JOURNAL OF MATERIALS SCIENCE 26 (1991) 3951–3954

Production of superconducting Cu–Nb–Sn alloy by hot extrusion of rapidly solidified powder

A. INOUE, T. MASUMOTO
Institute for Materials Research, Tohoku University, Sendai 980, Japan
L. ARNBERG
Department of Metallurgy, Norwegian Institute of Technology, 7034 Trondheim, Norway
N. BÄCKSTRÖM
Swedish Institute for Metals Research, Drottning Kristinas väg 48, 114 28 Stockholm, Sweden

A $Cu_{92.5}Nb_5Sn_{2.5}$ alloy has been rapidly quenched into a powder by ultrasonic gas atomization. The structure of the powder consists of finely dispersed Nb particles in a Cu–Sn matrix. The powder has been consolidated by hot extrusion at 650 °C. The extrusion does not change the phases present in the material appreciably but annealing for 100 h at 650 °C causes a transformation of the Nb particles to Nb_3Sn.

The extruded material shows superconductivity. The critical temperature T_c, of the as-quenched alloys is 8.0 K but increases to 15.6 K after annealing for 100 h at 923 K. The upper critical magnetic field, H_{c_2}, and critical current density, J_c, were 3.4 kOe at 4.2 K and 7.4×10^5 A m^{-2} at zero applied field and 4.2 K, respectively.

The appearance of superconductivity is attributed to the proximity effect of the Nb_3Sn phase particles which are sufficiently well distributed to satisfy the leak distance and the critical particle size.

1. Introduction

Investigation of rapidly quenched alloys with large miscibility gaps has shown that it is possible to produce mixed microstructures with the insoluble constituents very finely distributed [1, 2]. This has been utilized by Inoue *et al.* to produce rapidly solidified microstructures of Pb, Pb–Bi, Al–Si, Si–V and Nb–Sn particles in Al or Cu matrices [3–5]. These alloys show superconducting properties with transition temperatures characteristic of the dispersed phases. The superconductivity has been explained by the proximity effect which has been attributed to the very fine dispersion of the superconducting phase in the non-superconducting matrix. The test materials previously investigated by Inoue *et al.* have consisted of thin rapidly solidified ribbon samples. For many practical applications, however, a bulk material would be preferable. Such a bulk material can be produced by consolidation of rapidly solidified ribbons or powders, provided the consolidation does not significantly coarsen the fine microstructure. A consolidation process which includes a substantial amount of deformation such as hot extrusion or powder forging could be preferable since the superconducting phase can be further deformed to a fibrous structure, thereby increasing the ease of the formation of a superconducting circuit by the proximity effect.

Rapidly quenched $Cu_{88}Nb_8Sn_4$ ribbons have been investigated previously [5] and demonstrated attractive superconducting properties. The as-quenched alloy consists of Nb particles, finely dispersed in a Cu–Sn α-matrix, but after annealing for ~ 100 h at 650 °C the Nb-phase transforms to Nb_3Sn. The particle dispersion is still very fine, and the alloy shows a superconducting transition temperature, T_c, of 16 K, close to that of pure Nb_3Sn.

Ultrasonic gas atomization gives cooling rates and microstructures similar to those of rapidly solidified ribbons [6]. It has been shown previously that Cu alloys with finely dispersed second-phase particles can be produced by hot extruding rapidly solidified powders at temperatures of 600 to 650 °C [7, 8].

The present investigation was undertaken in order to see if a rapidly solidified Cu–Nb–Sn superconducting alloy could be produced in bulk shape by hot extrusion of a rapidly solidified powder. The paper will describe the production and report on the microstructure and superconducting properties.

2. Experimental procedure

A Cu–8 at % Nb–4 at % Sn master alloy was produced by vacuum induction melting pure elements in an alumina crucible. The master alloy (~ 5 kg) was chill

0022-2461/91 $03.00 + .12

cast in a copper mould. Attempts to atomize the alloy failed due to the high melting point (sufficient superheating of melt for efficient atomization could not be provided). The master alloy was, therefore, diluted by Cu to 5 at % Nb and 2.5 at % Sn. The melt was atomized from ~ 1800 °C with He at a dynamic pressure of 6.9 MPa in an ultrasonic gas atomization equipment [6]. The powder was collected under inert atmosphere but screened in air and the size fraction below 63 μm was put in cylindrical Cu cans with a diameter of 50 mm. The tap density of the powder was 51%. The cans were evacuated, sealed by welding and precompacted to 78% density by cold isostatic pressing. The precompacted cans were heated in a resistance furnace at the extrusion temperature for 45 min and then hot extruded to an area reduction of 20 : 1 in a 350 ton extrusion press. Initial attempts to extrude at 600 °C failed and therefore the billet temperature was increased to 650 °C. Even at this temperature the extrusion was interrupted as the available extrusion pressure 1750 MPa was exceeded, but sufficient material (200 mm of 11 mm diameter rod) for structure and superconductivity measurements could be obtained.

The microstructure of the powder and extruded material was investigated by light optical microscopy.

Measurements of superconducting properties, T_c, J_c(H) and $H_{c_2}(T)$ were made on pieces with a cross-section 0.5×0.1 cm^2, cut from the central part of the extruded bars. The d.c. method using four electrical probes was used. The temperature was measured with an accuracy of ± 0.01 K by a calibrated germanium thermometer. A magnetic field up to 9.0 T was applied perpendicular to the specimen surface and feed current.

3. Results and discussion

The atomized powder had a fine particle size, 79 wt % of the particles had diameters less than 40 μm. Powder particles in this size range have previously been shown to exhibit cooling rates $> 10^5$ K s^{-1}. The powder was spherical and was relatively free from satellites. The internal porosity was very low. Fig. 1a and b shows etched cross-sections of two size fractions of powder particles. It can be seen that the microstructure of the < 63 μm powder is below the resolution limit of the microscope. No distinct features can be seen in the etched structure. Some of the particles in the > 100 μm fraction, however, contain relatively coarse precipitates. The < 65 μm size fraction was therefore chosen for consolidation.

The original intention was to keep the extrusion temperature as low as possible to avoid diffusion of Sn to the Nb particles and thus formation of Nb_3Sn. The reason for avoiding Nb_3Sn formation during extrusion is that deformation of the particles during the extrusion was considered favourable for the superconductivity and this deformation will be prevented by transformation from ductile Nb to hard Nb_3Sn. It has been found previously that the transformation of Nb to Nb_3Sn at 650 °C is measurable after 1 h. An extrusion temperature of 600 °C was therefore chosen. It is, however, obvious that the combined strengthening effect of the 2.5 at % Sn and the fine Nb dispersion is appreciable and the available extrusion pressure (1750 MPa) was not sufficient to extrude the alloy. At 650 °C the pressure was just sufficient for ~ 50% of the material to extrude before the press stalled.

Fig. 2 shows the microstructure of the extruded material. The structural features are generally below the resolution limit of the microscope. It can, however, be seen that there are areas which have etched differently, probably originating from powder particles with lower Nb-concentration or different Nb-particle distribution. Occasionally, features like in Fig. 3 can be seen in the structure. These are most probably coarse Nb particles. It can be seen that most of the particles are relatively undeformed; the elongated, fibrous shape has not been achieved for these particles.

Fig. 4 shows the normalized electrical resistance R/R_n curve in the vicinity of T_c without an applied magnetic field for the as-extruded alloy. The transition temperature (at $R/R_n = 0.5$) is 8.0 K, and the transition is relatively wide; $\Delta T_1 = 2.5$ K. The value of T_c indicates that the superconducting phase is Nb rather than Nb_3Sn. The critical current density (J_c) of the as-extruded material at 4.2 K as a function of applied magnetic field is shown in Fig. 5. J_c at zero magnetic

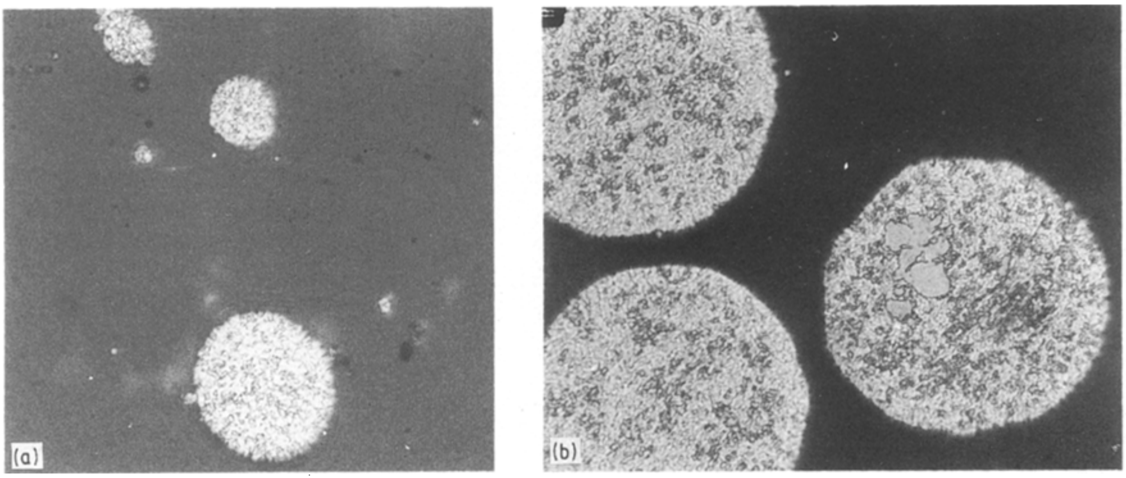

Figure 1 Etched cross sections of as-atomized Cu–5 wt % Nb–2.5 wt % Sn powder particles. (a) < 65 μm size fraction (b) > 100 μm size fraction.

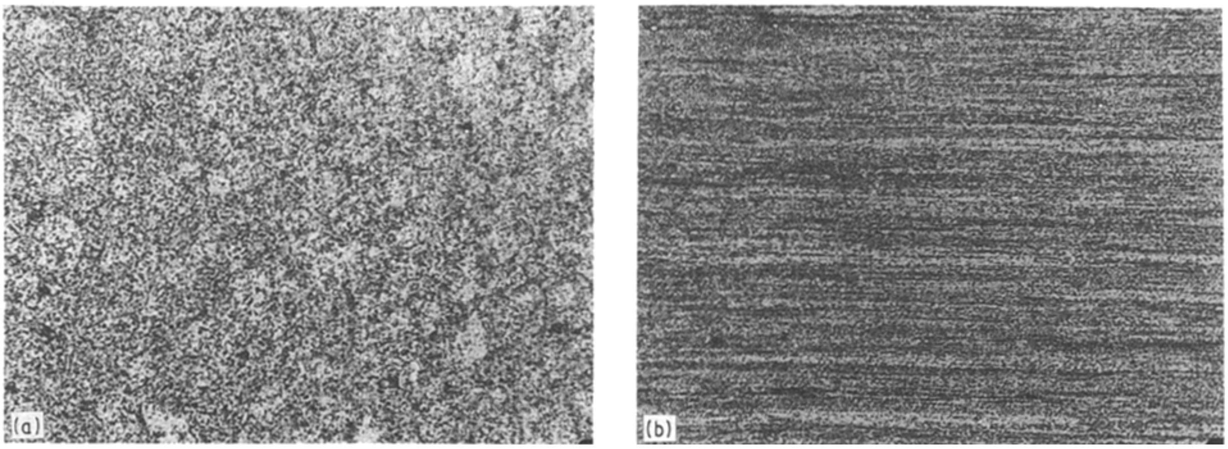

Figure 2 Etched sections of as-extruded Cu–5 wt % Nb–2.5 wt % Sn (a) Section perpendicular to the extrusion direction (b) Section parallel to the extrusion direction.

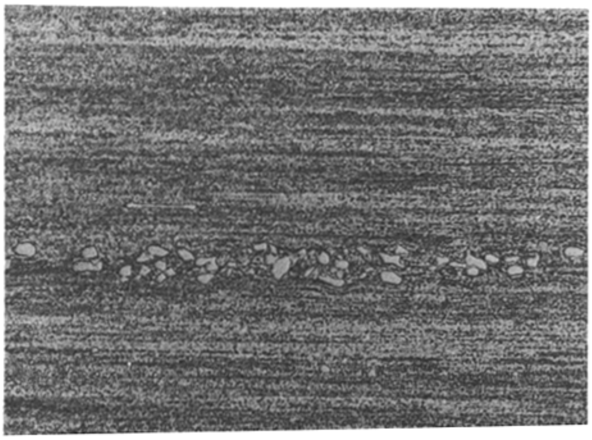

Figure 3 Etched section of as-extruded Cu–5 wt % Nb–2.5 wt % Sn parallel to the extrusion condition, showing inhomogeneous microstructure.

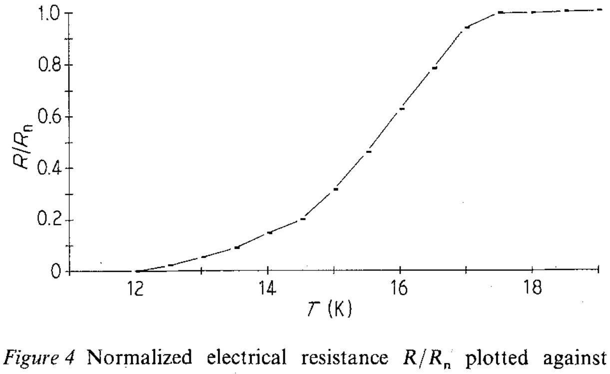

Figure 4 Normalized electrical resistance R/R_n plotted against temperature T, for as-extruded Cu–5 wt % Nb–2.5 wt % Sn.

field is 8.3×10^5 A m^{-2}. The critical magnetic field, H_{c_2} at $R/R_n = 0.5$ is 3.40 kOe.

Annealing of rapidly quenched Cu–Nb–Sn ribbons at 650 °C causes a relatively slow transformation of the Nb-phase originally present in the ribbons to Nb_3Sn [5]. This transformation is complete after 100 h, i.e., T_c of the material increases with annealing time and becomes constant after 100 h. The extruded material was, therefore, heat treated at 650 °C for 100 h. The resulting resistance – temperature curve is shown in Fig. 6. The critical temperature is 15.6 K but

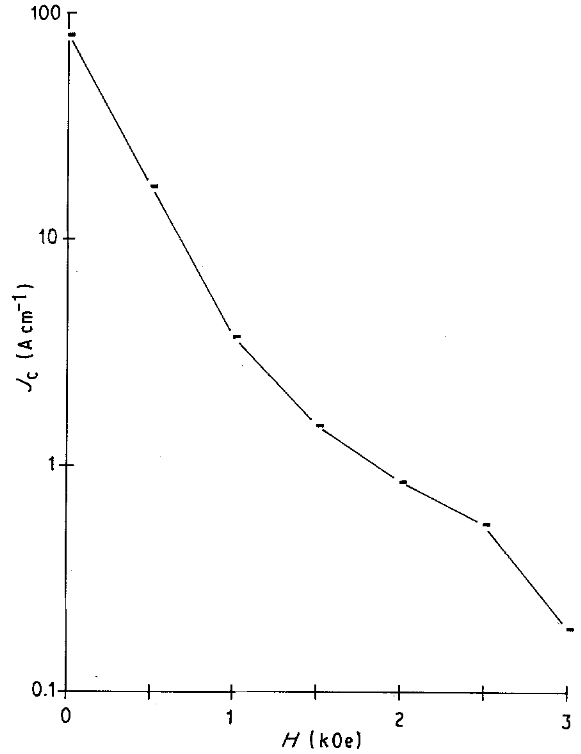

Figure 5 Critical current density J_c plotted against applied magnetic field, H, for as-extruded Cu–5 wt % Nb–2.5 wt % Sn.

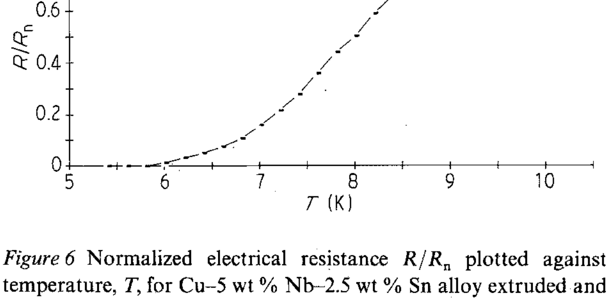

Figure 6 Normalized electrical resistance R/R_n plotted against temperature, T, for Cu–5 wt % Nb–2.5 wt % Sn alloy extruded and annealed at 650 °C for 100 h.

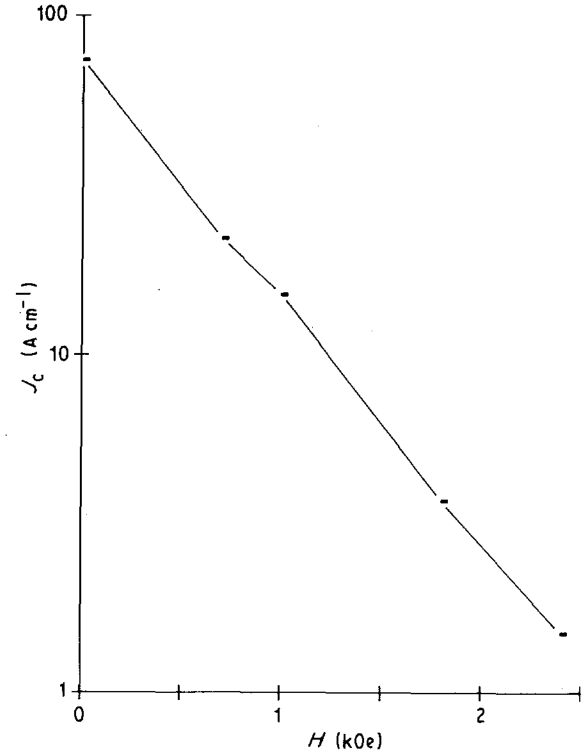

Figure 7 Critical current density, J_c, plotted against applied magnetic field, H, for Cu–5 wt % Nb–2.5 wt % Sn alloy extruded and annealed at 350 °C for 100 h.

the transition is still relatively wide; $\Delta T_c = 3.25$ K, indicating that the superconducting Nb_3Sn phase is not at equilibrium. The critical current density of the annealed material at 4.2 K as a function of applied field is shown in Fig. 7. J_c at zero magnetic field has decreased somewhat compared to the as-extruded alloy 7.4×10^5 A m^{-2}. The critical magnetic field H_c has also decreased to < 3 kOe after the annealing treatment.

The high critical temperature of the annealed alloy, 15.6 K is attractive, but the values of the critical current density and critical magnetic field are too low for most applications. The J_c value is two orders of magnitude lower than that of Cu–Nb–Sn ribbon [5]. The reason for this is not clear, but presumably the microstructure of the extruded material is considerably coarser than that of the ribbon. Furthermore, the fraction of superconducting phase in the ribbon material is 60% higher (the ribbon material contained 8 at % Nb and 4 at % Sn).

References

1. A. INOUE, M. OGUCHI, K. MATSUZAKI and T. MASUMOTO, *J. Mater. Sci.* **21** (1986) 260.
2. *Idem., Int. J. Rapid Solidification* **1** (1984–5) 173.
3. A. INOUE, N. YANO, K. MATSUZAKI and T. MASUMOTO, *J. Mater. Sci.* **22** (1987) 123.
4. *Idem., J. Mater. Sci.* **22** (1987).
5. A. INOUE, N. YANO, K. MATSUZAKI, L. ARNBERG, B. LEHTINEN and T. MASUMOTO. Unpublished work.
6. U. BACKMARK, N. BÄCKSTRÖM and L. ARNBERG, *Powder Met. Int.* **18** (1986) 338.
7. L. ARNBERG, U. BACKMARK, N. BÄCKSTRÖM and J. LAGNE, *Mat. Sci. Eng.* **83** (1986) 115.
8. A. M. HALLÉN, L. ARNBERG, N. BÄCKSTRÖM and U. BACKMARK, *Mod. Dev. of Powder Met.* **18–21** (1988).

Received 20 June
and accepted 26 June 1990