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Enhancement of superconductivity in Pb–Bi–Sn and Pb–Bi–In alloy filaments produced by glass-coated melt spinning

TOMOKO GOTŌ, AKINOBU MORI
Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi 466, Japan

The enhancement of T_c in Pb–Bi–Sn and Pb–Bi–In system alloy filaments produced by glass-coated melt spinning was investigated as a means of producing a new type of superconducting filament with high T_c. Long filaments of Pb–Bi–Sn alloy with T_c higher than 10 K and Pb–Bi–In alloy with T_c higher than 9 K were obtained from the molten state at a temperature of 1500 K with a winding speed of 2.63 m sec^{-1}. For example, a $Pb_{45}Bi_{35}Sn_{20}$ filament with T_c of 10.1 K was 15 μm in diameter and polycrystalline with a grain size of 100 nm. The structure of the filament was a mixture of ε, tin and bismuth phases and a metastable phase of mixed structure of bismuth and supersaturated solid solution of tin in ε-phase was detected. The T_c of the filament decreased on heat treatment. A metastable phase of mixed structure of bismuth and ε-phase was also detected for a $Pb_{45}Bi_{45}In_{10}$ filament with T_c of 9.3 K. As the metastable phase for the Pb–Bi–In filament was more unstable than that for the Pb–Bi–Sn filament, the T_c of the filament was drastically decreased by heat treatment. The metastable phase was considered to play an important role in the enhancement of T_c for Pb–Bi–Sn and Pb–Bi–In alloy filaments.

1. Introduction

New types of superconducting long filament with high crystal transition temperatures (T_c) were prepared using the glass-coated melt spinning method [1, 2]. This method gives filament at a cooling rate of more than 10^5 K sec^{-1} from the molten state with a metastable phase or micrograins. It is also possible to obtain a uniformly mixed alloy filament, even if each element is immiscible in the bulk form. In a previous paper, long filaments of Pb–Bi–Ge, Pb–Bi–Te alloys with T_c higher than 10 K were produced by this method and the interface between the tellurium or germanium and ε-phase was considered to play an important role in the enhanced T_c. The enhancement of T_c in another lead alloy filament was therefore examined and it was found that Pb–Bi–Sn filament with a T_c higher than 10 K and Pb–Bi–In filament with a T_c higher than 9 K were obtained. This paper describes details of the melt spinning of Pb–Bi–Sn and Pb–Bi–In ternary alloys employed to prepare superconducting long filaments with high T_c, and reports the microstructure of the filaments thus obtained.

2. Experimental procedure

The melt spinning of Pb–Bi–Sn and Pb–Bi–In alloys was carried out using the same method as described earlier [1]. A 1 g mixture of lead, bismuth and tin of appropriate compositions was placed in a Pyrex glass tube and melted by r.f. induction heating in an argon atmosphere. When the glass tube containing the molten alloy was drawn, the alloy was stretched to form a glass-coated metallic filament and was coiled on a winding drum. The glass coating was removed in a 45% hydrogen fluoride aqueous solution. The tensile strength of the filament produced by this method was measured with an Instron type machine and the microstructure of the filament was studied using an X-ray diffractometer, X-ray microanalyser (XMA) and the differential scanning calorimeter (DSC). The T_c of the filament was examined by resistivity measurement.

3. Results and discussion

3.1. Preparation of Pb–Bi–Sn and Pb–Bi–In alloy filaments with high T_c

The melt spinning of Pb–Bi–Sn alloys ($20 \leqq$ Pb $\leqq 70$, $20 \leqq$ Bi $\leqq 65$, $5 \leqq$ Sn $\leqq 50$) was carried out from the molten state at a temperature of about 1500 K and a winding speed of 2.63 m sec^{-1}. The continuous melt spinning of Pb–Bi–Sn alloy is difficult because of the high density and low boiling point of the molten alloy and the maximum obtainable length of the filament was only a few hundred metres. Fig. 1 shows the surface of the filaments having a circular cross section and some small pinholes. The average diameter, tensile strength and crystal structure of the filament obtained were measured and some results are given in Table I. The dependence of the diameter and strength on the composition of the filament was low. The filament was about 10 μm diameter and had tensile strength of about 20 MPa with elongation of 5%. The crystal structure of the filament was mixture of ε-phase and other phases.

The T_c of the filaments was determined by measuring

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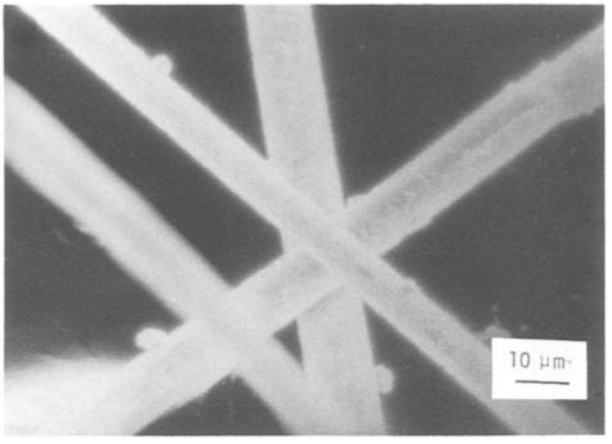

Figure 1 Scanning electron micrograph of $Pb_{45}Bi_{35}Sn_{20}$ filaments produced by melt spinning with Pyrex glass.

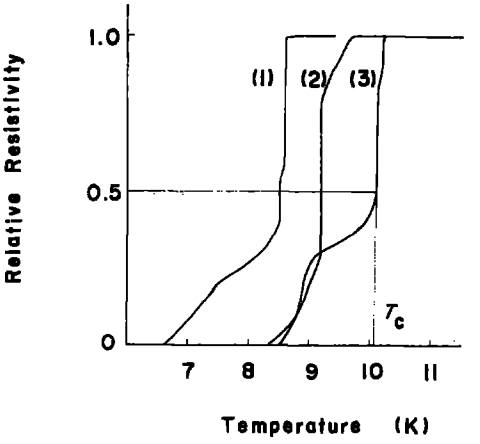

Figure 2 Electrical resistivity of Pb–Bi–Sn filaments. (1) $Pb_{30}Bi_{20}Sn_{50}$, (2) $Pb_{30}Bi_{60}Sn_{10}$, (3) $Pb_{45}Bi_{35}Sn_{20}$.

the changes in resistivity of the filament as a function of temperature using a chromel–gold + 0.007% iron thermocouple. The sample current density was of the order of $10^6 A\,m^{-2}$. Fig. 2 shows some resistivity measurement results. The filaments were found to be superconductive with a wide temperature range of normal–superconducting transition (ΔT_c) of 1.5 K. T_c was chosen as the temperature at which the filament resistance reached half its normal value. The $Pb_{45}Bi_{35}Sn_{20}$ filament had a high T_c of 10.1 K, whereas the Pb–Bi–Sn bulk alloy was reported to have T_c of 8.68 K [3]. The T_c values for filaments made from Pb–Bi–Sn alloys of various compositions were measured and plotted on the ternary diagram of Fig. 3. The addition of tin to Pb–Bi alloy thus results in an improvement in T_c. A high T_c of more than 10 K is observed for the $Pb_{50}Bi_{40}Sn_{10}$, $Pb_{45}Bi_{35}Sn_{20}$, $Pb_{40}Bi_{40}Sn_{20}$ and $Pb_{40}Bi_{35}Sn_{25}$ alloy filaments. It was found out the filament with high T_c consisted of a mixed structure of ε-phase (Pb_3Bi, hcp), bismuth (trigonal) and slight tin (bct) phases.

The melt spinning of Pb–Bi–In ternary alloys was also studied and long filaments of Pb–Bi–In alloys ($15 \leqq Pb \leqq 70$, $20 \leqq Bi \leqq 60$, $5 \leqq In \leqq 50$) were obtained as for the Pb–Bi–Sn ternary alloy. The average diameter, tensile strength and crystal structure of the filament obtained were measured, and some results are listed in Table II. The diameter of the filament obtained was about 10 μm. Most of the filaments had a mixed structure of four phases of ε, bismuth, lead and indium. The T_c of the filament was also measured and some resistivity results are shown in Fig. 4. The $Pb_{45}Bi_{45}In_{10}$ filaments have a high T_c of 9.3 K, while the $Pb_{25}Bi_{30}In_{45}$ filaments have a low T_c of 7.6 K. The ΔT_c of the Pb–Bi–In filament was larger than that for the Pb–Bi–Sn alloys. The T_c values for the filaments of Pb–Bi–In alloys with various compositions were measured and plotted on the ternary diagram of Fig. 5. The T_c of the filament increases if a small amount of indium is added and then decreases on addition of more than 20 at % In. It was also found that the filaments with T_c higher than 9 K consisted of a mixed structure of ε, bismuth, indium and lead phases.

3.2. Microstructure of $Pb_{45}Bi_{35}Sn_{20}$ and $Pb_{45}Bi_{45}In_{10}$ filaments

As the $Pb_{45}Bi_{35}Sn_{20}$ filaments exhibited superconductivity with a high T_c of 10.1 K, its microstructure was investigated to determine the cause of the high T_c. Melt spinning of $Pb_{45}Bi_{35}Sn_{20}$ alloy was carried out from the molten state at 1500 K at various winding speeds. The variations in average diameter, tensile strength and T_c of the filaments with winding speed

TABLE I Average diameter, strength and crystal structure of Pb–Bi–Sn alloy filaments produced by melt spinning with Pyrex glass

Alloy filament	Diameter (μm)	Tensile strength (MPa)	Elongation (%)	Crystal structure
$Pb_{20}Bi_{60}Sn_{20}$	11	23	2.3	ε* + Bi* + Sn*
$Pb_{20}Bi_{50}Sn_{30}$	10	24	4.1	ε + Bi + Sn
$Pb_{30}Bi_{65}Sn_5$	16	30	2.8	ε + Bi
$Pb_{30}Bi_{20}Sn_{50}$	8	19	5.0	ε + Bi + Sn
$Pb_{40}BI_{50}Sn_{10}$	12	12	12.7	ε + Bi
$Pb_{40}Bi_{25}Sn_{35}$	13	26	3.3	ε + Bi + Sn
$Pb_{45}Bi_{35}Sn_{20}$	15	35	1.6	ε + Bi + Sn
$Pb_{50}Bi_{45}Sn_5$	18	25	2.1	ε + Bi + Sn
$Pb_{50}Bi_{15}Sn_{35}$	12	14	23.1	ε + Sn + Pb*
$Pb_{60}BI_{30}Sn_{10}$	10	17	3.9	ε + Bi
$Pb_{60}Bi_{20}Sn_{20}$	12	35	2.1	ε + Pb
$Pb_{70}Bi_{20}Sn_{10}$	34	29	2.9	ε + Pb

*ε, hcp; Bi, trigonal; Sn, bct; Pb, fcc.

TABLE II Average diameter, strength and crystal structure of Pb–Bi–In alloy filaments produced by melt spinning with Pyrex glass

Alloy filament	Diameter (μm)	Tensile strength (MPa)	Elongation (%)	Crystal structure
$Pb_{15}Bi_{50}In_{35}$	12	13	3.6	ε + Bi + Pb + In*
$Pb_{20}Bi_{55}In_{25}$	17	16	2.6	ε + Bi + Pb + In
$Pb_{20}BI_{40}In_{40}$	15	32	1.1	Bi + Pb + In
$Pb_{30}Bi_{40}In_{30}$	11	42	1.2	ε + Bi + Pb + In
$Pb_{30}Bi_{60}In_{10}$	12	38	2.0	ε + Bi + In
$Pb_{40}Bi_{30}In_{30}$	17	20	3.8	ε + Bi + Pb + In
$Pb_{40}Bi_{55}In_{5}$	11	31	5.6	ε + Bi + Pb
$Pb_{45}Bi_{45}In_{10}$	14	25	4.6	ε + Bi + Pb + In
$Pb_{50}Bi_{20}In_{30}$	9	51	1.5	ε + Pb + In
$Pb_{50}Bi_{45}In_{5}$	15	26	2.9	ε + Bi
$Pb_{60}Bi_{30}In_{10}$	17	32	1.7	ε + Pb
$Pb_{60}Bi_{20}In_{20}$	13	51	1.7	Bi + Pb
$Pb_{70}Bi_{20}In_{10}$	10	46	1.4	ε + Pb

*In, fct.

were measured and the results are shown in Table III. The diameter of the filament is slightly increased with decreasing winding speed. Although the present method gives filaments for a cooling rate of more than 10^5 K sec^{-1} and the rate is approximately proportional to the winding speed [4], the T_c of the filament is independent of winding speed and the highest T_c is observed for the filament spun at a winding speed of 2.63 m sec^{-1} because of the strict spinning conditions for lead ternary alloys.

The surface and cross-section of the filament were examined by XMA. Fig. 6 shows an XMA micrograph of the cross-section of the filament. Although the tin, bismuth and lead were distributed homogeneously on the surface of the filament, segregation of tin element is observed in the cross-section of the filament. It was found out the bismuth and lead elements were distributed homogeneously in the filament but segregation of the tin was detected on a scale of about 1 μm.

As the appearance of the metastable phase is expected in the filament, the thermal stability of the filament was examined using DSC. Typical DSC curves of the filaments at a heating rate of 0.33 K sec^{-1} are shown in Fig. 7. The as-drawn filament exhibits a sharp endothermic peak at 365, 368 and 373 K and broad peaks at 389 and 423 K. After the first heating treatment, endothermic reactions take place at 368, 373, 384 and 423 K, respectively. The endothermic peak at 368 K is considered to be the eutectic point and peaks at 373, 384 and 423 K are considered to arise from the melting of ε, bismuth and tin phases, respectively. The first endothermic peak at 365 K for as-drawn filament is considered to arise from the melting of the metastable phase. However, the crystal structure of the filament annealed at 423 K for 36 ksec was apparently a mixed structure of ε, bismuth and tin phases as for the as-drawn filament. The filament was then annealed under various conditions. The tensile strength and T_c of the annealed filament were also measured and are given in Table IV. The ratio of the intensity of X-ray line profile of the {1 0 1} reflection of the tin phase and the {1 1 0} reflection of the bismuth phase to that of the {1 0 1} reflection of the ε-phase was measured for the annealed filament and the results are given in Table IV. The ratio of Sn {1 0 1}/ε{1 0 1} increased on heating at more than 423 K. On the other hand, the ratio of Bi {1 1 0}/ε{1 0 1} decreased on heating at 373 K and then increased on heating at more than 393 K. The metastable phase formed by rapid quenching from the liquid state was considered to be a mixed structure of trigonal and supersaturated solid solution of tin in the ε-phase. The trigonal structure had a lattice parameter of a = 47.9 nm α = 0.981 and the structure of the stable bismuth phase was trigonal with a = 47.2 nm and α = 1.01. These are similar values to the standard

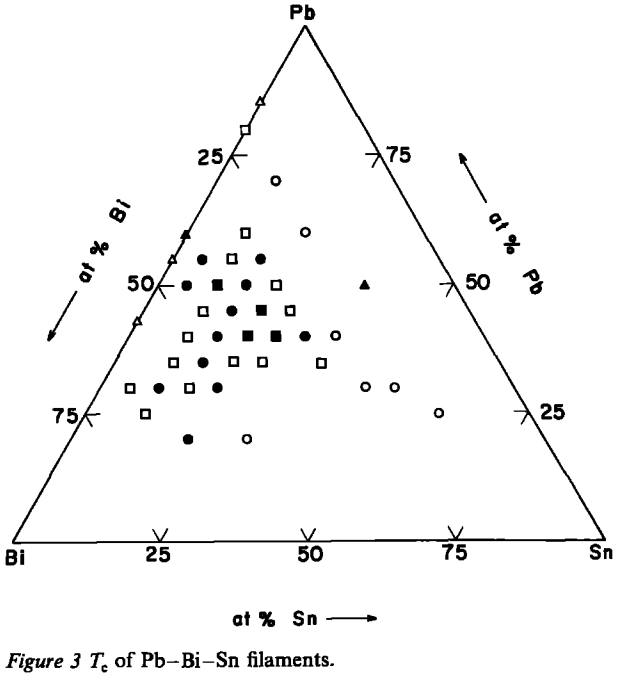

Figure 3 T_c of Pb–Bi–Sn filaments.

TABLE III Average diameter, strength and T_c of $Pb_{45}Bi_{35}Sn_{20}$ filaments spun at various windings speeds

Winding speed (m sec^{-1})	Diameter (μm)	Tensile strength (MPa)	Elongation (%)	T_c (K)
0.95	16	41	2.2	9.6
2.63	15	35	1.6	10.1
3.97	12	51	1.7	9.7

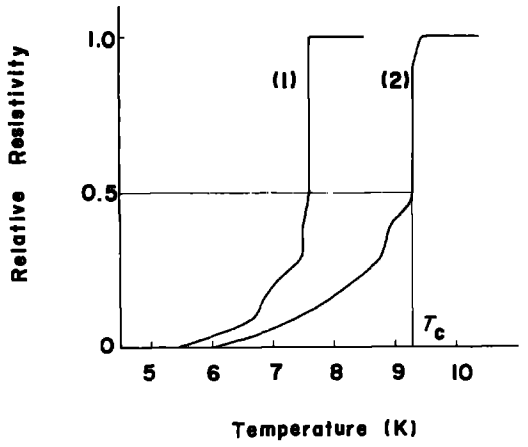

Figure 4 Electrical resistivity of Pb–Bi–In filaments. (1) $Pb_{25}Bi_{30}In_{45}$, (2) $Pb_{45}Bi_{45}In_{10}$.

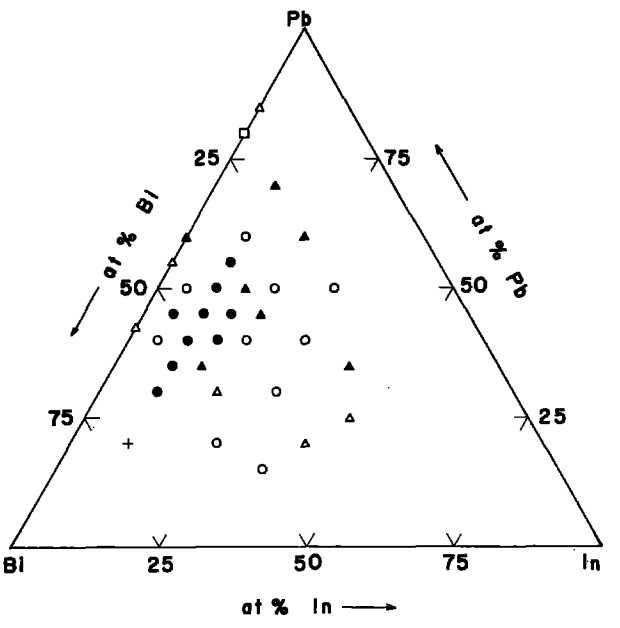

Figure 5 T_c of Pb–Bi–In filaments. (+) < 7.4 K, (△) 7.5 to 7.9 K, (▲) 8.0 to 8.4 K, (○) 8.5 to 8.9 K, (●) 9.0 to 9.5 K.

bismuth phase of $a = 47.36\,\text{nm}$ $\alpha = 0.998$ [5]. The T_c decreased on heat treatment and it was estimated that the metastable phase played an important role in the enhancement of T_c of the filament [6]. As the metastable phase transformed to the stable phase at a low temperature of 365 K, the relaxation at room temperature was examined. The T_c of the filament drastically decreased to 8.6 K for 7.5 Msec (87 days) after rapid quenching by melt spinning.

Several cross-sections of the filament after chemical etching in a mixture of acetic acid and hydrogen peroxide were observed by scanning electron microscopy (SEM) and are shown in Fig. 8. The filament is found to have a fine polycrystalline structure with a grain size of 100 nm as in the annealed filament. The heat-treatment had not caused the growth of the crystal grains.

The microstructure of the $Pb_{45}Bi_{45}In_{10}$ filament with a high T_c of 9.3 K was also examined. The filament was found to be fine polycrystalline with a grain size of 200 nm on examination by SEM. The XMA micrographs of the cross-section of the filament are shown in Fig. 9. It was found that bismuth was distributed homogeneously in the filament but segregation of indium was detected on a scale of about 3 μm in the lead element.

Typical DSC curves of the filament are shown in Fig. 10. The irreversible endothermic peaks are observed at 339 and 345 K for as-drawn filament. However, the filament annealed at 423 K for 36 ksec had a mixed structure of ε, bismuth, lead (fcc) and indium (fct) phases as in the as-drawn filament. The filament was then annealed under various conditions. The tensile strength, T_c and crystal structure of the annealed filament were measured and are given in Table V. The ratio of the intensity of X-ray line profile of the {1 1 1} reflection of lead and indium and the {1 1 0} reflection of bismuth to that of the {1 0 1} reflection of the ε-phase was measured. The bismuth and ε-phases decreased on heating at 353 K for 1.8 ksec and then increased on heating at 423 K for 1.8 ksec. The metastable phase formed by rapid quenching from the liquid state was considered to be of a mixed structure of trigonal and hcp phase with similar lattice parameter to bismuth and ε-phases. The T_c of the filament drastically decreased to 8.5 K on heating at 353 K for 1.8 ksec. It also decreased to 8.5 K at room temperature for 3.5 Msec (40 days) after rapid quenching by melt spinning. The metastable phase is considered to play an important role in the enhancement of T_c of the Pb–Bi–In alloy filament as in the Pb–Bi–Sn alloy filament. The metastable phase for Pb–Bi–In filament is unstable compared with Pb–Bi–Sn and the T_c of the Pb–Bi–In filament is drastically decreased by heat treatment.

4. Conclusions

Melt spinning of the Pb–Bi–Sn and Pb–Bi–In system alloys with a Pyrex glass was investigated by producing

TABLE IV Strength, T_c and crystal structure of $Pb_{45}Bi_{35}Sn_{20}$ filaments annealed under various conditions

Heat treatment	Tensile strength (MPa)	Elongation (%)	T_c (K)	Crystal structure	
				Sn {1 0 1} / ε {1 0 1}	Bi {1 0 0} / ε {1 0 1}
As-drawn	35	1.6	10.1	0.08	0.27
373 K, 1.8 ksec	46	2.7	9.8	0.08	0.08
393 K, 1.8 ksec	–	–	–	0.14	0.33
423 K, 1.8 ksec	24	0.7	9.3	0.20	0.23
423 K, 36 ksec	–	–	–	0.20	0.20
room temp. 7.5 Msec	–	–	8.5	0.10	0.23

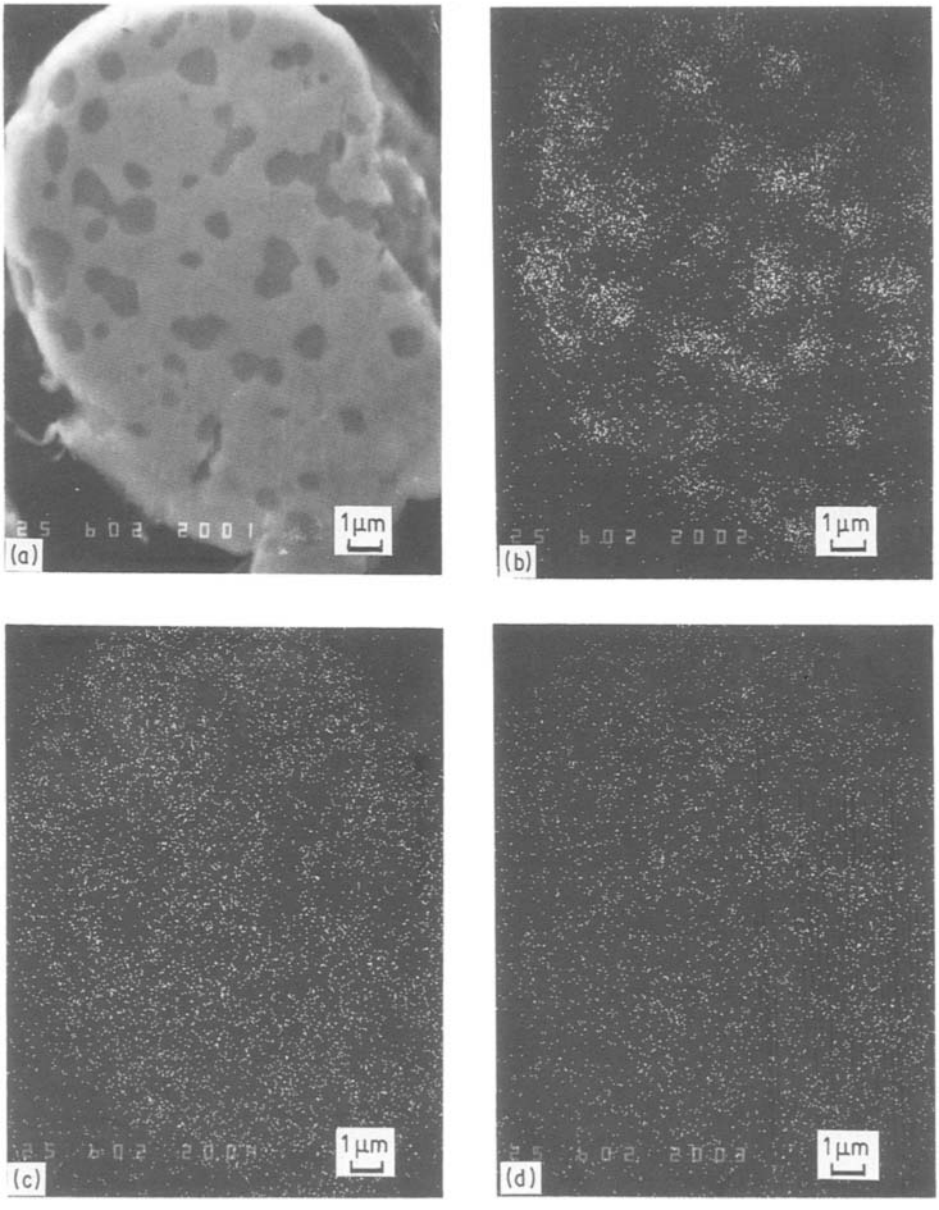

Figure 6 X-ray microanalysed micrography of cross-section of $Pb_{45}Bi_{35}Sn_{20}$ filament. (a) Reflection pattern, (b) tin, (c) lead, (d) bismuth.

a new type of superconducting long filament with high T_c. Pb–Bi–Sn filaments with T_c higher than 10 K and Pb–Bi–In filaments with T_c higher than 9 K were obtained from the molten state at a temperature of 1500 K with a winding speed of 2.63 m sec^{-1}. For example a $Pb_{45}Bi_{35}Sn_{20}$ filament with T_c of 10.1 K was 15 μm in diameter and polycrystalline with a grain size of 100 nm and had a mixed structure of ε, tin and bismuth phases. A metastable phase of mixed structure of bismuth and supersaturated solid solution of

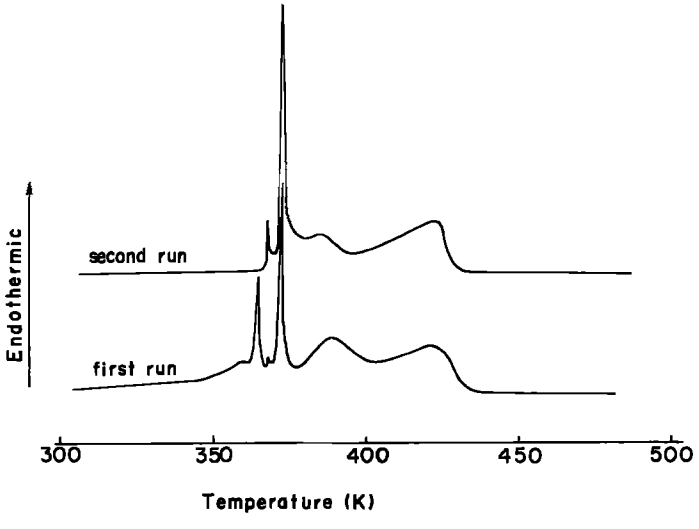

Figure 7 DSC curve for $Pb_{45}Bi_{35}Sn_{20}$ filaments.

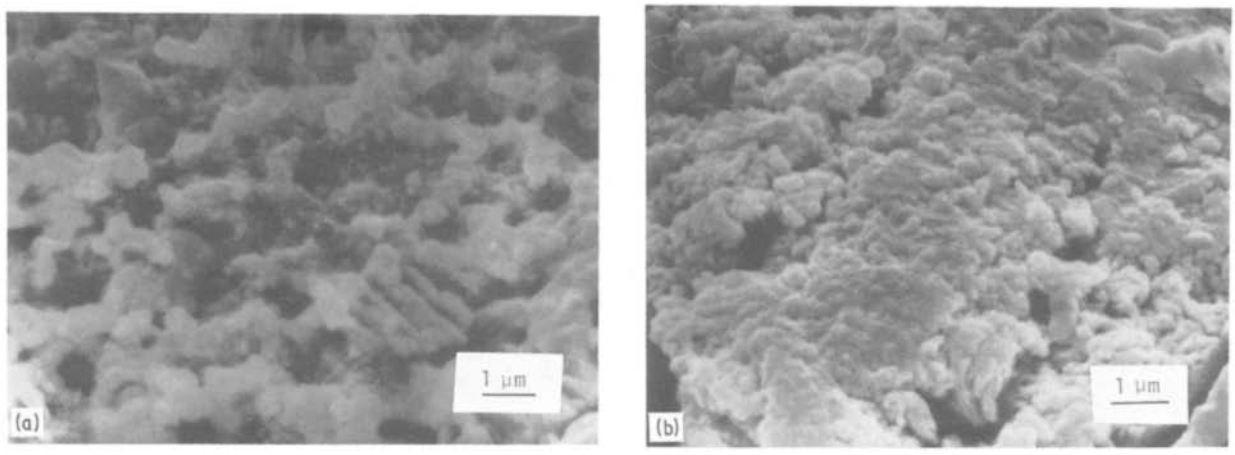

Figure 8 Scanning electron micrographs of cross-section of $Pb_{45}Bi_{35}Sn_{20}$ filaments after chemical etching: (a) as-drawn, (b) annealed at 423 K for 1.8 ksec.

tin in ε-phase was detected. The T_c decreased on heat treatment.

A metastable phase of mixed structure of bismuth and ε-phase was also detected for the $Pb_{45}Bi_{45}In_{10}$ filament with T_c of 9.3 K. This was unstable compared to that for Pb–Bi–Sn filament and the T_c of the Pb–Bi–In filament was drastically reduced on heat treatment. It was estimated that the metastable phase played an important role in the enhancement of T_c of the Pb–Bi–Sn and Pb–Bi–In alloy filaments.

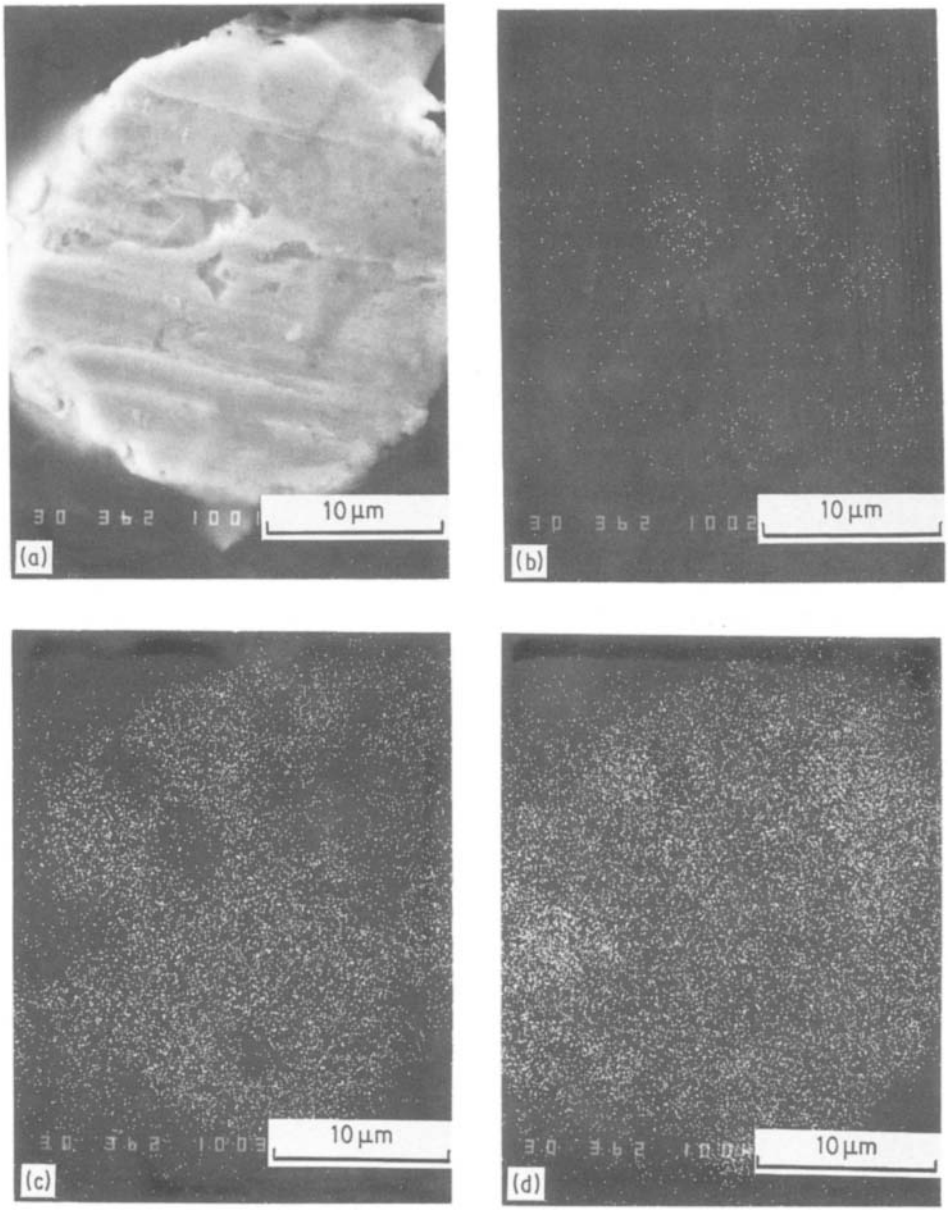

Figure 9 X-ray microanalysed micrography of cross-section of $Pb_{45}Bi_{45}In_{10}$ filament. (a) Reflection pattern, (b) indium, (c) lead, (d) bismuth.

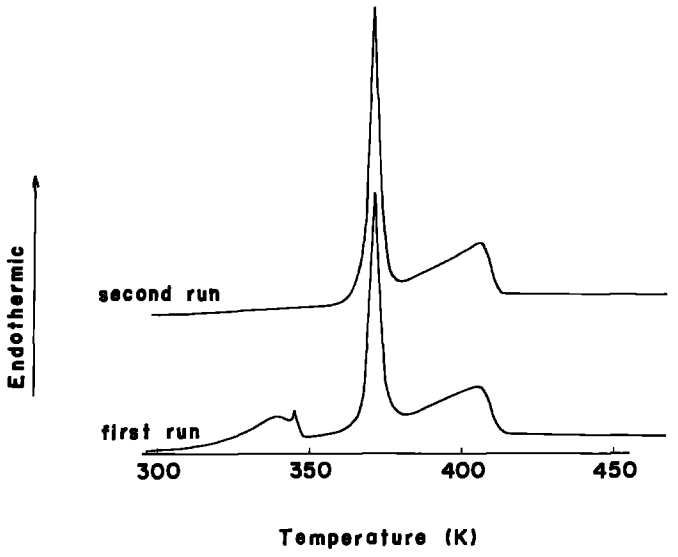

Figure 10 DSC curves for $Pb_{45}Bi_{45}In_{10}$ filaments.

TABLE V Strength, T_c and crystal structure of $Pb_{45}Bi_{45}In_{10}$ filaments annealed under various conditions

Heat treatment	Tensile strength (MPa)	Elongation (%)	T_c (K)	Crystal structure		
				Pb {1 1 1} / ε {1 0 1}	Bi {1 1 0} / ε {1 0 1}	In {1 1 1} / ε{1 0 1}
As-drawn	26	4.6	9.3	0.5	1.9	2.7
353 K, 1.8 ksec	24	3.8	8.4	3.0	1.3	4.4
383 K, 1.8 ksec	–	–	–	2.7	0.9	2.1
423 K, 1.8 ksec	18	1.5	8.4	0.4	1.2	0.4
room temp. 3.5 Msec	–	–	8.5	0.1	1.4	0

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