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Superconductivity in dilute Cu-Nb-Sn alloys containing Nb_3Sn precipitates

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The dilute Cu–Nb–Sn alloys containing small amounts of Nb and Sn less than 1 at % exhibited superconductivity after quenching from the liquid state and ageing. The best superconducting properties (T_{c_2} = 12.0 K and J_c = 130 A cm^{-2}) in a Cu–0.30 at % Nb–0.15 at % Sn alloy were obtained when the sample was aged at 550° C for 384 h. This sample exhibited a structure of fine Nb_3Sn precipitates of 200 to 500 Å diameter distributed homogeneously in the Cu matrix, and therefore it was concluded that superconductivity in these alloys resulted from the proximity effect of Nb_3Sn particles. In spite of the similar structure obtained by ageing at 800° C, the Cu–Nb–Sn alloys showed inferior superconducting properties compared to the Cu–0.4 at % Nb alloy and this would be explained qualitatively by the difference in the mean free path in the two alloys.

1. Introduction

It is well known that pure copper is not a superconductor even at very low temperatures (0.05 K) [1]. However, it was reported that Cu with small amounts of dispersed particles of superconductors exhibited superconductivity. For example, Raub *et al.* [2–4] reported that the Cu alloys containing Pb or $Nb_3Al_{0.8}Ge_{0.2}$ particles showed superconducting transition temperatures near those in the bulk superconductors. Tsuei *et al.* [5, 6] and Gupta *et al.* [7] discussed the characteristics of superconductivity in Cu alloys with small amounts of Nb particles. The reason why these alloys exhibit superconductivity is believed to be due to the proximity effect [8–11] of superconducting particles dispersed in the Cu matrix. Therefore, superconductivity is considered to depend on the size and the spacing as well as the nature of the superconductor. This is a very interesting problem from the metallurgical aspect, but there is no systematic research on the relationship between the superconducting properties and the structure in those alloys.

The purpose of this study is to make clear the nature of superconductivity in Cu allloys containing small amounts of superconducting particles prepared by quenching from the liquid state and ageing under various conditions. The reason why the Cu–Nb–Sn alloys were chosen for this study is that the A-15 type intermetallic compound Nb_3Sn (T_c = 18.0 K) [12] is expected to precipitate in the Cu matrix, and that the superconductor Nb_3Sn has a more promising nature than Nb and Pb metals. The nature of superconductivity in dilute Cu–Nb–Sn alloys was determined by resistive measurement and their structure was observed using a transmission electron microscope.

2. Experimental procedure

2.1. Specimen preparation

The starting materials consisted of 99.99% pure Cu, 99.5% pure Nb and 99.9% pure Sn. At first, a Cu–20 wt % Nb master alloy was arc-melted in the water-cooled Cu hearth and then three Cu–Nb–Sn alloys given in Table I were prepared by induction melting or arc-melting. These alloys

TABLE I Chemical compositions of Cu–Nb–Sn alloys.

Material	Content (at %)	
	Nb	Sn
Cu–0.30 Nb–0.15 Sn	0.30	0.15
Cu–0.56 Nb–0.26 Sn	0.56	0.26
Cu–1.10 Nb–0.53 Sn	1.10	0.53

were quenched from the liquid state to a tape shape about 1 mm wide and about 0.03 mm thick by the rotating drum method [13, 14] at a cooling rate of about 10^5 °C $\sec^{-1}$. Samples were cut to about 30 mm in length, put into evacuated quartz ampoules, and aged at various temperatures for various times. A Cu–0.30% Nb–0.15% Sn alloy was used for the most part of the present study.

2.2. Superconducting measurements

Among the superconducting properties, the superconducting transition temperature (T_c) and the superconducting critical current (I_c) were determined by electrical resistivity measurements using a standard 4-probe technique in a temperature-variable cryostat. Samples held on the Cu block in the evacuated sample chamber were suspended vertically in a liquid helium cryostat. The temperature was controlled by varying the small electrical current through the heater wound around the Cu block and measured by an Allen Bradly carbon resistor thermometer placed close to the sample. I_c was measured in liquid helium (at 4.2 K) and the distance between voltage probes was about 20 mm.

2.3. Structural observations

Since T_c and I_c in materials which exhibit superconductivity by the proximity effect are considered to connect closely with their microstructure, the structures were observed using a transmission electron microscope operated at 200 kV after polishing electrolytically in a solution of phosphoric acid, ethyl alcohol and water.

3. Experimental results

3.1. Superconducting properties

It is a prominent feature that materials exhibiting superconductivity by the proximity effect have a wide range of temperatures for the super-normal transition. Fig. 1 shows an example of the change of the electrical resistance of the Cu–0.30% Nb–0.15% Sn alloy aged at 800° C for 384 h as a function of the sample current. In Fig. 1, the

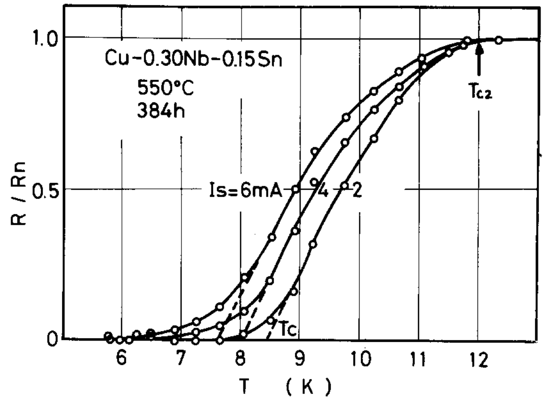

Figure 1 Superconducting transition curve as a function of sample current in the Cu–0.30% Nb–0.15% Sn alloy aged at 800° C for 384 h.

resistance (R) is normalized to that in the normal state (R_n). T_c was varied with the sample current (I_s) as shown in Fig. 1 and then the superconducting transition temperature T_{c_1} was defined as follows. At first, T_c at each sample current was determined as the temperature at which the resistance of the sample vanished completely, as can be seen in Fig. 1, and then this T_c was extrapolated to zero sample current in order to obtain T_{c_1}. The superconducting onset temperature (T_{c_2}) is also shown in Fig. 1 and depends very little on I_s.

I_c was measured at 4.2 K without the externally applied magnetic field. I_c was defined as the current where the resistance appeared with increasing I_s and the overall superconducting critical current density (J_c) was calculated by dividing I_c by the average sample cross-sectional area estimated by a weighing method.

3.1.1. Superconducting transition curves

It should be mentioned first that the as-quenched sample showed no superconductivity at 4.2 K. The temperature and the width of the superconducting transition depended strikingly on the ageing conditions. Fig. 2 shows the superconducting transition curves at $I_s = 2$ mA in the Cu–0.30% Nb–0.15% Sn alloy aged isochronally for 192 h. The sample aged at 550° C had the highest T_c and T_c markedly decreased with increasing ageing temperature. The sample aged at 700° C had T_{c_2} as low as 6.3 K and T_{c_1} could not be observed above 4.2 K. When the samples were aged at higher temperatures, i.e. 800° C, no superconductivity was detected at 4.2 K even for short ageing time (4 h).

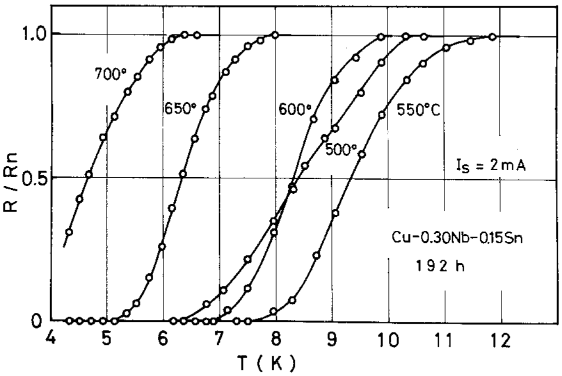

Figure 2 Superconducting transition curve as a function of ageing temperature in the Cu–0.30% Nb–0.15% Sn alloy aged for 192 h.

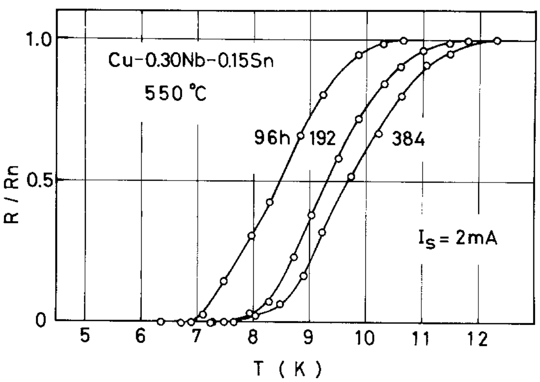

Figure 3 Superconducting transition curve as a function of ageing time in the Cu–0.30% Nb–0.15% Sn alloy aged at 550° C.

Fig. 3 shows the superconducting transition curves in the Cu–0.30% Nb–0.15% Sn alloy aged at 550° C. The highest T_c was obtained when the sample was aged for 384 h, that is, the longest time in this study. Under this ageing condition $T_{c_1} = 8.6$ K and $T_{c_2} = 12.0$ K were obtained, which were the highest values in the present study.

3.1.2. Superconducting critical current density

Fig. 4 shows some typical examples of the resistance (R) as a function of I_s for determining I_c. The sample aged at 800° C was not a superconductor at 4.2 K but the sample aged at 550° C exhibited superconductivity at low I_s as shown in Fig. 4.

The change of J_c with ageing temperature in Cu–0.30% Nb–0.15% Sn alloys aged isochronally is shown in Fig. 5. The change of T_{c_2} is also shown in Fig. 5. In the case of 192 h ageing, the sample

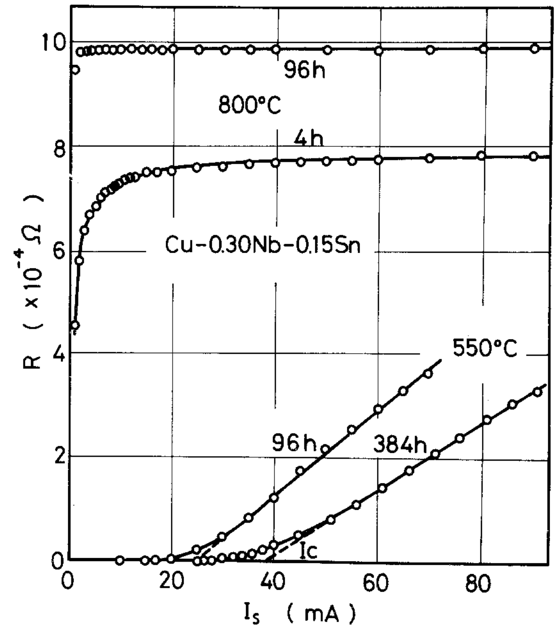

Figure 4 Electrical resistance (R) as a function of sample current (I_S) in the Cu–0.30% Nb–0.15% Sn alloy for determining the critical current (I_c).

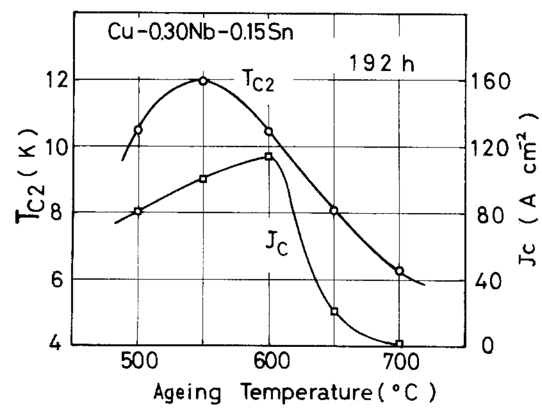

Figure 5 Superconducting transition temperature (T_{c_2}) and critical current density (J_c) as a function of ageing temperature in a Cu–0.30% Nb–0.15% Sn alloy aged for 192 h.

aged at 600° C had the highest J_c, i.e. 115 A cm^{-2}. J_c decreased rapidly with increasing ageing temperature above 650° C.

The highest J_c and T_{c_2} in the present study were obtained under the same ageing condition, namely at 550° C for 384 h, and the highest value of J_c was 130 A cm^{-2}.

3.1.3. Compositional dependence of T_c and J_c

The influence of the alloy composition on T_c and J_c was studied in three Cu–Nb–Sn alloys given

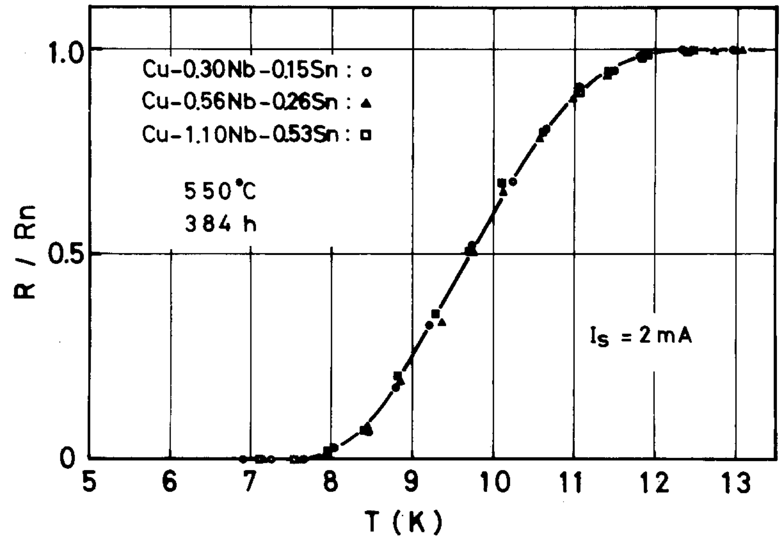

Figure 6 Superconducting transition curve as a function of composition of Cu–Nb–Sn alloys.

in Table I. These alloys were aged at 550° C for 384 h since the best superconducting properties of a Cu–0.30% Nb–0.15% Sn alloy were obtained under these ageing conditions. Fig. 6 shows the superconducting transition curves of these three alloys at $I_s = 2$ mA. There is no dependence of the alloy composition on T_c in the present study, as shown in Fig. 6. J_c also did not depend on the alloy composition.

3.2. Structural observations

The superconducting properties varied with ageing conditions as mentioned above. This is thought to result from the change of the distribution of precipitates by ageing. This explanation became clear from the transmission electron microscope observations.

Electron micrographs of the Cu–0.30% Nb–0.15% Sn alloy are shown in Figs. 7 to 9. Fig. 7 shows the structure of the as-quenched sample in which the very fine precipitates, though they are not so obvious, are observable in the grain and on the grain boundary, but this sample exhibited no superconductivity at 4.2 K. Fig. 8 shows the structure of the coarse precipitates in the sample aged at 800° C for 4 h, which had low T_c and low I_c values ($T_{c_2} = 5.0$ K, $T_{c_1} < 4.2$ K and $I_c = 0$ mA). The precipitates with 0.1 to 0.2 μm diameter exist on the position thought to be the original grain boundaries at the earlier time of

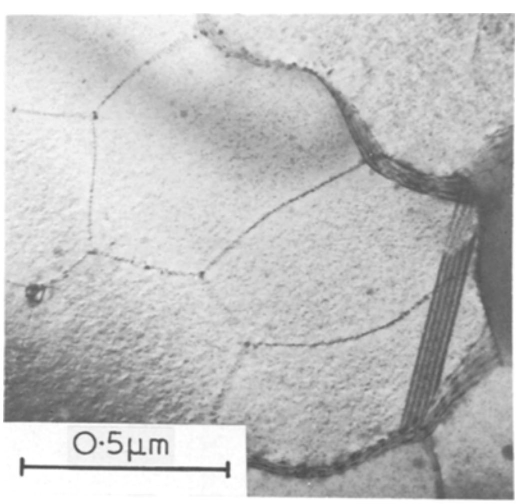

Figure 7 Electron micrograph of the as-quenched Cu–0.30% Nb–0.15% Sn alloy.

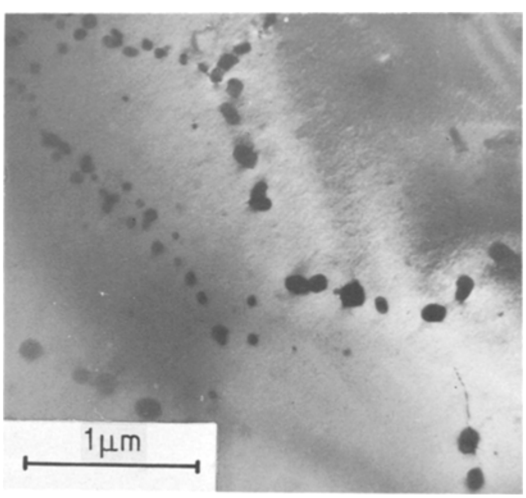

Figure 8 Electron microstructure of the distribution of coarse precipitates in the Cu–0.30% Nb–0.15% Sn alloy aged at 800° C for 4 h.

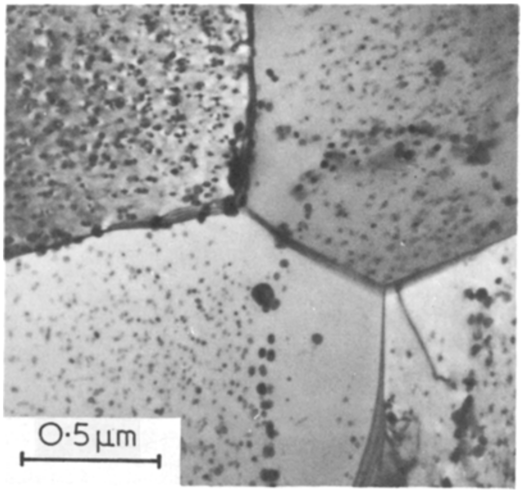

Figure 9 Electron microstructure of the distribution of fine precipitates in the Cu–0.30% Nb–0.15% Sn alloy aged at 550° C for 384 h.

ageing. The spacing of the precipitates is 0.2 to 0.6 µm. Fig. 9 shows the structure of the sample aged at 550° C for 384 h, which showed the best superconducting properties. As shown in Fig. 9, fine precipitates of 200 to 500 Å in diameter are distributed homogeneously with the spacing less than 500 Å. It is thought that this structure is responsible for good superconductivity in the Cu–Nb–Sn alloys. Fig. 10 shows the electron diffraction pattern from the fine precipitates in the Cu–0.30% Nb–0.15% Sn alloy aged at 500° C for 384 h. By analysing this spot pattern, it was concluded that the precipitates were of the A-15 type intermetallic compound Nb_3Sn ($a = 5.2908$ Å).

4. Discussion

The Cu–Nb–Sn alloys containing small amounts of Nb and Sn (less than 1 at %), exhibited superconductivity above 4.2 K after proper ageing and the superconducting properties in these alloys were strongly dependent on the ageing conditions. This suggests that T_c and J_c are closely related to the nature and the distribution, that is, the size and the spacing of the superconducting particles dispersed in the normal Cu matrix.

Let us discuss first the nature of the particles, both in the as-quenched and aged samples. Though there have been a few investigations [15, 16] on the phase diagram of the Cu–Nb–Sn system, the phase diagram of Cu-rich corner is not established yet and therefore the Cu-rich portion of the Cu–Nb binary system [17] is shown in Fig. 11. The very fine particles observed in the as-quenched sample (Fig. 7) are considered to be the Nb particles since Sn easily makes a solid solution with Cu. Although some parts of Nb precipitated during quenching from the liquid state, as shown in Fig. 7, it is thought that Nb is partially retained in the Cu matrix, as expected from Fig. 11. As can be seen in Fig. 10, the electron beam diffraction from the fine precipitates in the sample aged at 550° C for 384 h was identified as the Nb_3Sn intermetallic compound. The volume fraction of precipitates will decrease slightly with increasing ageing temperature as expected from the phase diagram in Fig. 11. The structure difference in the Cu–Nb–Sn alloys aged at 550° C for 384 h with various solute contents could not be made clear by transmission electron microscopy,

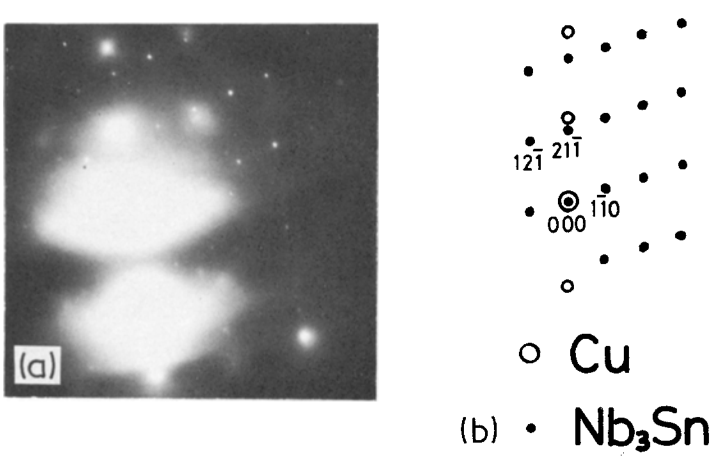

Figure 10 Electron diffraction pattern from fine precipitates in the Cu–0.30% Nb–0.15% Sn alloy aged at 550° C for 384 h. (a) Electron diffraction pattern shows the (1 1 3) reciprocal lattice plane of the Nb_3Sn intermetallic compound. (b) Key diagram of (a).

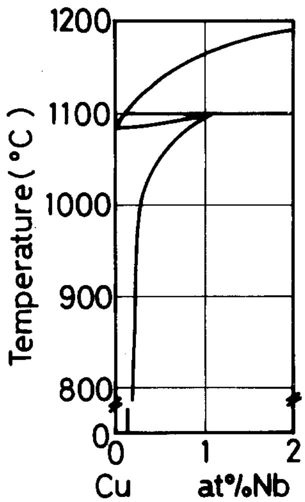

Figure 11 Copper-rich portion of the Cu–Nb phase diagram [17].

and no distinguishable change with composition in the volume fraction of precipitates was observable, irrespective of the phase diagram in Fig. 11. It is considered, however, that some coarse precipitates which we failed to observe might exist in the Cu–Nb–Sn alloy with increasing the solute content. But it did not become clear why the structure and superconducting properties are not dependent on the solute content in this study.

Let us consider, secondly, the intercorrelation between the distribution of Nb_3Sn precipitates and T_c. In the present study, high T_c (= 12 K) was obtained in the sample aged at 550° C for 384 h, and the structure showed that fine Nb_3Sn precipitates of 200 to 300 Å diameter were distributed homogeneously in the Cu matrix, with spacing less than 500 Å (Fig. 9). The sample aged at 800° C for 4 h exhibited a structure of relatively large Nb_3Sn particles of 0.1 to 0.2 μm diameter, precipitated onto the grain boundaries, with spacings of 0.2 to 0.6 μm (Fig. 8), and exhibited low T_c (< 5 K). On the contrary, although, the Cu–0.4 at % Nb alloy [18] prepared by the same method as the present study showed a similar structure to the Cu–0.30% Nb–0.15% Sn alloy when the samples were aged at the same conditions, the Cu–0.4% Nb alloy showed no superconductivity at 4.2 K when aged at 500 to 600° C, but exhibited superconductivity above 4.2 K when aged at 800° C, and the highest T_c, i.e. 5.8 K, was obtained when aged at 800° C for 4 h. Therefore, superconductivity in a Cu–0.4% Nb alloy was thought to result from the superconducting path of the network of the relatively coarse Nb precipitates, i.e. 0.1 to 0.2 μm diameter and 0.2 to 0.6 μm spacing, by the proximity effect [18]. The discrepancy in these alloys implies that the superconducting properties should be discussed with respect to the size and the spacing as well as the nature of the superconducting precipitates.

When the normal metal containing the superconducting particles shows superconductivity by the proximity effect, the relationship between particle size and T_c is deduced by the theory proposed by Silvert *et al.* [9]. This theory predicts that the condition at which superconductivity appears is given by $a > 2.965\xi_0$, where a is the radius of the superconducting particles and ξ_0 is the coherence length of the bulk superconductor. ξ_0 values in Nb and Nb_3Sn are about 400 Å and about 100 Å, respectively [19]. The critical size of the superconducting particles for exhibiting superconductivity is about $6\xi_0$ when the critical particle sizes for the Cu–Nb and the Cu–Nb–Sn alloys become about 2400 Å and about 600 Å, respectively. Our result that superconductivity in the Cu–Nb–Sn alloys is observed at smaller sizes of precipitates compared with the Cu–Nb alloys qualititatively agrees with the theory of Silvert *et al.* and thus the difference in the size of precipitates where superconductivity was observed in the Cu–Nb and the Cu–Nb–Sn alloys is reasonably understood. It should be said that ξ_0 plays an important role in superconductivity by the proximity effect.

The theory of Silvert *et al.* also predicts that T_c approaches that of the bulk superconductor with increasing radius of the superconducting particles. However, the present results show that, although the size of Nb_3Sn precipitates in the Cu–0.30% Nb–0.15% Sn alloy became as large as 0.1 to 0.2 μm, T_c was depressed (Figs. 3, 5 and 8). This suggests that T_c is dependent not only on the size but also on the spacing of the precipitates. The model used by Silvert *et al.* was too simple and did not consider the spacing of the precipitates.

The condition for showing superconductivity for the materials containing the dispersed Nb_3Sn precipitates in the normal Cu matrix, is thought to be that the spacing of Nb_3Sn precipitates must be shorter than the leakage distance of the superconducting Cooper pairs. When a superconducting metal (S) is in contact with a normal metal (N), the superconducting Cooper pairs can leak from S to N [8] and if the coherence length (ξ_N) in N is small compared to the mean free path (l_N) in N, i.e., if the metal N is "clean", the thickness (K^{-1}) of the leakage region on the N side is given by $K^{-1} = \hbar v_F / 2\pi k_B T$, where v_F is the Fermi velocity in a normal metal and others are usual meanings. If $\xi_N > l_N$, i.e., if the metal N is "dirty", the leakage distance (ξ_N) of the pairs is given by $\xi_N = (\hbar v_F l_N / 6\pi k_B T)^{1/2}$. As v_F in Cu is 1.56×10^8 cm sec^{-1}, K^{-1} is a function of temperature (T) alone but ξ_N is a function of T and l_N. Thus, it is important in determining the leakage distance of the pairs to consider whether the normal matrix metal is "clean" or "dirty". Applying this theory to the materials containing the superconducting particles, we can deduce that if the spacing is shorter than $2K^{-1}$ or $2\xi_N$, then the superconducting path will be established by the proximity effect. In the study of a Cu–0.6 at % Nb alloy by Gupta *et al.* [7] the highest T_c was 6.3 K and the corresponding spacing was 0.6 μm. This is in good agreement with the theory as the alloy is supposed to be "clean" and similar results were obtained in a Cu–0.4% Nb alloy [18]. Since Nb is sparingly soluble in the Cu matrix, as can be seen in Fig. 11, it is reasonable to say that the Cu–Nb alloys are "clean". On the other hand, the Cu–Nb–Sn alloys are supposed to be "dirty" due to the following reasons. While the specific resistivity (ρ) of the Cu–0.4% Nb alloy aged at 800° C for 4 h was $5.30 \times 10^{-8}\,\Omega$ cm at 6 K [20], ρ of the aged Cu–0.30% Nb–0.15% Sn alloys was always higher than ρ of the Cu–0.4% Nb alloy, for example, ρ of the sample aged at 550° C for 384 h showing the best superconducting properties in the present study was $2.66 \times 10^{-7}\,\Omega$ cm at 13 K. This is reasonable because Sn is more soluble in Cu than Nb. It is considered therefore that l_N in the Cu–0.30% Nb–0.15% Sn alloy is about one fifth of l_N in the Cu–0.4% Nb alloy since l_N is inversely proportional to ρ. Thus, the Cu–0.30% Nb–0.15% Sn alloy is thought to be "dirty" as are the Cu–V–Ga alloys [20] and ξ_N is therefore dependent on l_N. In consequence, ξ_N of the Cooper pairs from the superconducting particles in the Cu–Nb–Sn alloys is expected to be much shorter than K^{-1} in the Cu–Nb alloys, and therefore the Cu–Nb–Sn alloys lose superconductivity due to the narrow spacing of particles compared with the Cu–Nb alloys.

In the case of 192 h isochronal ageing of the Cu–0.30% Nb–0.15% Sn alloy, the sample aged at 550° C shows the highest T_c (Figs. 2 and 5). It is considered that the increase in T_c with increasing ageing temperature below 550° C is due to the increase in the size of Nb_3Sn precipitates in agreement with the theory by Silvert *et al.* [9], and that the decrease in T_c with increasing ageing temperature above 550° C is the result of increasing the average distance between Nb_3Sn precipitates in spite of the enlargement of Nb_3Sn precipitates with increased ageing temperature.

In the case of the S–N film junction, T_c could be estimated as a function of the thickness of the superconductor by various theories [11, 21–24]. Silvert reported that the evaluation of the dependence of T_c on the thickness of the N metals was difficult [11], and it is not clear therefore whether T_c in our alloys depends on such a parameter as the spacing of the precipitates or not. However, it should be said that the spacing of the precipitates as well as ξ_0, K^{-1} and ξ_N play an important role in superconductivity in materials containing superconducting particles. Thus, the superconductivity in these alloys should be studied further both theoretically and experimentally.

Finally, let us discuss J_c in the Cu–0.30% Nb–0.15% Sn alloy. J_c had stronger dependence on the ageing condition than T_c (Fig. 5). It is said that J_c in the bulk superconductor is very sensitive to the structure of the superconductor [25] but there is no theory predicting J_c in the case of the proximity effect. However, it would be considered that J_c is also dependent of the size, the spacing and ξ_0 of the superconducting precipitates, just as in T_c, and in addition, on the volume fraction of them. Further development is necessary in the theoretical fields.

5. Conclusions

(1) The Cu–Nb–Sn alloys containing small amounts of Nb and Sn quenched from the liquid state and then aged properly, exhibitied superconductivity above 4.2 K.

(2) The superconducting properties were dependent on ageing temperature and time, and the highest T_c ($T_{c_2} = 12$ K and $T_{c_1} = 8.7$ K) and J_c (130 A cm^{-2}) were obtained when the sample was aged at 550° C for 384 h.

(3) This sample showed a structure with fine precipitates of 200 to 500 Å diameter distributed

homogeneously with a spacing of less than 500 Å in the Cu matrix. These precipitates were identified as the Nb_3Sn intermetallic compound by electron beam diffraction.

(4) By comparing the results of the Cu–Nb–Sn alloys and the Cu–Nb alloy [18], the minimum size of precipitates for exhibiting superconductivity was dependent on ξ_0 in accordance with the theory by Silvert *et al.*

(5) Even though the Cu–0.4%Nb alloy and the Cu–0.30%Nb–0.15%Sn alloy showed a similar structure of coarse precipitates and wide spacing when aged at 800° C, the Cu–0.4%Nb alloy exhibited better superconductivity than the Cu–0.30%Nb–0.15%Sn alloy. This would be explained qualitatively by the difference in the mean free path in both alloys.

(6) Superconductivity in the present study is considered to result from the superconducting path of the Nb_3Sn precipitates in the Cu matrix by the proximity effect.

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