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Polymer coating for filamentary $YBa_2Cu_3O_x$ superconductors

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Polymer coating for filamentary $YBa_2Cu_3O_x$ superconductors was examined. The precursor filaments were prepared by solution spinning through aqueous poly(vinyl alcohol) solution containing mixed acetates of Y, Ba and Cu. The as-drawn filaments were heated to remove volatile components and to generate a superconducting phase. The synthesis of polyamide acid for the polymer coating was made. The filamentary superconductors were coated with the polyamide acid and cured to convert to the polyimide. The surface of the sample was an insulator. The critical current (I_c) value of the filamentary sample at 77 K was preserved by the polyimide coating. Moreover, the I_c for the polyimide-coated sample was maintained after holding at room temperature for more than 6 months. After thermal cycling between 77 K and room temperature 10 times, the I_c for the coated sample did not deteriorate, whereas the I_c for the sample without polymer coating disappeared. Polymer coating using epoxy resin applied to the filamentary superconductors was also examined.

1. Introduction

It is well known that $Y_1Ba_2Cu_3O_x$ (Y123) high-T_c-superconductors (T_c: critical temperature) exhibit poor mechanical properties and are degraded by CO_2 and H_2O in the atmosphere [1]. Good thermal cycle properties between 77 K and room temperature for Y123 superconductors are important for cryogenic applications operating at 77 K, such as magnetic bearings, permanent magnets, energy storage devices, electric motors and current leads. Therefore polymer coating of the superconductors is necessary for such applications. In the case of $RE_1Ba_2Cu_3O_y$ superconductors (RE: Y, Nd, Sm, Eu, Gd etc.) prepared by the melt textured growth process, the gas generation during the heat treatment gives rise to porosity and tetragonal to orthorhombic phase transformation by oxygen annealing produces cracks. For superconductors containing porosity and cracks, the thermal stress produced by refrigeration using liquid nitrogen extends the cracks, deteriorates the superconductivity and sometimes leads to destruction of the sample.

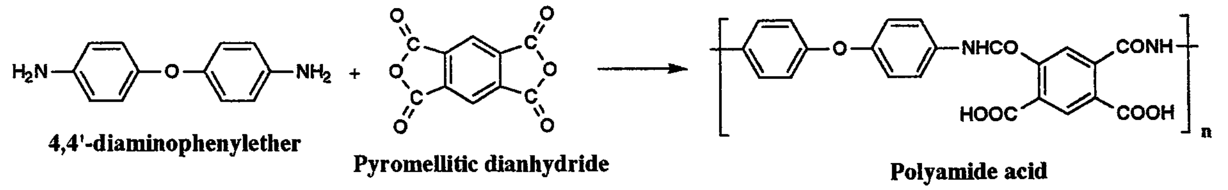
Recently, Tomita *et al.* reported [2] that epoxy resin impregnation into bulk superconductors in vacuum resulted in disappearance of the microcracks and porosity, and the mechanical properties were improved. In addition, the epoxy resin impregnation prevented the superconductivity from deteriorating due to CO_2 and H_2O in the atmosphere even after long term exposure.

We have studied the preparation of filamentary superconductors by solution spinning through aqueous poly(vinyl alcohol) solution containing mixed acetates of Y, Ba and Cu [3]. The filamentary superconductors have to be coated by polymer for the cryogenic applications. Polyimide is a heat-resistant polymer and is suitable for coating of Y123 superconductors operating at 77 K [4]. In this paper, polyimide coating for the filamentary Y123 superconductors is studied.

2. Experimental procedure

2.1. Synthesis of polyamide acid

Polyimide was prepared by curing of polyamide acid. The polyamide acid was synthesized as follows [5].



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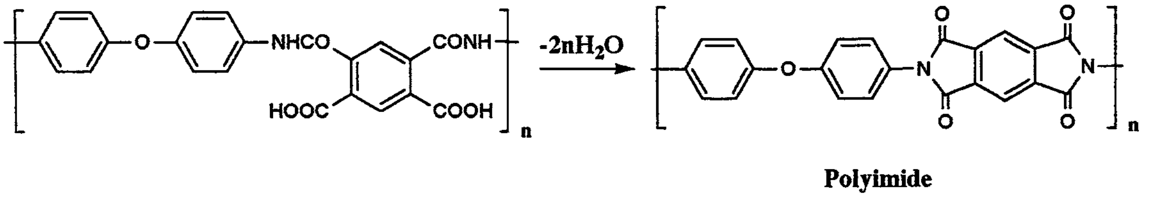
4,4′-diaminophenylether (0.01 mol) and pyromellitic dianhydride (0.01 mol) were added to a 100 ml three-necked flask with a magnetic stirrer. After the flask was purged with nitrogen gas for 10 min, dry dimethylacetoamide (DMAc; 40×10^{-6} m^3) was added at room temperature. The polyamide acid was synthesized by stirring the reaction mixture for 1 h. The synthesized polyamide acid was preserved at −15°C. DMAc (Wako Co. Ltd., 98%) was distilled under reduced pressure. 4,4′-diaminophenylether (Wako Co. Ltd., 98%) and pyromellitic dianhydride (Wako Co. Ltd., 95%) were used without further purification.

The obtained polyamide acid was precipitated in ethylether and was filtered. Then the ethylether and DMAc were evacuated. The polyamide acid powder was characterized by measurement of ^{1}H nuclear magnetic resonance (^{1}H-NMR) and gel permeation chromatography (GPC). ^{1}H-NMR spectra (in dimethylsulfoxide (DMSO)-d_6) were observed on a JEOL JNM-GX200 FT-NMR spectrometer at room temperature. The molecular weight and polydispersity index (M_w/M_n) of the polyamide acid were measured by GPC with a Toso DP-8020/RI-8012 chromatograph (eluent: dimethylformamide with a flowing rate of $10^{-6}m^3$/min at 40°C, columns: TSKgel GMH_{XL}, $G5000H_{XL}$, calibrated with polystyrene standards).

On the other hand, the solution of polyamide acid was poured on a plastic plate and dried in air to cast into a film. Infra red (IR), thermogravimetric-differential thermal analysis (TG-DTA) and elemental analysis of the polyamide acid film were measured. IR spectra were recorded with a Nicolet Impact 400D spectrometer. TG-DTA measurement was performed using a Seiko Instruments TG/DTA-220 in the temperature range from 50 to 500°C (first heating) and to 600°C (second heating) at a heating rate of 20°C/min in flowing N_2 ($200 \times 10^{-6}m^3$/min). Elemental analysis was performed using Yanagimoto MT-3 CHN.

A polyimide film was prepared by curing the polyamide acid film in a tube furnace at 80°C for 3 h, 150°C for 1 h, 200°C for 1 h and 300°C for 1 h in flowing Ar ($10^{-3}m^3$/min) according to the following reaction.



IR and elemental analysis of the polyimide film were measured.

X-ray diffraction (Rigaku CN2013) was used to measure the crystal structure of the films, employing Cu K_α radiation.

2.2. Polymer coating on filamentary Y123 superconductors

The preparation of filamentary Y123 superconductors has been reported elsewhere [3]. The precursor filaments were prepared by solution spinning through a homogeneous aqueous solution containing mixed acetates of Y, Ba and Cu. Acetates of Y, Ba and Cu were weighed with an atomic ratio of Y:Ba:Cu = 1 : 2 : 3 and were dissolved in water. Propionic acid, 2-hydroxy isobutyric acid and poly(vinyl alcohol) with a degree of polymerization of 2450, saponification degree of 88 mol% were added to the aqueous solution. The solution was concentrated to obtain a stable viscous homogeneous spinning dope. The dope was deaerated at 80°C for one day and then extruded as a filament into a hot air zone and coiled on a winding drum. The as-drawn filaments were heated to 450°C at a heating rate of 25°C/h to remove any volatile components and rapidly heated to 900°C and maintained for 15 min to generate a superconducting phase, followed by furnace cooling in flowing O_2 ($10^{-3}m^3$/min). Then the filaments were rapidly heated to 1040°C and partially melted for 30 min and cooled to 920°C at a cooling rate of 60°C/h and cooled to 860°C at a cooling rate of 30°C/h and cooled to room temperature at a cooling rate of 100°C/h in flowing O_2 ($10^{-3}m^3$/min).

As a comparison, poly(vinyl formal) (PVF: kindly supplied Tisso Co. Ltd.), varnish (Supplied by Hitachikasei Co. Ltd., WM-446) and epoxy resin (Supplied by GRACE Japan Co. Ltd., STYCAST 1264) were used for polymer coating. The filamentary Y123 samples were passed through the polymer solution for coating. The samples coated with PVF and varnish were baked at 400°C for 5 min, however, the baking leads to destruction of the sample. Then the samples coated with polyimide, PVF and varnish were heated in a tube furnace at 80°C for 3 h, 150°C for 1 h, 200°C for 1 h and at 300°C for 1 h in flowing Ar ($10^{-3}m^3$/min). These treatments (coating and heating) were repeated twice. The samples coated with epoxy resin were cured for 48 h at room temperature.

Silver was sputtered onto four locations on the samples and silver paint was used to connect the silver sputtered parts of the sample to Ag electrodes. To confirm the insulating property of the surfaces of the samples, the electric resistance at room temperature was measured by the two-probe method using a tester (Kaise MODEL SK-2: maximum resistance is $10^6\Omega$). The cross-section and surface of the samples were observed with a scanning electron microscope (SEM) (Hitachi SSM-2).

The critical current (I_c) of the sample at 77 K and zero field was measured by a standard four-probe resistive method. A criterion of 100 μV/m was used for the I_c measurement. The samples with high I_c more than 0.5 A were coated with the polyimide, epoxy resin and the degradation of the I_c was examined. The I_c

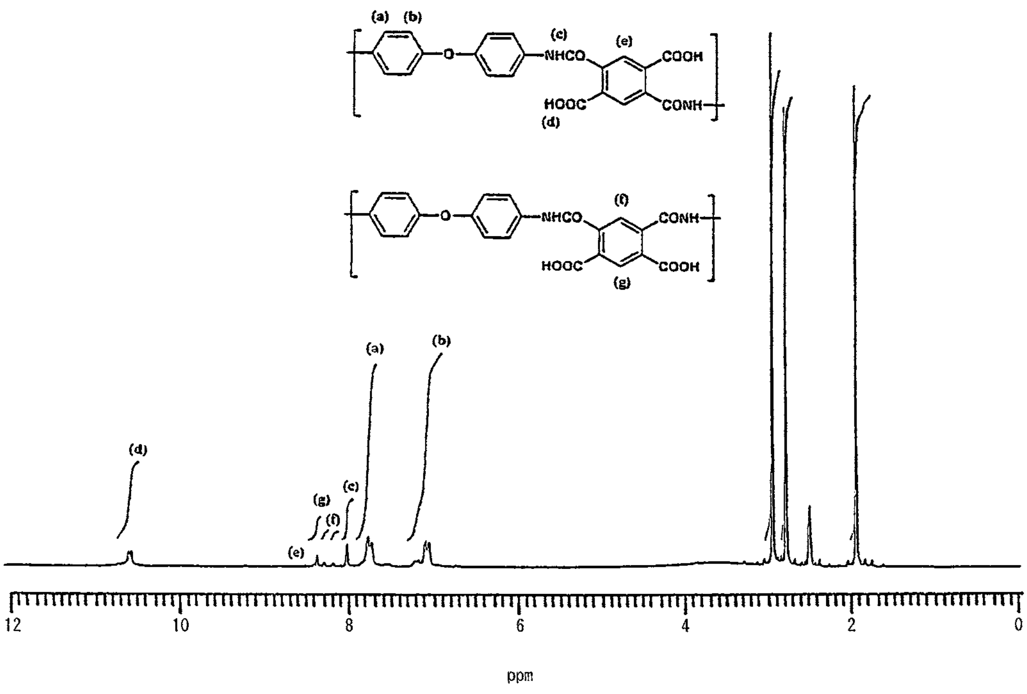


Figure 1 ^{1}H-NMR spectrum for the polyamide acid (200 Mhz, in DMSO-d_6).

deterioration of the sample coated with polyimide was also measured after holding at room temperature for more than 6 months.

After the I_c measurement by immersing in liquid nitrogen, the samples were maintained at room temperature for 10 min and again subjected to the I_c measurement. The thermal cycle was repeated 10 times.

3. Results and discussion

3.1. Characterization of the synthesized polyamide acid and polyimide

Fig. 1 shows ^{1}H-NMR spectra of the prepared polyamide acid. A small peak due to the carboxyl group (–COOH) is observed at 10.5 ppm as shown in the inset chemical formula (d) in Fig. 1. A small peak at 8 ppm is ascribed to the proton of the amide group (–NHCO–) as presented in the inset (c). Proton peaks of the benzene ring appear at 7–8.5 ppm as shown in the inset (a, b, e, f, g). DMAc peaks of the solvent are also observed at 2–3 ppm. These spectra data indicate that the synthesized polymer has a chemical formula of the polyamide acid as shown in the inset of Fig. 1.

The GPC measurement of the polyamide acid was performed. The number average molecular weight of the polyamide acid was 80,000. The molecular weight polydispersity was 2.7.

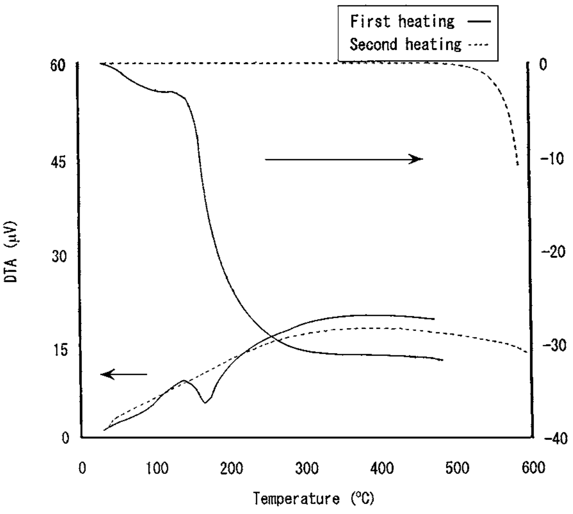


Figure 2 TG-DTA curves for the polyamide acid (heating rate of 20°C/min, in flowing N_2).

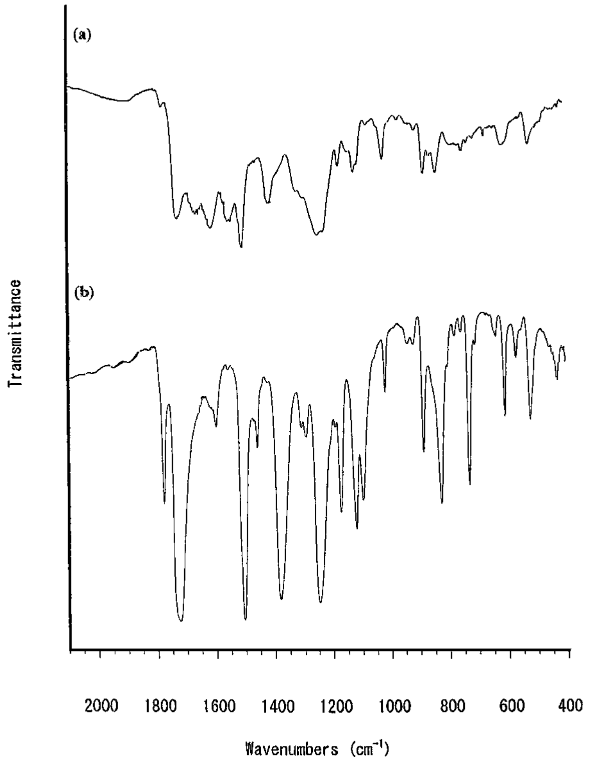


Figure 3 FT-IR spectra of the polymer. (a) Polyamide acid, (b) polyimide.

Fig. 2 shows TG-DTA curves of the polyamide acid. The sample was heated up to 500°C in the first run. After cooling, the sample was again heated up to 600°C. A weight loss of polyamide acid appears at 150°C and an endothermic peak is observed at 150°C on the first heating run due to the imidization of the polyamide acid. In the second heating run, both peaks disappear and a weight loss due to the decomposition of polyimide appears at 550°C.

Fig. 3 shows IR spectra of the polyamide acid and the cured polyimide films. The polyamide acid film shows absorption bands at 1550 and 1650 cm^{-1} for the amide group (–NHCO–). After the curing, these peaks become much smaller as shown in Fig. 3b. Strong peaks at 600, 720 and 1780 cm^{-1} due to the imide ring newly appear for the polyimide film. These indicate the conversion from the polyamide acid to the polyimide.

Elemental analysis for polyamide acid and polyamide is listed in Table I. The observed values for the polyamide acid disagree with the calculated values owing to the inclusion of solvent. The observed data for the polyimide agree with the calculated values.

From the X-ray diffraction pattern of the films, the polyamide acid and polyimide were amorphous.

3.2. I_c for the filamentary superconductors with polymer coating

The insulating property on the surface of the filamentary superconductor coated with the polyimide was measured at room temperature and the results are listed in Table II. As a comparison, electric resistance of the samples coated with PVF, varnish and epoxy resin are also listed. The samples coated with polyimide and epoxy resin are sufficiently

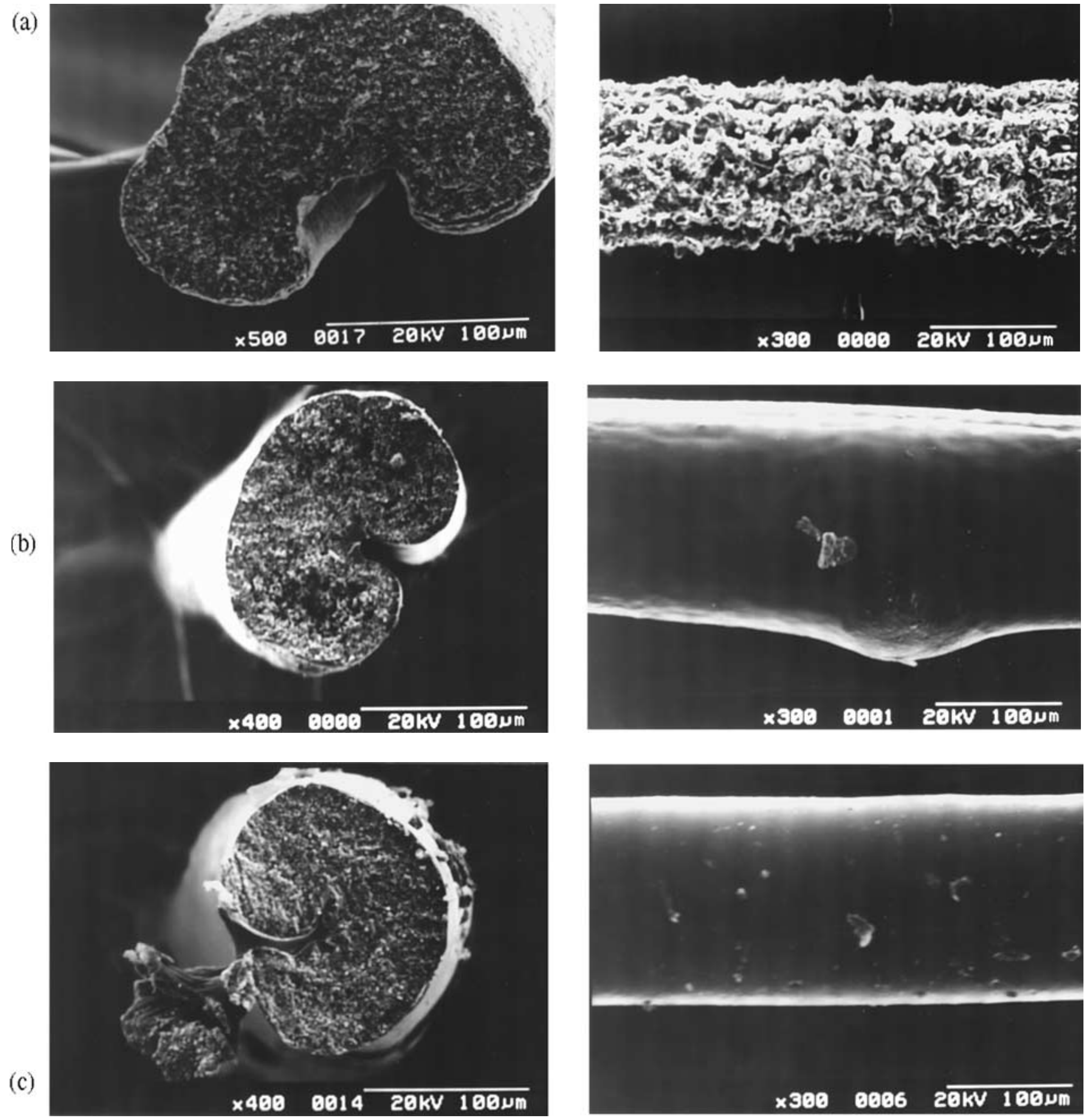


Figure 4 The cross-section and surface of the samples. (a) Without coating, (b) coated with polyimide, (c) coated with epoxy resin.

TABLE I Elemental analysis for the Polyamide acid and polyamide

Sample	Composition		C(%)	H(%)	N(%)	C/N
Polyamide acid	$C_{22}H_{14}N_2O_7$	Calculated	63.16	3.37	6.69	9.44
		Found	58.60	4.86	7.88	7.44
Polyimide	$C_{22}H_{10}N_2O_5$	Calculated	69.11	2.63	7.32	9.44
		Found	68.05	2.67	6.95	9.79

TABLE II Electrical resistance on the surface of the filamentary Y123 superconductors coated with polymer

Polymer	Electric resistance (Ω)
Polyimide	$>10^6$
PVF	5×10^3
Varnish	10^5
Epoxy	$>10^6$

TABLE III Variation of the I_c at 77 K and zero field for the samples by repeating the thermal cycle

Number of repeating	Without coating A (A)	Without coating B (A)	Polyimide (A)	Epoxy resin (A)
1	>0.5	>0.5	>0.5	>0.5
2	>0.5	0.45	>0.5	>0.5
3	>0.5	0.45	>0.5	>0.5
4	0.5[a]	0.43	>0.5	>0.5
5	–	0.43	>0.5	>0.5
6	–	–[b]	>0.5	>0.5
7	–	–	>0.5	>0.5
8	–	–	>0.5	>0.5
9	–	–	>0.5	>0.5
10	–	–	>0.5	>0.5

[a] Destroyed by applying the current of 0.5 A.

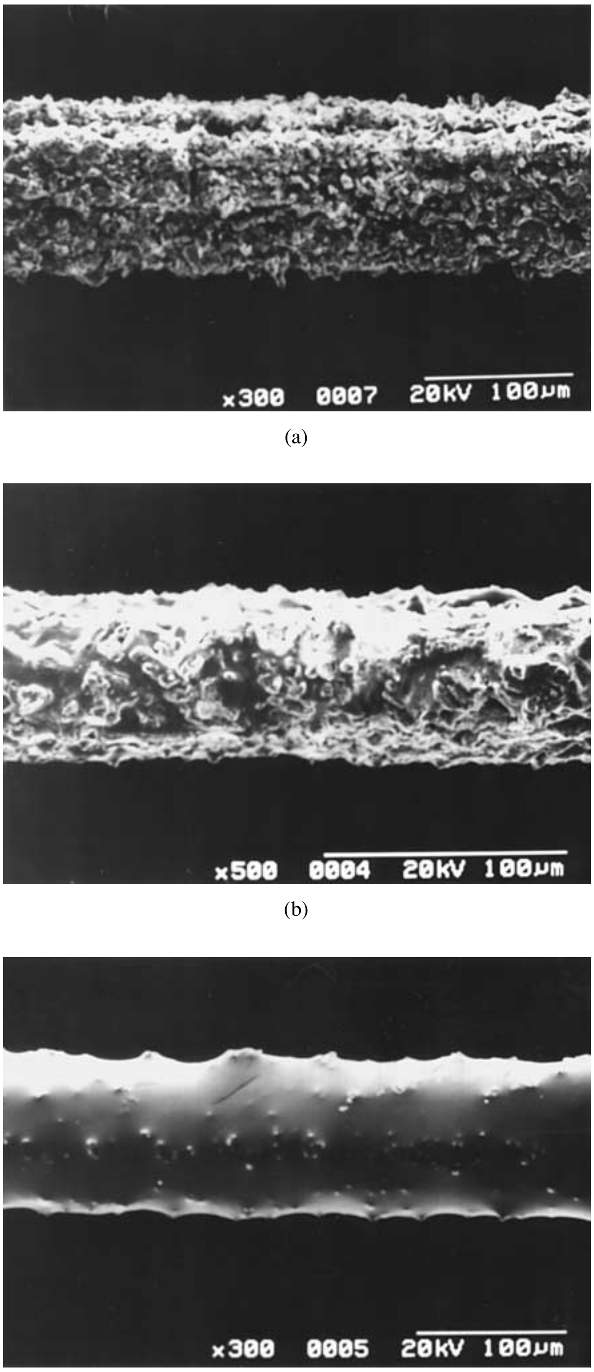
[b] Destroyed by cooling.

insulated. On the other hand, the samples coated with PVF and varnish are not sufficiently insulated. As the heat treatment was not suitable for the samples coated with PVF and varnish, some cracks appeared on the surface of the samples. The cross-section and surface of the samples without coating, coated with polyimide and epoxy resin are shown in Fig. 4. The rough surface of the sample turns into a smooth surface after polymer coating. The thickness of the polymer coating is about 1.5 μm.

The I_c at 77 K for the sample coated with polyimide ($I_c > 0.5$ A) was maintained after holding at room temperature for more than 6 months. A polyimide coating prevents the superconductivity from the deterioration by CO_2 and H_2O in the atmosphere.

After the I_c measurement by immersing in liquid nitrogen, the samples were maintained at room temperature for 10 min and again subjected to the I_c measurement. The thermal cycle was repeated 10 times. Table III presents the I_c of superconductors measured after repeating the thermal cycle. The I_c for the samples coated with the polyimide and epoxy resin is maintained at more than 0.5 A at 77 K and zero field. On the contrary, the I_c for the samples without polymer coating gradually deteriorated and disappeared after thermal cycling less than 6 times. It is considered that the thermal stress produced by the thermal cycle and the exposure to the moisture extended the cracks in the samples. Polymer coating is effective in improving the thermal cycle properties of filamentary superconductors.

Fig. 5 shows the surface of the samples without coating, coated with polyimide and epoxy resin after 10 times repeating the thermal cycle. The smooth surface of the sample coated with polyimide become rough after the repeating. The polyimide coating is partially peeled. On the other hand, the surface of the sample coated with epoxy resin is smooth. Thermal elongation of Y123 superconductors, polyimide and epoxy resin is



(a)

(b)

(c)

Figure 5 The surface of the samples after the thermal cycle measurement. (a) Without coating, (b) coated with polyimide, (c) coated with epoxy resin.

approximately 1.4–1.7 × 10^{-5}/°C, 2.0 × 10^{-5}/°C and 12.5 × 10^{-5}/°C respectively. The thickness of the polymer coating was so thin (such as 1.5 μm) that the effect of the difference of the thermal elongation of Y123 and epoxy resin was minor. As the decomposition of the imide ring by water is often known [4], it is considered that a condensation of the moisture during the thermal cycle measurement affects the degradation of the polyimide coating. For the application of the polyimide coated high-T_c-superconductors, taking sufficient care to shield from moisture is necessary.

4. Conclusion

We examined polymer coating for filamentary Y123 superconductors. The synthesis of polyamide acid for polymer coating was made. The filamentary superconductors were coated with the polyamide acid and cured to convert to the polyamide. The I_c value of the filamentary superconductors was preserved by the polyimide coating. Moreover, the I_c of polyimide-coated samples (>0.5 A) was maintained after holding at room temperature for more than 6 months.

The I_c for the samples coated with polyimide and epoxy resin was maintained after thermal cycling between room temperature and 77 K 10 times. On the other hand, the I_c of the samples without polymer coating progressively deteriorated and disappeared by the sixth thermal cycle.

Acknowledgments

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