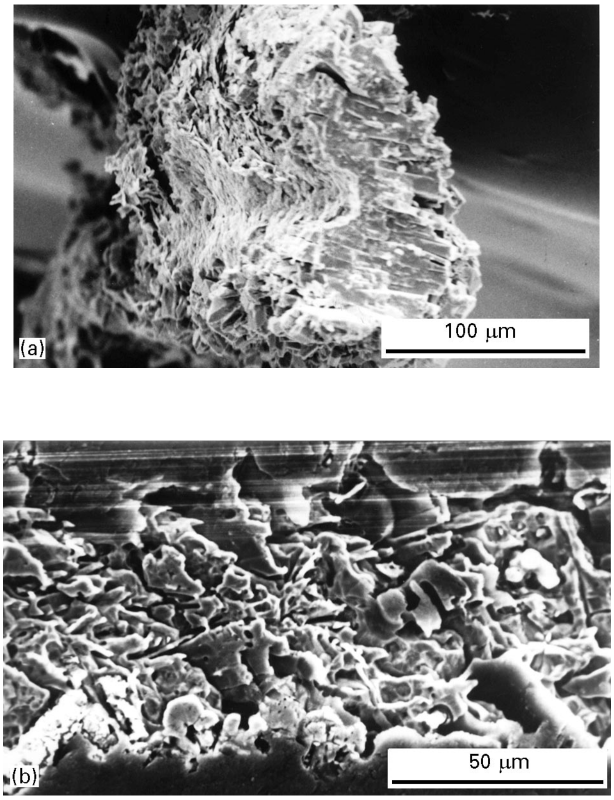

Figure 10 Scanning electron micrographs of the filament with $J_c = 1.9 \times 10^3$ A cm^{-2} at 77 K and 0 T, where the filament was spun from the PVA solution with a DS of 71 mol% and partially melted: (a) fracture surface; (b) the polished and etched surface on the longitudinal cross-section.

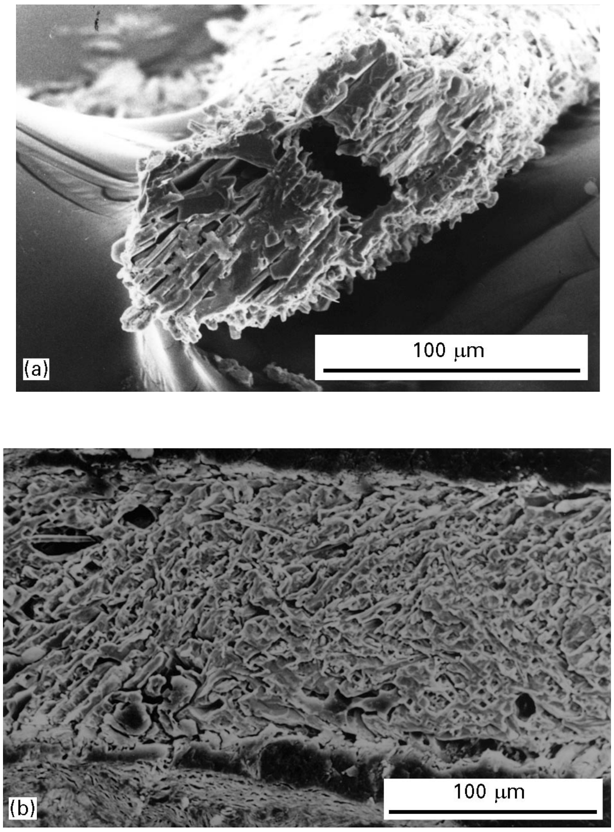

Figure 11 Scanning electron micrographs of the filament with $J_c = 8.9 \times 10^3 \mathrm{A\ cm^{-2}}$ at 77 K and 0 T, where the filament was spun from the PVA solution with a DS of 65 mol% and partially melted: (a) fracture surface; (b) the polished and etched surface on the longitudinal cross-section.

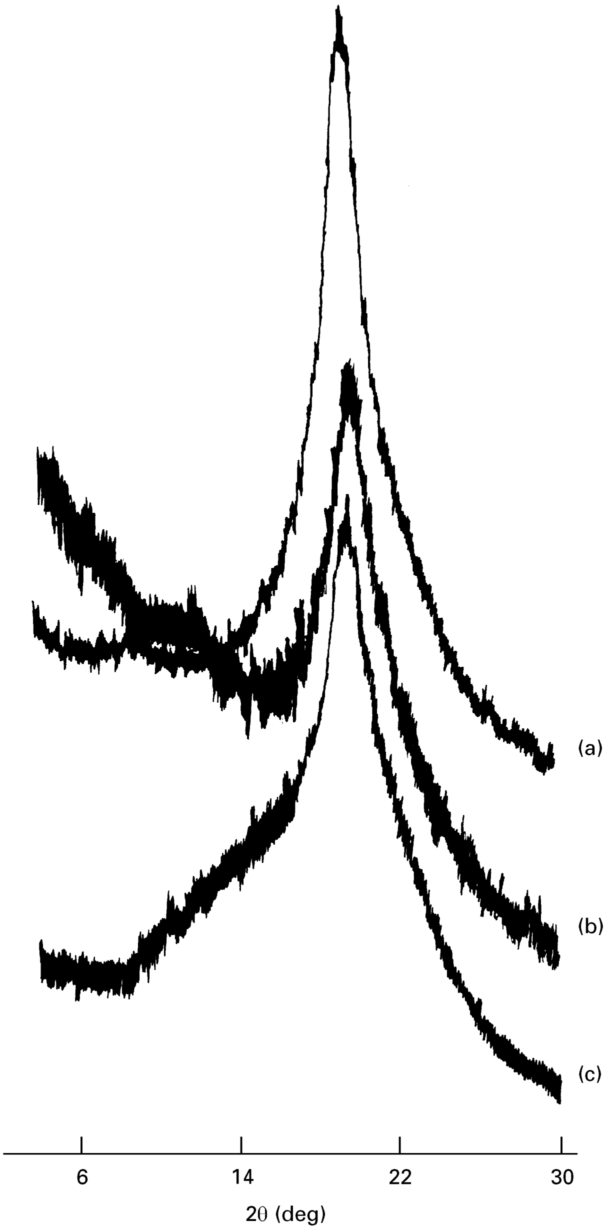

Figure 12 X-ray diffraction patterns of the PVA with DSs of 81 mol% (curve (a)), 71 mol% (curve (b)) and 65 mol% (curve (c)) (Cu Kα radiation).

4. Discussion

Summarizing the above results, the DS of the PVA in the precursor filament affected the J_c value of the heated Y-123 filament. A very low J_c was observed for the filament with a DS of 71 mol% sintered at 920 °C for 15 min. In the case of partially melted filaments, J_c increased with increase in the DS ranging from 67 to 81 mol%. However, the filament with the lowest DS of 65 mol% showed a very high J_c. This suggested that the configuration of the PVA in the precursor filament affects the superconductivity of the heated filament.

Therefore, the crystal structure of the PVA used was investigated by means of X-ray diffraction. Fig. 12 shows the X-ray diffraction patterns of the PVA used. The PVA had a sharp peak at $2\theta = 20°$ which arises from the [101] reflection of crystal structure formed by hydrogen bonding of the hydroxy groups [9]. The intensity of the peak for the PVA with a DS of 71 mol% was lower than that of the other peaks. The PVA with a DS of 65 mol% has a broad peak at around $2\theta = 14°$ in addition to the peak at $2\theta = 20°$. The broad peak at around $2\theta = 14°$ for the PVA with the lowest DS is considered to indicate the formation of another structure due to the unsaponified acetate group. It is pointed out that the hydroxy groups are not distributed randomly but rather in blocks along the polymer chain during the saponification process [10]. This suggests that the hydroxy groups in the present PVA with the lowest DS of 65 mol% are formed as a blocky type. As the DS increases, the hydroxy groups tend to distribute homogeneously.

In the basic research on the spinning dopant, the formation of a multimetal polynuclear complex attached to the hydroxy groups on PVA in the Y-123 precursor filament was reported [11]. For the present PVA with the lowest DS of 65 mol%, the configuration of the complex is blocky along the polymer chain, and the complexes are aligned heterogeneously throughout the filament. The bulky complex is beneficial for the partial melting and a relative high J_c is observed.

On the other hand, a homogeneous distribution of the complex occurs throughout the filament for the PVA with a DS of 71 mol% owing to the random distribution of the hydroxy groups. It was confirmed that liquid-phase sintering in the whole filament from the PVA with a DS of 71 mol% was observed owing to the homogeneous complex distribution. However, the dilute fine complex resulted in a low J_c in partial melt processing. As the amount of hydroxy groups increases, the complex alignment increases, and J_c for the filament partially melted increases.

Therefore, J_c for the heated filament depends on the configuration of PVA used in the precursor filament.

5. Conclusion

The effect of the DS of PVA in the precursor filament on J_c for the heated filament was examined. The precursor Y-123 filament was produced by dry spinning from a starting homogeneous aqueous solution containing PVA and Y, Ba and Cu acetates. The solution spinning was successfully performed through the PVA solution with DSs ranging from 65 to 81 mol%. The filament was pyrolysed to remove volatile components and then sintered in flowing oxygen. A very low J_c was observed for the filament with a DS of 71 mol% sintered at 920 °C for 15 min, and liquid-phase sintering occurred throughout the filament. The pyrolysed filaments were partially melted to enhance J_c. The highest J_c of $3.5 \times 10^4\ \mathrm{A\,cm^{-2}}$ at 77 K and 0 T was achieved for the filament with the highest DS of 81 mol%, whereas the filament with a DS of 71 mol% showed the minimum J_c. These behaviours arise from the alignment and distribution of the complex in the precursor filament. The configuration of PVA in the precursor filament dominates the superconductivity of the heated filament.

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