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Fabrication of uniform Al–Pb–Bi monotectic alloys under microgravity utilizing the Space Shuttle: microstructure and superconducting properties

H. FUJII, T. KIMURA, H. KITAGUCHI, H. KUMAKURA, K. TOGANO
National Research Institute for Metals, 1-2-1, Sengen, Tsukuba-Shi, 305, Japan
M. MOHRI
National Space Development Agency of Japan, 2-1-1, Sengen, Tsukuba-Shi, 305, Japan

Al–Pb–Bi monotectic alloys with three different compositions were melted and solidified under a microgravity environment in the Space Shuttle. The (Pb, Bi) particles were dispersed uniformly in the aluminium matrix, while evident sedimentation was observed in the reference sample processed under 1 *G*. Slow cooling was also effective to obtain homogeneous microstructure because of the absence of Marangoni force. The alloys were cold-worked into wires and the superconducting properties of the wires were investigated. The distance between (Pb, Bi) fibres for the alloys prepared under microgravity was so small that the wires showed complete zero resistance below 9 K due to the proximity effect.

1. Introduction

Under a microgravity environment, new excellent materials are expected to be fabricated, because gravitational segregation hardly takes place. For example, the Al–Pb–Bi ternary system separates into two liquid phases, aluminium-rich and (Pb, Bi)-rich phases, above the monotectic reaction temperature [1, 2]. Fig. 1 schematically shows the phase diagram of the pseudo-binary system of Al–(Pb,Bi). When the alloy is cooled from a single liquid phase, it separates into two liquid phases, L_1 and L_2 at the miscibility line. These two phases segregate gravitationally under a 1 *G* environment because of a great difference in density. Therefore, this ternary alloy is rarely prepared uniformly. Under microgravity, on the other hand, (Pb, Bi)-rich particles are expected to disperse homogeneously in the aluminium-rich liquid matrix forming a uniform composite structure during solidification. The Al–Pb–Bi composite alloy is also interesting from a view point of an *in situ* processed superconductor. By deforming the Al–Pb–Bi ingot into a wire, (Pb, Bi) superconducting particles are elongated into Pb–Bi filaments in the aluminium matrix. When the distance between the filaments becomes smaller than the distance of a Cooper pair leakage in the aluminium matrix (coherence length), the wire is expected to show complete zero resistance due to the proximity effect.

Kitaguchi and Togano [3] and Mohri *et al.* [4] reported the microstructure of Al–(Pb, Bi) alloys melted and solidified under low-gravity conditions utilizing a parabolic flight of an aircraft. Kitaguchi and Togano showed that (Pb, Bi) particles dispersed uniformly in the aluminium matrix below ~ 0.02 *G*, while evident gravitational segregation was observed in 1 *G*. Mohri *et al.* performed unidirectional solidification, and compared the microstructure of the samples prepared under low- and high-gravity conditions [4]. They reported that the sample prepared under lower gravity showed a higher critical temperature, T_C. Tachikawa and Togano [5] fabricated Al–Pb–Bi wires by deforming the ingots prepared by chill casting under 1 *G* and investigated the superconducting properties. They showed that the values of T_C, the upper critical field, H_{C2}, and the critical current density, J_C, depended on the content of (Pb, Bi) alloys. However, the scatter of J_C values in their measurements was large due to the heterogeneity of (Pb, Bi) particle distribution in the ingot. These results suggest that fabrication of uniform ingots is the key factor to obtain wires with excellent superconducting properties.

In previous reports, the melt-solidification under microgravity had to be finished in a very short time [3, 4]. This results in a large cooling rate, and hence, large temperature gradient in a sample. A large temperature gradient induces a large Marangoni force which brings about a movement of (Pb, Bi) particles. Recently, we had an opportunity to perform long-term microgravity experiments utilizing the Space Lab-3 (SL-3) mission of the Space Shuttle launched in September 1992. In this paper we report the microstructure of Al–Pb–Bi ingots solidified in the Space Shuttle. We also report the superconducting properties of wires fabricated using these ingots.

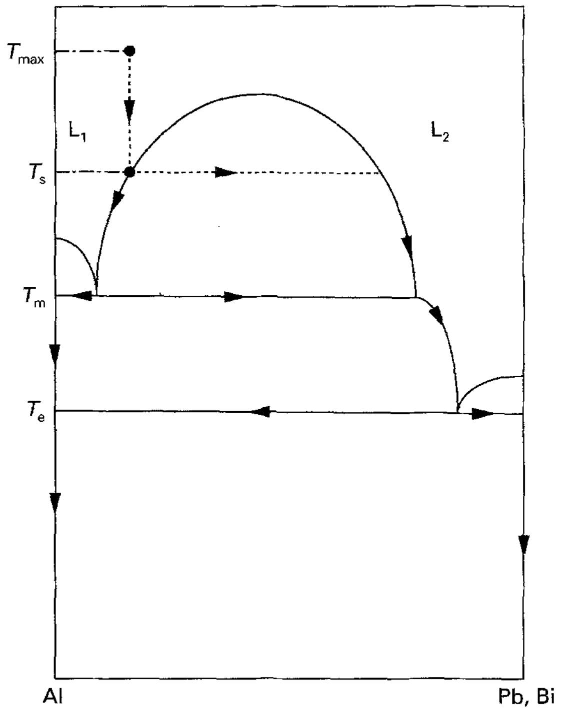

Figure 1 A schematic phase diagram of the pseudo-binary system, Al–(Pb, Bi).

2. Experimental procedure

The alloys were melted and solidified in the Space Shuttle *Endeavour* on 13 September 1992 as one of the subjects of the First Material Processing Test (FMPT'92) organized by National Space Development Agency of Japan. The starting Al–Pb–Bi alloy was prepared on Earth as follows. Aluminium, lead and bismuth (99.999% purity) with three different compositions were melted above 1373 K under 1 atm Ar gas and were quenched into a copper mould to reduce gravitational segregation. The compositions of the ingots were Al–1 at % Pb–1 at %Bi, Al–2 at % Pb–2 at % Bi and Al–3 at % Pb–3 at % Bi. These samples are denoted by CHF-11, CHF-13 and CHF-15, respectively. The atomic ratio of lead to bismuth was chosen to be 1 : 1 because our preliminary results show that the superconducting properties of the Pb–Bi system are the best for this composition. Each ingot was cut to the size of 6 mm diameter and 30 mm long and put into a BN crucible and then sealed in a double tantalum capsule for safety, as shown in Fig. 2. The capsules were sealed in a cartridge for heat treatment using a continuous heating furnace (CHF). The temperature of the sample was measured using an *R* thermocouple located at the edge of the capsule. The samples were heated to 1577–1580 K in 10 min and held for 34 min at this temperature, and then cooled in a cooling chamber by filling the chamber with helium gas. The temperature decreased to 873 K in about 70 s. The melt–solidification under 1 *G* was also performed with the same heat-treatment procedure for comparison.

A solidified sample was cut in quarters in the longitudinal direction. One of them was sheathed in a copper tube, and then cold-worked with grooved rolling and drawing machines to a wire of 0.35 mm diameter with intermediate annealings at 573 K under 1×10^{-4} torr (1 torr = 133.322 Pa).

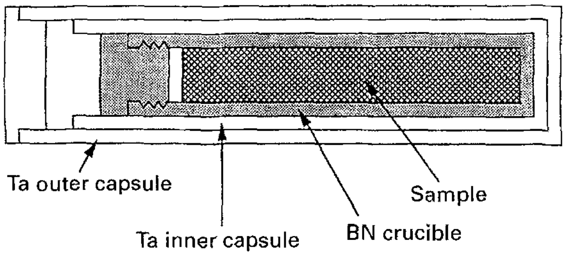

Figure 2 Schematic longitudinal cross-section of the sample container for the heat treatment using a continuous heating furnace (CHF).

Microstructure observation was performed for both bulk and wire samples with an optical microscope and a scanning electron microscope (SEM, Jeol JSM-840F). For the SEM observation, both secondary electron image (SEI) and backscattering electron image (BEI; composition image) were recorded. The size distribution of (Pb, Bi) particles was measured for several areas on the longitudinal cross-section. The particle size is the diameter measured on the plane of observation. Energy dispersive X-ray spectroscopy (EDS) was performed using a spectrometer attached to the SEM in order to determine the composition. Analysis of light elements such as boron, nitrogen and oxygen was performed by electron probe microanalysis (EPMA) using a Jeol JXA-8900R.

T_C, H_{C2} at 4.2 K and J_C at 4.2 K were measured for wires by a four-probe resistive method. Before measurement, the copper sheath was removed by etching with a nitric acid solution. J_C was obtained by dividing the critical current by the cross-sectional area of a wire. In the H_{C2} measurement, the magnetic field was applied perpendicular to the wire. H_{C2} was defined as the lowest field where J_C became zero.

3. Results and discussion

After the flight, the samples were transparently photographed with X-rays before removal from the capsules. The photographs showed that neither capsules nor crucibles were damaged for any of the three samples. In order to remove the ingots, the crucibles were broken because the ingots were stuck to the inner wall.

The BEIs of the longitudinal cross-section of the CHF-11, 13 and 15 ingots are shown in Fig. 3 a–c, respectively. In these images, the dark area corresponds to light elements and the bright area to heavy ones. EDS analysis shows that the bright and dark areas consist of Pb–Bi and aluminium, respectively. These images show that (Pb, Bi) particles are dispersed uniformly in the aluminium matrix. There are large voids in all the samples, especially in the CHF-11 and 15 ingots. These voids were probably produced from gas contamination during sample preparation on Earth. Their formation mechanism is discussed later. Fig. 4a and b show BEIs for the longitudinal cross-sections of the Al–2 at % Pb–2 at %Bi and Al–3 at % Pb–3 at %Bi ingots solidified under 1 *G*, respectively. Sedimentation of (Pb, Bi) particles are

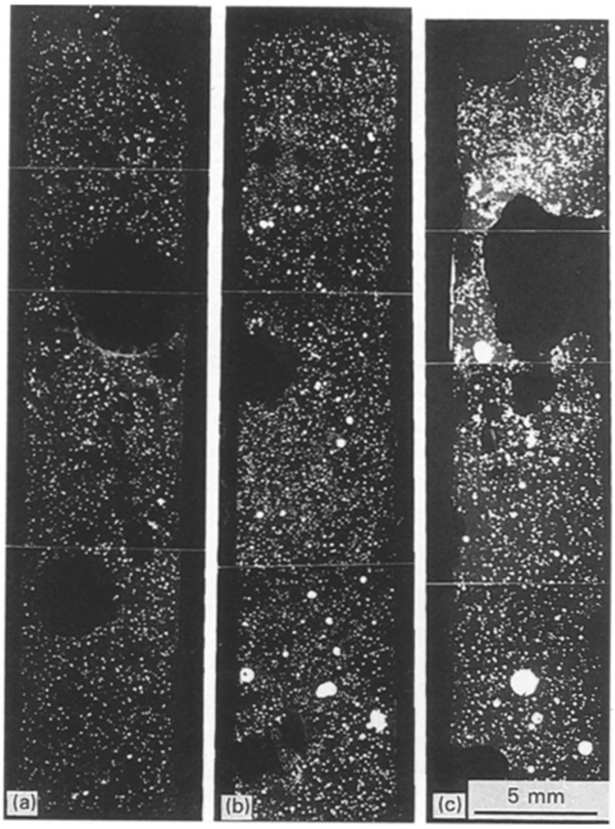

Figure 3 Backscattering electron images of the longitudinal cross-section of (a) Al–1 at % Pb–1 at % Bi (CHF-11), (b) Al–2 at % Pb–2 at %Bi (CHF-13) and (c) Al–3 at % Pb–3 at % Bi (CHF-15) ingots. Dark and bright areas correspond to the aluminium matrix and (Pb, Bi) particles, respectively.

clearly observed for both ingots. For the Al–3 at % Pb–3 at %Bi ingot, some (Pb, Bi) layers are observed between the ingot and the crucible because of the wettability of (Pb, Bi) with the BN crucible.

The distribution of particle size in the CHF-13 ingot for upper, middle and lower parts of the ingot is shown in Fig. 5a–c, respectively. A weak dependence of size distribution on the part of the sample is observed. Particle diameter ranges from several to hundreds of micrometres but the diameter of most of the particles is below 50 μm. The other two samples also have uniform microstructure. For the ingots melt–solidified under 1 *G*, on the other hand, the (Pb, Bi) particle size is more strongly dependent upon the regions in the ingot, as shown in Fig. 6a and b. The large particles fall to the bottom due to gravitational sedimentation.

The (Pb, Bi) particles were formed by two different mechanisms. According to the phase diagram in Fig. 1, the liquid began to separate into aluminium- and (Pb, Bi)-rich liquid phases at T_s, and at T_m a monotectic reaction occurred. It is considered that large (Pb, Bi) particles were produced at stage two of the liquid-phase separation and fine particles at the monotectic reaction. At T_e, the eutectic reaction took place and the (Pb, Bi)-rich liquid phase was solidified. Fig. 7 shows a BEI for the cross-section of a (Pb, Bi) particle. Fine aluminium precipitates obtained during the eutectic reaction were observed.

In the previous experiment performed in an aircraft, samples were cooled with directional gas flow, which brought about a large temperature gradient. Therefore, Marangoni force acted on the (Pb, Bi)-rich liquid particles in the aluminium liquid matrix and drove these liquid particles into a higher temperature region [6]. Because the mobility caused by this driving force depends on particle size, the size distribution differed greatly from part to part. In this experiment, we can conclude from the homogeneous microstructure that there is no Marangoni force acting during solidification.

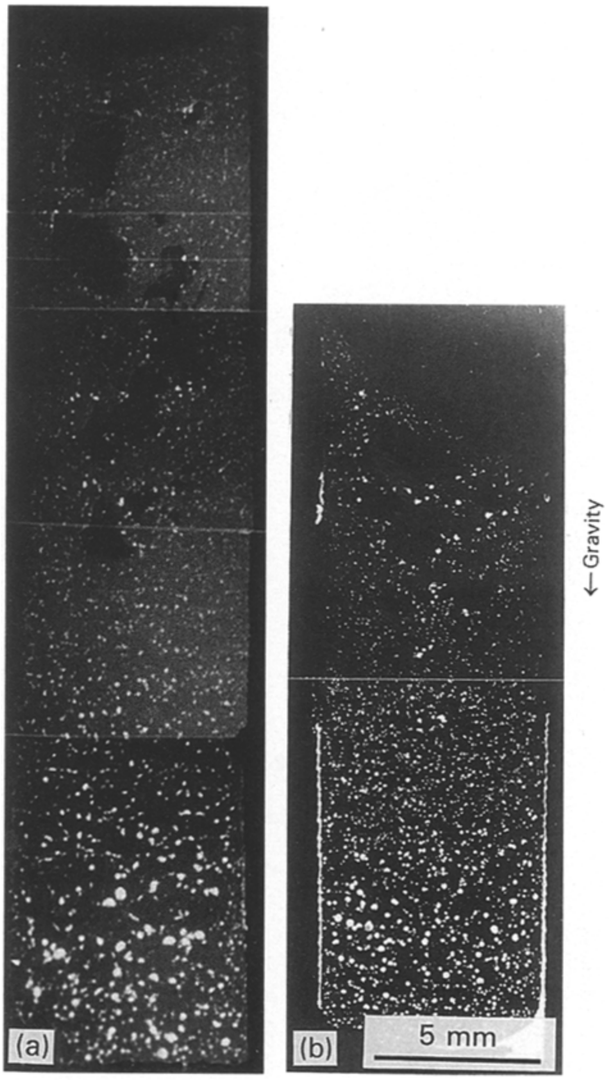

Figure 4 Backscattering electron images of the longitudinal cross-sections of (a) Al–2 at % Pb–2 at % Bi and (b) Al–3 at % Pb–3 at % Bi ingots solidified under 1 *G*.

An optical micrograph of a cross-section of the CHF-13 ingot is shown in Fig. 8a. Not only (Pb, Bi) particles but also needle-like structures are observed in the aluminium matrix. The needle-like structure is also observed for the CHF-11 and 15 ingots and the samples solidified under 1 *G*. This microstructure, however, was not observed for the samples solidified by quenching from high temperature in an aeroplane under 0.02 *G* [3, 4]. Fig. 8b shows a BEI of the needle-like structure observed in the CHF-13 ingot. The needle is darker than the aluminium matrix, although the extent of the darkness changes from needle to needle. This result implies that the needle contains light elements, such as boron, nitrogen and oxygen,

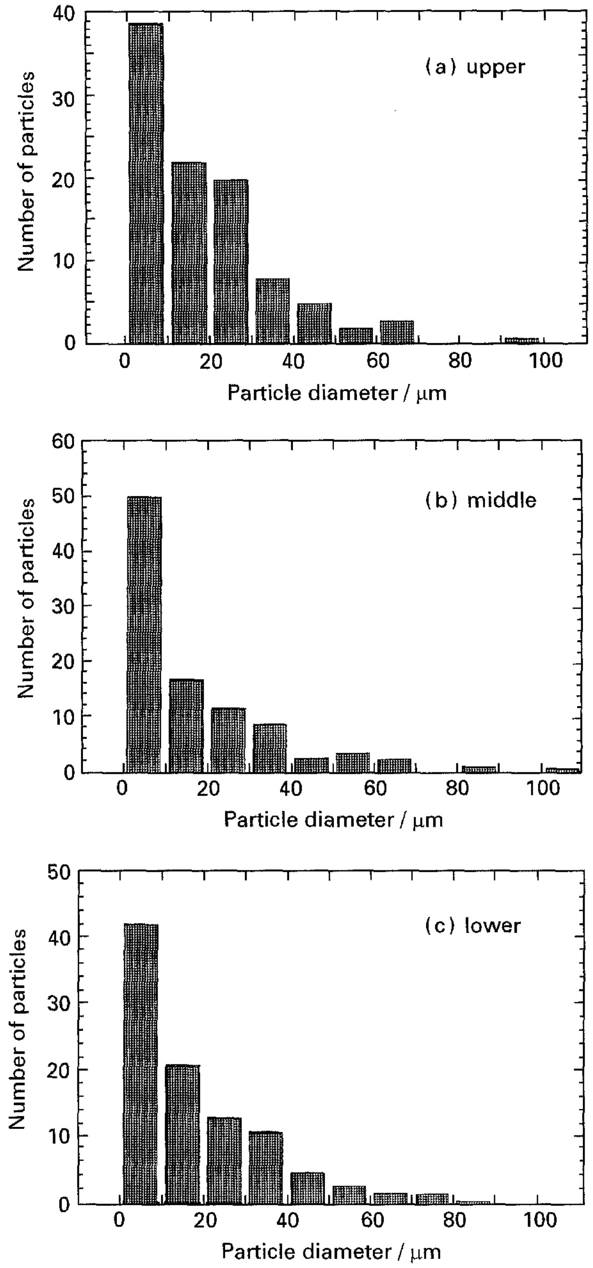

Figure 5 (Pb, Bi) particle-size distribution for the (a) upper, (b) middle and (c) lower parts in the Al–2 at % Pb–2 at % Bi (CHF-13) ingot. The terms "upper" and "lower" are used for distinction of both sides for convenience.

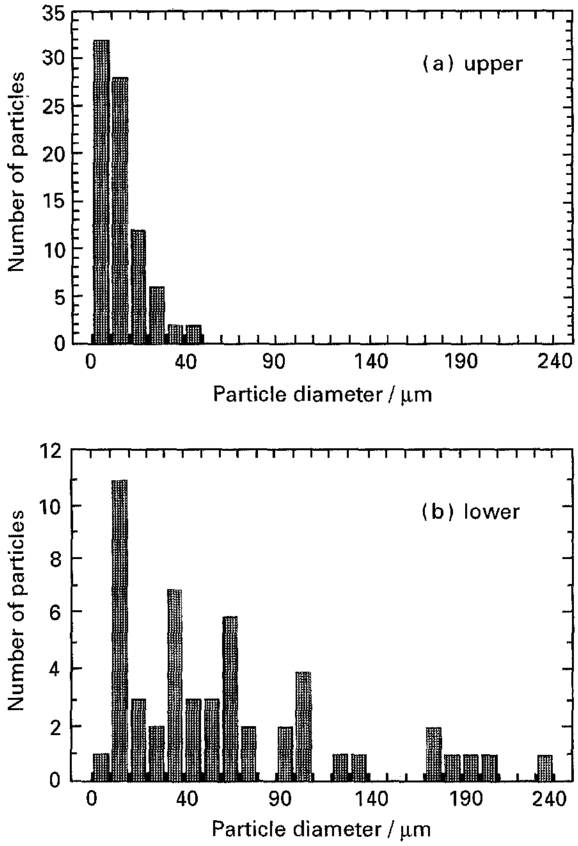

Figure 6 (Pb, Bi) particle–size distribution for the (a) upper and (b) lower parts in the Al–2 at % Pb–2 at % Bi ingot processed under 1 *G*.

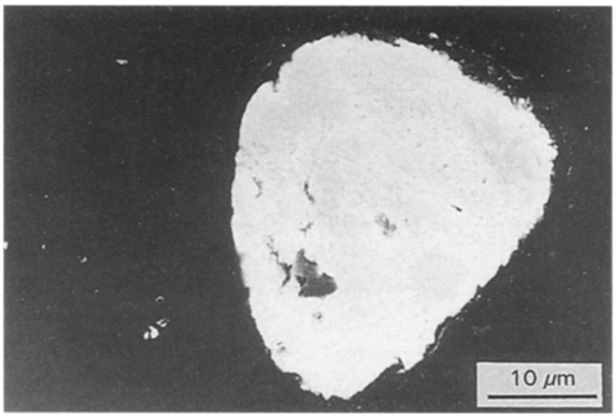

Figure 7 A backscattering electron image of a (Pb, Bi) particle in the Al–2 at % Pb–2 at % Bi (CHF-13) ingot.

and that there is a scattering of the concentration in the needles. The results of EPMA measurement showed that the needles contain boron, which is attributed to the reaction with the BN crucible. The difference in the darkness of the structure is due to the distribution of the boron content. This result is in good agreement with the microstructure after polishing. The surrounding aluminium was polished selectively due to the difference in hardness, dependent on whether or not they contained boron. The reason why this structure was not observed in the samples processed in the aircraft is attributed to the fact that the melt–solidification was performed over a short period of time, just a few minutes. In this experiment, the long-term experiment allowed the reaction between Al–Pb–Bi and BN to occur.

A BEI for the longitudinal cross-section of the wire prepared using the CHF-13 ingot is shown in Fig. 9. The (Pb, Bi) particles were cold-worked and elongated into fine filaments. Although the distance between the filaments ranges over several micrometres, some of them are under 1 μm smaller than 1.6 μm, which is the superconducting coherence length of aluminium [7]. Fig. 10 shows the resistive transition of the wire obtained from the CHF-13 ingot. Sharp superconducting transition was observed with a midpoint transition temperature of 8.7 K. Because the coherence length of the aluminium matrix is larger than the distance between the filaments in most cases, the wire shows zero resistance due to the proximity effect.

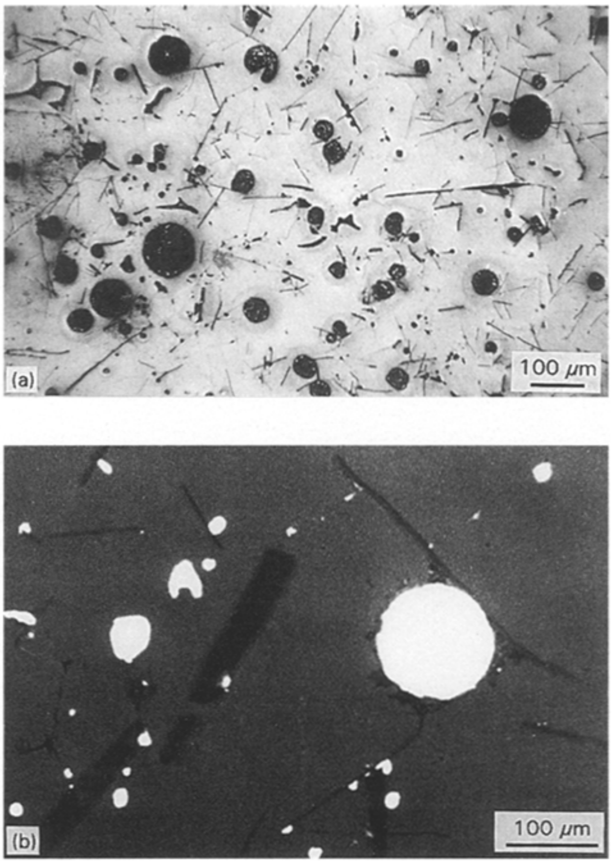

Figure 8 (a) Optical micrograph of the cross-section of the Al–2 at % Pb–2 at % Bi (CHF-13) ingot. (b) A backscattering electron image of a needle-like structure in the sample ingot.

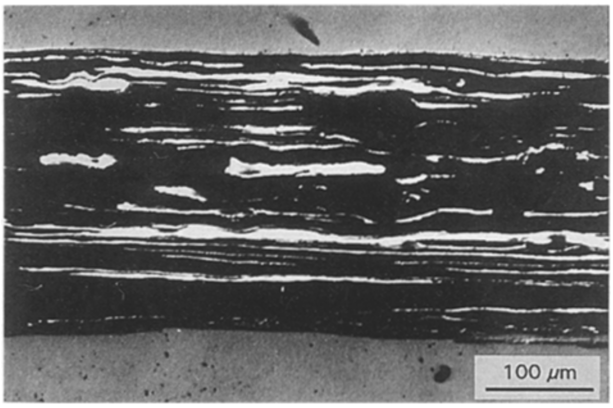

Figure 9 A backscattering electron image of the longitudinal cross-section of the Al–(Pb, Bi) wire fabricated using the Al–2 at % Pb–2 at % Bi (CHF-13) ingot.

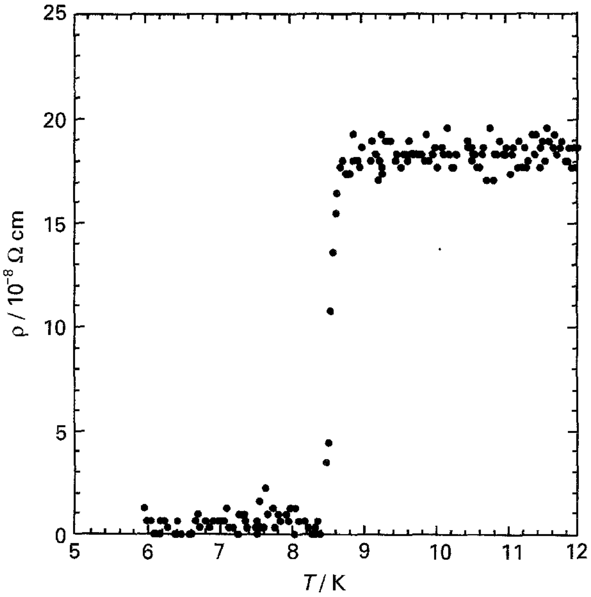

Figure 10 Resistivity, ρ, versus temperature, *T*, plot for the Al–(Pb, Bi) wire fabricated from the Al–2 at % Pb–2 at % Bi (CHF-13) ingot.

TABLE I Superconducting properties, T_C, H_{C2} and J_C, of three samples.

	T_C/K	H_{C2} (4.2 K) / T	J_C (4.2 K, 0 T)/A cm^{-2}
CHF-11	8.6	1.9	2600
CHF-13	8.7	1.9	7800
CHF-15	8.8	1.9	4700

The results of T_C, H_{C2} and J_C measurements on the wire are shown in Table I. The T_C and H_{C2} values are 8.7 K and 1.9 T for the CHF-13 ingot, respectively. Almost the same values are obtained for the other two ingots, indicating that T_C and H_{C2} are independent of the (Pb, Bi) contents. On the other hand, the J_C value, ranging from 2600–7800 A cm^{-2}, strongly depends on the (Pb, Bi) contents and becomes maximum for the CHF-13 ingot. It is reported that the higher the (Pb, Bi) concentration, the higher are the J_C values [5]. The reason why the J_C value becomes maximum not at the composition of the CHF-15 Al–3 at % Pb–3 at %Bi) ingot but at that of the CHF-13 (Al–3 at % Pb–3 at %Bi), is not clear, but it is probably related to the quality of the original ingots. The number of voids in the CHF-13 ingot is the smallest of the three ingots, as shown in Fig. 3. These voids were formed in the following two ways: one is that gas absorbed into the starting materials may be released during the melt–solidification (it is known that aluminium easily absorbs hydrogen); the other is attributed to the gas release from the BN crucible. Many voids were observed close to the inner wall. The gas was not purged from the ingots because of the absence of gravity.

4. Conclusion

We have succeeded in preparing uniform Al–Pb–Bi monotectic alloy under microgravity in space utilizing the Space Shuttle. The (Pb, Bi) particles were dispersed uniformly in the aluminium matrix. Particle size ranged from a few to hundreds of micrometres but most particles were below 50 μm diameter. The uniform cooling much decreased the Marangoni force which induces movement of the particles, which is also effective to obtain uniform microstructure. A needle-like structure was observed in the aluminium matrix. The result of EPMA measurement showed that this structure was composed of Al–B solid solution or compounds formed by the reaction with the BN crucible.

The T_C and H_{C2} at 4.2 K are around 8.7 K and 1.9 T for all wires, respectively. The J_C value ranged from 2600–7800 A cm^{-2}, depending on the (Pb, Bi) contents.

One of the most important issues for material processing under microgravity is to resolve the problems of void formation during melt–solidification.

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