The preparation of high transition temperature superconducting Pb–Bi–Ge alloy filaments using the method of glass-coated melt spinning

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The melt spinning of Pb–Bi–Ge alloys with Pyrex glass was investigated as a means of producing a superconducting long filament with high T_c. Continuous filaments with maximum T_c of more than 10 K of $Pb_{100-x-y}Bi_xGe_y$ ($15 \leqslant x \leqslant 37$ and $7 \leqslant y \leqslant 25$) were obtained from the molten state at 1500 K with a winding speed of $0.95\,m\,sec^{-1}$. The $Pb_{49}Bi_{33}Ge_{18}$ filament, which was 34×10^{-6} m diameter and a ductile material with a tensile strength of 20 MPa and elongation of 2.7%, exhibited superconductivity at the highest T_c of 14.3 K. These filaments were found to be polycrystalline with a grain size of more than 5000×10^{-10} m and had a mixed structure of germanium (diamond) ϵ (h c p) and bismuth phases. The germanium element distributed homogeneously in the filament.

1. Introduction
Superconductors with high superconducting transition temperatures ($T_c > 10$ K) are usually brittle and difficult to fabricate into tapes or wires, which are useful in large-scale engineering applications such as superconducting magnets, power transmission lines etc. We have developed a fabrication technique for the glass-coated melt spinning of metals whereby fine filaments can be produced directly from the molten metal in one stage. This technique was used to produce a continuous superconducting long filament [1–3]. In previous papers, the $Pb_{80}Bi_{20}$ filament with a high T_c of 11.0 K was prepared using this method [2], and an enhancement of T_c was observed for the Ge–Sn filament [3]. This paper describes the melt spinning of Pb–Bi–Ge alloys for producing a superconducting long filament with a high T_c and microstructure of the filament obtained. Although lead and bismuth are immiscible in germanium, the present method gives a filament for a cooling rate of more than $10^5\,K\,sec^{-1}$ and it is possible to obtain a continuous alloy filament.

2. Experimental procedure
The melt spinning of Pb–Bi–Ge alloys was carried out using the same method as that for germanium alloys [3]. 1 g mixture of lead, bismuth and germanium of appropriate composition was placed in a Pyrex glass tube and melted by 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 filaments produced by this method was measured with an Instron-type machine and the T_c of the filament was examined by the resistive method. The microstructure of the filament with high T_c was studied using an X-ray diffractometer and an X-ray microanalyser.

3. Results and discussion
3.1. Preparation of Pb–Bi–Ge long filament
The melt spinning of $Pb_{100-x-y}Bi_xGe_y$ ($11.25 \leqslant x \leqslant 42.5$ and $7 \leqslant y \leqslant 25$) was carried out from the molten state at a temperature of about 1500 K with winding speeds of $0.95\,m\,sec^{-1}$. Fig. 1 shows the surface of the filament obtained. Some cracks and pinholes are observed in the present filament,

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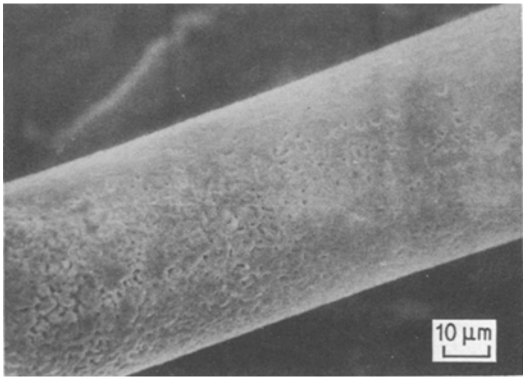

Figure 1 Scanning electron micrograph of Pb–Bi–Ge system alloy filament produced by melt spinning with Pyrex glass

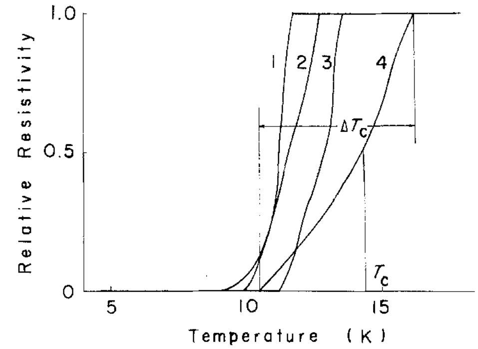

Figure 2 Electrical resistivity of Pb–Bi–Ge filament spun at a winding speed of $0.95\,m\,sec^{-1}$. 1, $Pb_{57}Bi_{30}Ge_{13}$; 2, $Pb_{57}Bi_{22}Ge_{21}$; 3, $Pb_{53}Bi_{26}Ge_{21}$; 4, $Pb_{49}Bi_{33}Ge_{18}$.

whereas the filaments produced by this method usually had a lustrous smooth surface and were free of pinholes. As the $Pb_{49}Bi_{33}Ge_{18}$ and $Pb_{57}Bi_{30}Ge_{13}$ alloys tended to segregate, melt spinning of these alloys for several tens of times was tried in order to obtain the long filament. The average diameter and tensile strength of the filament obtained were measured and the results are shown in Table I. The dependence of diameter and tensile strength on composition of the filament is minor. The filament is about 40×10^{-6} m diameter and has a tensile strength of 30 MPa with an elongation of 1.2%. The plasticity of the filaments was observed on the stress–strain curves and fracture morphologies.

TABLE I Average diameter and tensile strength of Pb–Bi–Ge system alloy filament produced by melt spinning with Pyrex glass

Alloy filament	Diameter ($\times 10^{-6}$ m)	Tensile strength (MPa)	Elongation (%)
$Pb_{63.75}Bi_{11.25}Ge_{25}$	30	29	1.6
$Pb_{60}Bi_{15}Ge_{25}$	35	36	1.3
$Pb_{56.25}Bi_{18.75}Ge_{25}$	32	42	1.7
$Pb_{50}Bi_{25}Ge_{25}$	35	29	1.1
$Pb_{45.2}Bi_{29.8}Ge_{25}$	64	36	1.9
$Pb_{42}Bi_{33}Ge_{25}$	46	30	1.9
$Pb_{36.5}Bi_{38.5}Ge_{25}$	51	22	0.8
$Pb_{60.25}Bi_{18.75}Ge_{21}$	41	30	1.5
$Pb_{57}Bi_{22}Ge_{21}$	41	23	1.3
$Pb_{53}Bi_{26}Ge_{21}$	55	25	1.1
$Pb_{49}Bi_{30}Ge_{21}$	58	26	1.1
$Pb_{45}Bi_{34}Ge_{21}$	51	48	1.3
$Pb_{60}Bi_{22}Ge_{18}$	25	31	1.3
$Pb_{57}Bi_{25}Ge_{18}$	53	46	1.6
$Pb_{55}Bi_{27}Ge_{18}$	50	32	1.6
$Pb_{49}Bi_{33}Ge_{18}$	34	20	2.7
$Pb_{45}Bi_{37}Ge_{18}$	70	22	0.8
$Pb_{39.5}Bi_{42.5}Ge_{18}$	26	43	0.8
$Pb_{63}Bi_{24}Ge_{13}$	38	20	1.7
$Pb_{57}Bi_{30}Ge_{13}$	62	25	1.4
$Pb_{53}Bi_{34}Ge_{13}$	25	19	1.0
$Pb_{49}Bi_{38}Ge_{13}$	31	17	0.9
$Pb_{71}Bi_{22}Ge_{7}$	71	24	1.3

T_c of the filament was determined by measuring 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 the same resistivity measurement results for the filament with high T_c. The filament is found to show superconductivity with a wide temperature range of normal-superconducting transition (ΔT_c). The T_c is chosen as the temperature where the filament resistance has reached half of its normal value. ΔT_c increases with increasing T_c. The T_c for the filament of various compositions of Pb–Bi–Ge alloys was measured. The maximum T_c of the filament is plotted on the trilinear coordinates of Fig. 3. Most of the filaments exhibit a superconductivity of more than 10 K. The addition of germanium results in the enhancement of T_c. The $Pb_{49}Bi_{33}Ge_{18}$ filament, especially has the highest T_c such as 14.3 K. It is noted that such a high T_c of 14.3 K has not been reported yet for lead alloys. The highest T_c of 9.02 K was reported for Pb–Bi alloys after ion implantation with bismuth in a saturated Pb–Bi alloy [4].

3.2. Microstructure of the filament with high T_c

The $Pb_{49}Bi_{33}Ge_{18}$, $Pb_{53}Bi_{26}Ge_{21}$, $Pb_{57}Bi_{22}Ge_{21}$ and $Pb_{57}Bi_{30}Ge_{13}$ filaments exhibited superconductivity at high T_c more than 11.0 K. Therefore, the microstructure of these filaments was investigated.

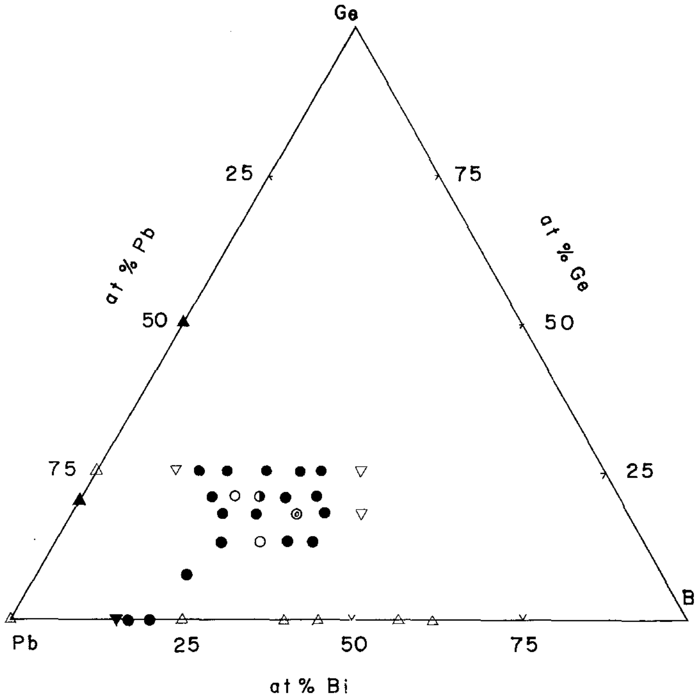

Figure 3 The maximum T_c of Pb–Bi–Ge system alloy filament spun at a winding speed of 0.95 m sec^{-1}. ▲ up to 7.0 K; △ 7.1–8.0 K; ▼ 8.1–9.0 K; ▽ 9.1–10.0 K; ● 10.1–11.0 K; ○ 11.1–12.0 K; ◑ 12.1–13.0 K; ◐ 13.1-14.0 K; ◎ 14.1–15.0 K.

The melt spinning of $Pb_{49}Bi_{33}Ge_{18}$, $Pb_{53}Bi_{26}Ge_{21}$, $Pb_{57}Bi_{22}Ge_{21}$ and $Pb_{57}Bi_{30}Ge_{13}$ alloys was carried out from the molten state at a temperature of about 1500 K with winding speeds ranging from 0.95 to 3.97 m sec^{-1}. The variations in the average diameter and tensile strength of the filaments with winding speed were measured and the results are shown in Table II. The diameter of the filament obtained decreases with increasing winding speed and ranges from 62×10^{-6} to 13×10^{-6} m. Several cross-sections of the filament after chemical etching in a mixture of acetic acid

TABLE II Average diameter, strength, T_c and crystal structure of Pb–Bi–Ge system alloy filament spun at various winding speeds

Alloy, filament winding speed (m sec^{-1})	Diameter ($\times 10^{-6}$ m)	Tensile strength (MPa)	Elongation (%)	T_c (K)	ΔT_c (K)	Crystal structure			
						Ge-phase* a ($\times 10^{-10}$ m)	ε-phase† c/a	Bi-phase‡ c/a	Ge/ε§
$Pb_{49}Bi_{33}Ge_{18}$									
0.95	44	20	2.7	14.3–10.4	5.6–0.7	5.57	1.66	2.45	1.6
2.63	21	20	1.4	13.0– 9.9	4.0–0.5	5.59	1.66	2.44	0.8
3.97	13	20	0.9	10.8– 9.3	4.1–1.4	5.64	1.66	2.39	0.8
$Pb_{53}Bi_{26}Ge_{21}$									
0.95	55	24	1.1	13.0–10.6	2.0–0.7	5.63	1.66	2.50	1.8
2.63	44	25	0.8	11.4– 9.1	1.8–0.6	5.59	1.65	2.52	0.7
3.97	22	23	0.7	9.9– 8.4	1.8–0.7	–	1.66	–	0
$Pb_{57}Bi_{22}Ge_{21}$									
0.95	41	23	1.3	11.4– 9.7	2.2–0.5	5.66	1.65	2.50	1.7
2.63	30	26	1.6	10.6– 9.7	2.1–0.6	5.64	1.65	2.50	1.3
3.97	22	22	1.7	11.5– 9.9	2.1–0.7	5.69	1.66	2.52	1.1
$Pb_{57}Bi_{30}Ge_{13}$									
0.95	62	24	1.4	11.2– 9.3	3.6–0.9	5.59	1.66	2.48	0.8
2.63	30	34	1.8	10.2– 8.9	1.4–0.8	5.61	1.65	2.49	0.5
3.97	25	–	–	11.1–10.5	2.4–2.1	5.69	1.66	2.50	2.4

*Diamond type, $a = 5.658 \times 10^{-10}$ m (stable phase).
†h c p, $a = 3.503 \times 10^{-10}$ m, $c = 5.791 \times 10^{-10}$ m, $c/a = 1.65$ (stable phase).
‡h c p, $a = 4.736 \times 10^{-10}$ m, $c = 11.862 \times 10^{-10}$ m, $c/a = 2.50$ (stable phase).
§Intensity of (1 1 1) plane of Ge-phase/intensity of (1 0 3) plane of ε-phase.

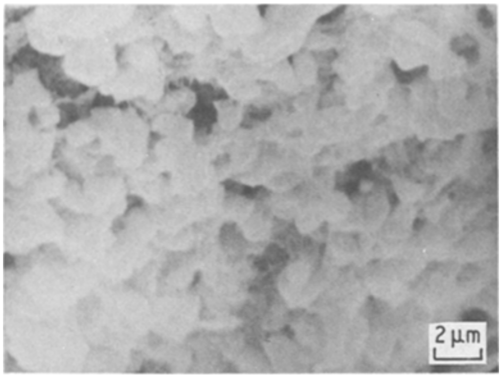

Figure 4 Scanning electron micrograph of the cross-section of $Pb_{49}Bi_{33}Ge_{18}$ filament after chemical etching.

30×10^{-5} m^3 and hydrogen peroxide solution 10×10^{-5} m^3 were observed by scanning electron microscopy. Fig. 4 shows a typical cross-section of the filament. The filament is found to be polycrystalline with a grain size of more than 5000×10^{-10} m. T_c of the filaments spun at various winding speeds was also measured and the results are listed in Table II. The T_c of the $Pb_{49}Bi_{33}Ge_{18}$ and $Pb_{57}Bi_{30}Ge_{13}$ filaments decreases with increasing winding speed. ΔT_c of $Pb_{49}Bi_{33}Ge_{18}$ and $Pb_{57}Bi_{30}Ge_{13}$ filaments is larger than that of others. This is related to the difficulty of the spinning process and their coarse texture.

The crystal structure of the filament was investigated using X-ray diffraction and the results are also shown in Table II. Most of the filaments are a mixture of germanium (diamond), ϵ (h c p) and bismuth (h c p) phases. The lattice parameter of the diamond-type germanium phase and the axes of two h c p structures are similar to that of the stable phases. The thermal stability of these filaments was examined using differential scanning calorimetry. A metastable phase, such as $Pb_{80}Bi_{20}$

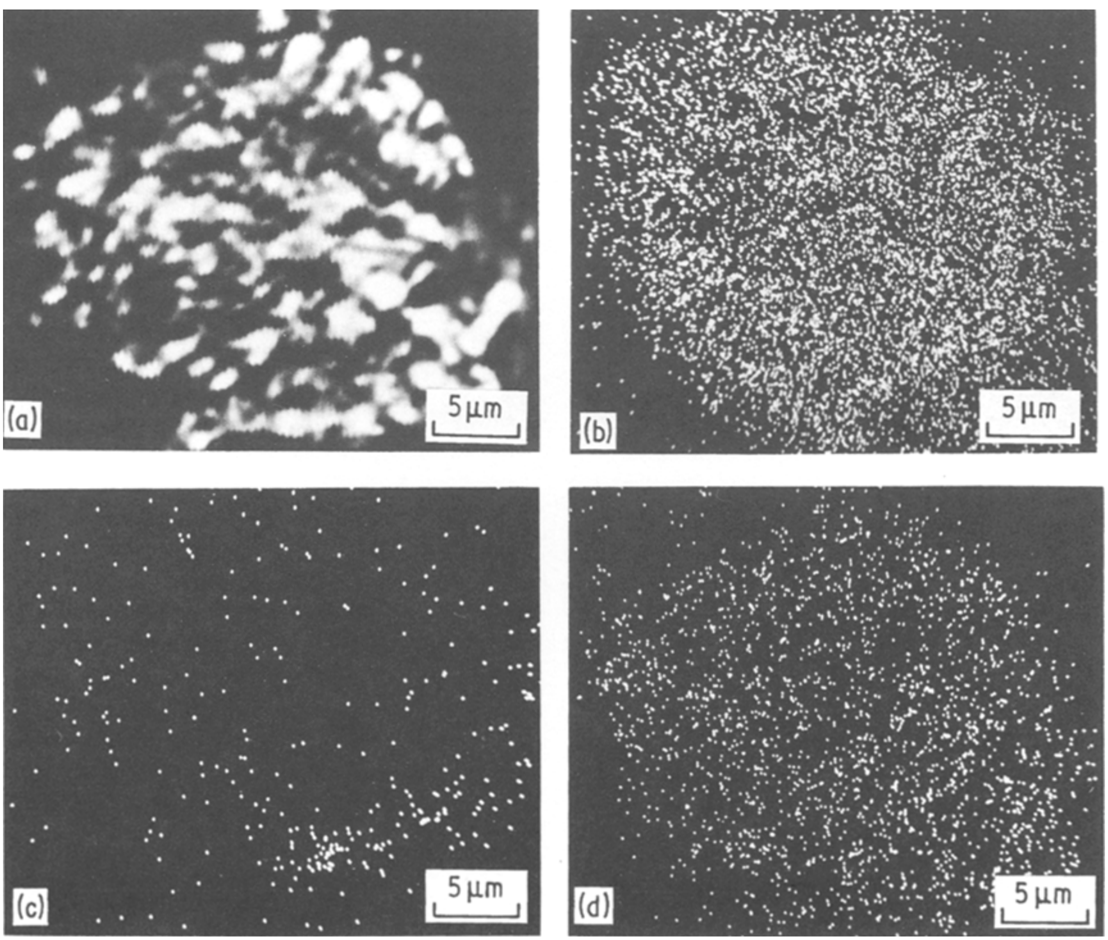

Figure 5 X-ray microanalysed micrography of the cross-section of $Pb_{49}Bi_{33}Ge_{18}$ filament spun at a winding speed of 0.95 m sec^{-1}. (a) Reflection pattern. (b) Germanium. (c) Lead. (d) Bismuth.

filament, was not found. As an exception, the $Pb_{53}Bi_{26}Ge_{21}$ filament, which was spun at a winding speed of $3.97\,m\,sec^{-1}$, consists of a single ϵ-phase due to rapid quenching and has a relatively low T_c. The T_c increases with increasing ratio of the intensity of the (111) plane of germanium (diamond) phase and that of the (103) plane of the ϵ-phase.

Fig. 5 shows the X-ray microanalysed micrography of the cross-section of the $Pb_{49}Bi_{33}Ge_{18}$ filament. It was found that the germanium and bismuth elements were distributed homogeneously in the filament.

It has already been reported that the Ge–Bi filament, which had a mixed structure of germanium (diamond) and bismuth (h c p) phases, did not exhibit a superconductivity higher than 4.2 K [3]. It is considered that the Ge–ϵ interface mainly had an influence upon the high T_c for the present filament. It is not well understood whether this can be explained by the exciton mechanism [5, 6], the wide ΔT_c is probably due to a scattered distribution of germanium and ϵ-phases.

4. Conclusion

A continuous filament of $Pb_{100-x-y}Bi_xGe_y$ ($15 \leqslant x \leqslant 37$, $7 \leqslant y \leqslant 25$) alloys could be produced from the molten state at a temperature of about 1500 K with winding speeds of $0.95\,m\,sec^{-1}$. The filament obtained was about 40×10^{-6} m diameter and was a ductile material with a tensile strength of 30 MPa and an elongation of 1.2%. The filament exhibited superconductivity at more than 10 K, in particular the $Pb_{49}Bi_{33}Ge_{18}$ filament which had a maximum T_c of 14.3 K. The filament was found to be polycrystalline with a grain size greater than 5000×10^{-10} m. The structure of the filament was a mixture of germanium (diamond), ϵ (h c p) and bismuth (h c p) phases. The germanium was distributed homogeneously in the filament.

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References

1. T. GOTŌ, *Trans. J.I.M.* **22** (1981) 753.
2. *Idem, ibid.* **25** (1984) 319.
3. *Idem,* in Proceedings of the 5th International Cryogenic Material Conference, Colorado Springs, August 1983, under the title "Advances in Cryogenic Engineering (materials)", Vol. 30 (Plenum Press, New York) p. 699.
4. C. GAUSS, Report KFK-2814 (1979) 68, C.A.93 (1980) 59331 g.
5. V. L. GINZBURG and D. A. KIRZHNITS, "High Temperature Superconducting" (Plenum, New York, 1982) p. 283.
6. D. ALLENDER, J. BRAG and J. BARDEEN, *Phys. Rev.* **B-7** (1973) 1020.

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