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Superconductivity of copper containing small amounts of niobium

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Superconductivity of copper containing small amounts of niobium has been investigated by measuring the electrical resistivity, superconducting volume fraction and by metallographic studies. Small amounts of niobium added to copper has a drastic effect on the low temperature resistivity of the alloys. The annealed alloy $Cu_{99.5}Nb_{0.5}$ shows zero resistance at a current density of 200 A cm^{-2} below 3K. The estimated superconducting volume fraction of this alloy at 2K is about fifty times the physical volume fraction of the Nb in the alloy.

When more Nb is added these effects unexpectedly become much smaller than those observed in the dilute alloys (< 1.5 at. % Nb). Metallographic results indicate that in all the Cu-Nb alloys studied there are two distinct types of Nb particles in the Cu matrix. The large particles (average size $\sim$ 10 μm) randomly distributed in the alloy are probably formed at high temperature when the bulk of the alloy is still in the liquid state. The small Nb particles (size $\leqslant$ 1 μm, interparticle distances < 0.2 μm) probably form through a solid state precipitation. It has been found that the large precipitates are more abundant in the alloy containing more than 1.5 at. % Nb, than in alloys containing less than 1.5 at. % Nb. The observed superconducting properties of alloys $Cu_{99.8}Nb_{0.2}$ and $Cu_{99.5}Nb_{0.5}$ have been attributed to the proximity effect of the small Nb particles whose interparticle distances are compatible with the coherence length in the Cu matrix. The very wide superconducting transition shown in both the resistivity and the inductance measurements suggested a distribution in the Nb particle sizes as well as in the interparticle distances.

1. Introduction

It is well established experimentally that pure copper does not become a superconductor even at the millidegree temperature range [1]. However, if high purity copper is melted in a niobium crucible under a helium atmosphere, the resulting Cu ingot exhibits evidence of superconductivity [2] at about 6 to 8 K. The evidence consisted of observing both the persistent current at a current density about 5A cm^{-2} and the flux quantization, using a Nb-contaminated Cu as part of a superconducting ring. It was uncertain, however, that the observed superconductivity was a bulk effect (i.e. a property of the Cu-Nb solid solution) or was due to the presence of niobium-rich filaments in a Cu matrix. The purpose of the present study is to clarify the nature of the superconductivity observed in the Cu-Nb alloys. A systematic study of Cu-Nb alloys of various compositions was performed by measuring the resistivity and the superconducting transition temperature (inductive method). The structures of some alloys, after various heat treatments, were examined metallographically.

2. Experimental procedure

Alloys of compositions $Cu_{100-x}Nb_x$ in which x = 0.1, 0.2, 0.5, 1.5, 3.0 and 5.0 were prepared by induction melting of the appropriate quantities of the constituents (99.999%-pure Cu and 99.98%-pure Nb) in glassy carbon crucible under an argon atmosphere. The alloys were then cooled slowly in the crucible. The weight losses were less than 0.2% and the nominal compositions of the alloys were taken as the actual ones. After melting, there was a silvery coating on the ingot which was removed by boiling H_2SO_4. The ingot was rolled into an approximately rect-

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angular rod with a 25% reduction in cross-section area. Then it was cut into two pieces which were machined into 2 × 20 mm rods. These two rods were designated as specimens I and II.

Specimen I was etched in dilute nitric acid to reduce its diameter to less than 1 mm. Its electrical resistivity as a function of temperature was measured by using a standard four-probe technique at a current density of about 200 A cm^{-2}. The superconducting transition temperature of the same sample was also measured by a standard a.c. inductance Wheatstone bridge using a PAR lock-in amplifier to detect the imbalance of the bridge. With the lock-in amplifier operating in a linear region, it was found that the bridge output is proportional to the volume of a given superconductor. Based on this fact, the inductance measurement was used to roughly estimate the volume fraction of the sample from which the flux is excluded (hereafter called superconducting volume fraction) by monitoring the amplitude change of the output of the lock-in amplifier in the bridge circuit. This was done by attaching a small piece of pure Nb of known weight (~ 10 mg) to the Cu-Nb sample and measuring the inductance change as a function of temperature. From the weight of the Nb and that of the Cu-Nb sample and from the changes of the bridge output at the superconducting transition temperatures of both the standard Nb and the specimen, the superconducting volume fraction (SVF) of the Cu-Nb alloy can be estimated within 10%.

The rod designated as specimen II was annealed at 800°C for about 2 days, and its diameter was reduced by etching. The resistivity and the superconducting transition temperature were then measured as for specimen I. The same samples were then examined under the optical microscope. For the purpose of comparison, metallographic study was also performed on two alloys (0.5 and 3.0% Nb) in the as-cast condition.

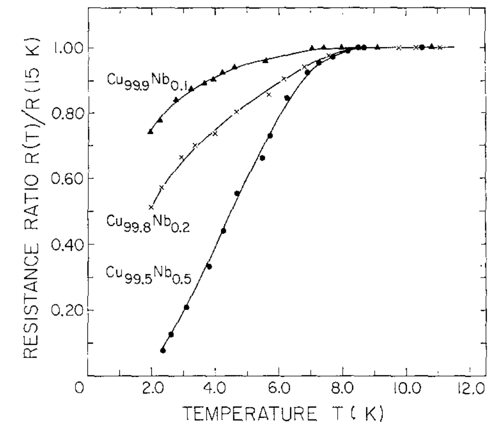

Figure 1 Resistance ratio $R(T)/R\,(T = 15\,K)$ as a function of temperature for copper alloys containing 0.1, 0.2 and 0.5 at. % Nb as-rolled.

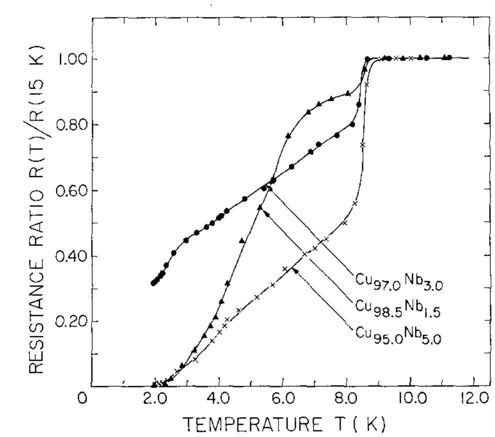

Figure 2 Resistance ratio $R(T)/R\,(T = 15\,K)$ as a function of temperature for copper alloys containing 1.5, 3.0 and 5.0 at. % Nb as-rolled.

3. Results

The values of the resistivity (normalized to those at 15K) are presented in Figs. 1 to 4 as a function of temperature and composition. The results for the as-rolled samples (specimen I) are shown in Figs. 1 and 2 and those for the annealed ones (specimen II) in Figs. 3 and 4. It is remarkable that, at a current density of about 200 A cm^{-2} the annealed $Cu_{99.8}Nb_{0.2}$ and $Cu_{99.5}Nb_{0.5}$ show no electrical resistance below 3K. By no resistance it is meant that the potential drop across a rod ~ 10 × 0.5 mm is less than 10^{-8} V at a current of 0.5 A.

The superconducting volume fraction as a function of temperature can be estimated from the inductance change of samples and the calibration procedure described in Section 2. The results of such measurements are shown in Figs. 5 to 8 for the as-rolled and annealed alloys. From the results shown in Figs. 1 to 8 and the microstructures shown in Fig. 9, the following observations can be made.

1. Small amounts of niobium added to copper has a drastic effect on the low temperature resistivity of the alloys at a current density of

about 200 A cm^{-2}. For the low concentrations, such as $Cu_{100-x}Nb_x$, with $x = 0.1$, 0.2 and 0.5, the low temperature resistivity for $T < 15$K instead of being constant as that of pure copper decreases with decreasing temperature starting at about 8K (Fig. 1). This effect becomes more pronounced with increasing Nb concentration.

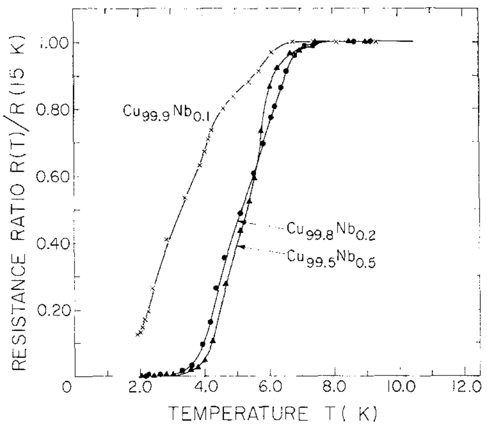

Figure 3 Resistance ratio $R(T)/R$ (T=15K) as a function of temperature for copper alloys containing 0.1, 0.2 and 0.5 at. % Nb after annealing.

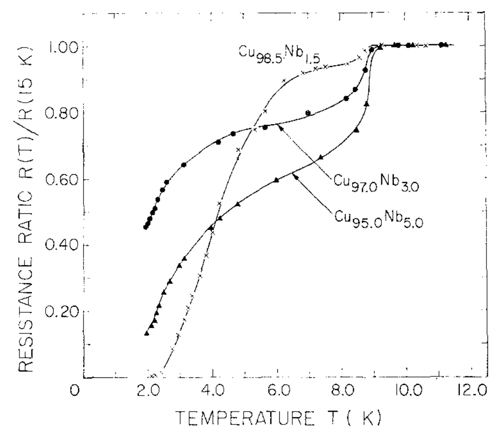

Figure 4 Resistance ratio $R(T)/R$ (T = 15K) as a function of temperature for copper alloys containing 1.5, 3.0 and 5.0 at. % Nb after annealing.

At 2K, the resistivity of the alloy $Cu_{99.5}Nb_{0.9}$ is reduced to about 4% of the resistivity at 15K. This trend is interrupted as more niobium is added to the copper. For alloys with relatively high niobium content,the resistivity as a function of temperature first shows a sharp drop at about 9K, then continues to decrease with decreasing temperature. The data presented in Fig. 2 indicates that the resistivity of the alloys $Cu_{98.5}Nb_{1.5}$ and $Cu_{95.0}Nb_{5.0}$ is nearly zero at 2K. The alloy $Cu_{97.0}Nb_{3.0}$ exhibits a relatively high resistivity at 2K (~ 30% of the resistivity at 15K). This indicates that the effect of adding Nb in Cu on resistivity of the alloys does not depend linearly on concentration.

2. The effect of annealing at 800°C for ~ 2 days on resistivity is shown in Figs. 3 and 4. For the most dilute alloy studied in this investigation, i.e. $Cu_{99.9}Nb_{0.1}$, annealing reduces the resistivity at 2.0K to ~ 10% of its value at 15K. This is to be compared with 75% for the same alloy in the as-rolled state. After annealing both $Cu_{99.8}Nb_{0.2}$ and $Cu_{99.5}Nb_{0.5}$ alloys become superconducting below 3K. As indicated in Fig. 3, the resistivity of the annealed $Cu_{99.5}Nb_{0.5}$ decreases with decreasing temperature at a faster rate than that of the annealed $Cu_{99.8}Nb_{0.2}$. The effect of annealing on the resistivity of the alloys with higher Nb concentration is manifested in two aspects: (a) the magnitude of the resistivity drop around 9K is

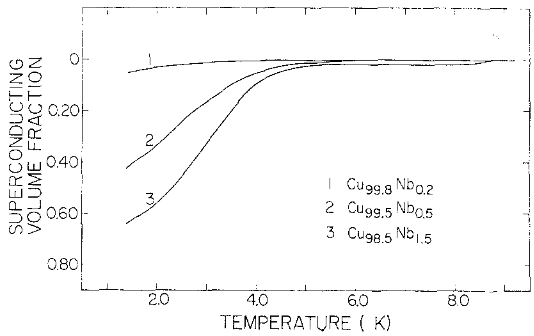

Figure 5 Estimated superconducting volume fraction as a function of temperature for copper alloys containing 0.2, 0.5 and 1.5 at. % Nb as-rolled.

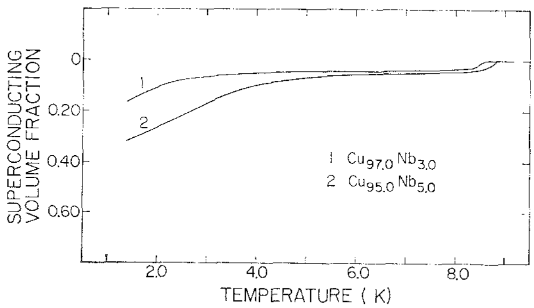

Figure 6 Estimated superconducting volume fraction as a function of temperature for copper alloys containing 3.0 and 5.0 at. % Nb as-rolled.

reduced; (b) below 8 K, the rate of decrease in resistivity is lower than that of the as-rolled samples. This effect, however, is less pronounced for the alloy $Cu_{98.5}Nb_{1.5}$.

3. From the results presented in Figs. 5 to 8, the estimated superconducting volume fraction (SVF) of the Cu-Nb alloys studied as a function of temperature is in general consistent with the results of the resistivity measurement. At low concentration, i.e. for alloys $Cu_{100-x}Nb_x$, with $x = 0.1, 0.2, 0.5$ and 1.5, the SVF increases with increasing Nb content for both the as-rolled and the annealed samples.

It should be noticed that the magnitude of the SVF shown by these alloys is about fifty times the physical volume fraction of niobium. For example, in the alloy $Cu_{99.5}Nb_{0.5}$, Nb would occupy at most $\sim 0.75\%$ of the total volume if all the Nb is assumed to be present as a second phase in the Cu matrix. The data shown in Fig. 7 indicate a superconducting volume fraction of about 50% at 2 K. The alloys containing higher Nb concentrations, i.e. $Cu_{100-x}Nb_x$, $x = 3$ and 5, show a relatively small SVF as compared with that in alloys $Cu_{99.5}Nb_{0.5}$ and $Cu_{98.5}Nb_{1.5}$. At about 9 K a step-like increase in SVF has been observed for alloys $Cu_{100-x}Nb_x$, with $x = 1.5$, 3, and 5. This corresponds to the resistivity drop at the same temperature as shown in Figs. 2 and 4. For a typical annealed $Cu_{97.0}Nb_{3.0}$, the initial increase of SVF is about 3%. At about 1.5 K, the SVF of the same alloy increases to about 35%. It has been found that annealed samples generally exhibit a larger SVF than rolled ones.

4. The metallographic results as shown in Figs. 9a to b, indicate that there are two distinct types of precipitates in the Cu-matrix. The large precipitates (average size ~ 10 μm) randomly distributed in the alloy are probably formed at high temperature when the bulk of the alloy is still in the liquid state. The small precipitates that are visible under the magnification used ($\times$ 750) appear to be discrete particles of average size < 1 μm. It is probable that there are even smaller size particles in between these relatively small precipitates. It is to be noted that the smaller precipitates tend to form along grain boundaries and probably result from solid state precipitation. As shown in Fig. 9b, the effect of cold rolling the $Cu_{99.5}Nb_{0.5}$ alloy is to align the precipitates in the rolling direction and the average interparticle distance along a line is about 0.2 μm. It has been found also that the large precipitates are more abundant in alloys containing more than 1.5 at. % Nb than in alloys containing less than 1.5 at. % Nb, and the reverse is true for small precipitates.

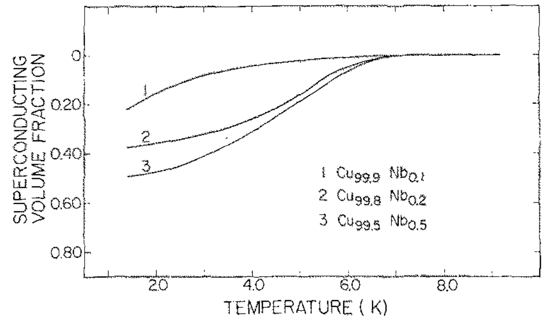

Figure 7 Estimated superconducting volume fraction as a function of temperature for copper alloys containing 0.1, 0.2 and 0.5 at. % Nb after annealing.

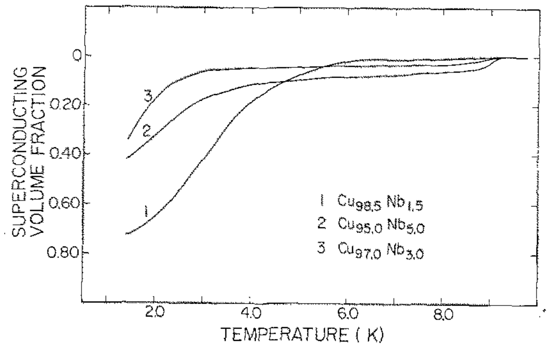

Figure 8 Estimated superconducting volume fraction as a function of temperature for copper alloys containing 1.5, 3.0 and 5.0 at. % Nb after annealing.

4. Discussion

In interpreting the experimental results obtained in this investigation, it is necessary to know the phase diagram of the Cu-Nb alloys. The most complete investigation of this phase diagram was published by Popov and Shiryaeva [3]. Their paper contains more information than is shown in the diagram given in [4] which is somewhat confusing since the horizontal phase boundary line at 1550°C does not satisfy the phase rule. All the data points reported in Tables in [3] are shown in Figs. 10 and 11, and the phase boundaries have been traced in accordance with these data points. A two-liquid phase field between about 20 and 33 at. % Nb has been included as suggested in [3], and by doing so the phase rule is satisfied. The copper-rich side of the diagram is

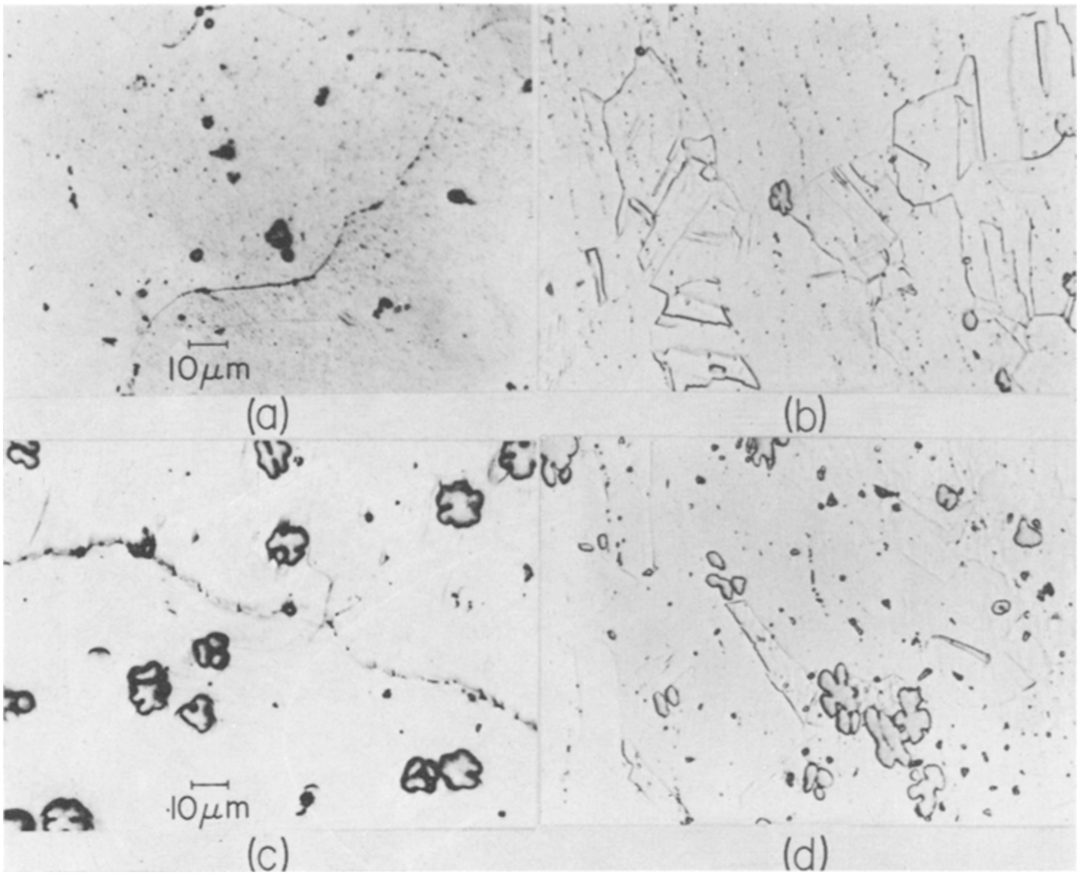

Figure 9 Photomicrographs of copper-niobium alloys; (a) 0.5 at. % Nb as-cast, (b) 0.5 at. % Nb after annealing, (c) 3.0 at. % Nb as-cast, (d) 3.0 at. % Nb after annealing.

rather well documented as shown in Fig. 10 and the solubility of Nb in Cu is less than 1 at. % just below 1100° C. This solubility decreases very fast with decreasing temperature, and the room temperature solubility is estimated to be about 0.10 at. %. In alloys cooled at rates in the range of those used in this investigation, the solubility is probably about 0.15 at. %.

The phase boundaries on the Nb rich side of the diagram are very poorly known. The boundaries shown in [3] and reproduced in [4] (curve 1 in Fig. 11) are not based on any data points. The solubility of Cu and Nb deduced from a microstructure examination [5] and from electrical resistivity measurements [6] would be 0.07 at. % at 1000° C. Possible phase boundaries consistent with this low solubility are shown by curves 2 and 3 in Fig. 11.

In summary, the data shown in the phase diagram indicate that at room temperature, the solubility of Nb in Cu (α solid solution) is limited to less than 0.10 at. % Nb and that Cu is almost insoluble in Nb. In equilibrium, the alloys containing more than 0.15 at. % Nb at room temperature should consist of two phases, Cu-rich α solid solution and Nb-rich solid solution containing less than 0.07 at. % Cu.

The microstructures observed in this work are consistent with the phase diagram shown in Fig. 10. The large particles can be identified as primary niobium crystallized above the peritectic temperature. In view of the fact that the alloys were in non-equilibrium conditions during cooling from the liquid state, it may be energetically favourable to form large particles for the alloys with higher Nb-content (> 1 at. % Nb), thus reducing the quantity of secondary precipitates.

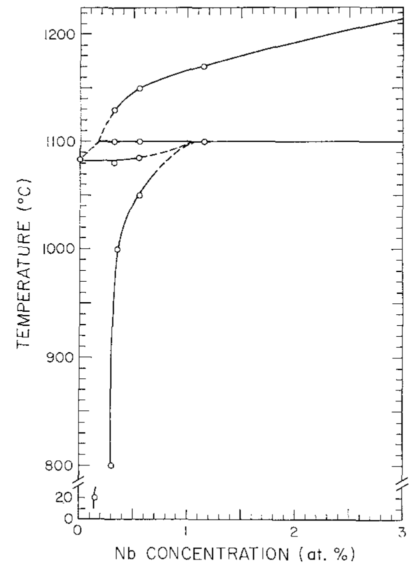

Figure 10 Copper rich portion of the Cu-Nb phase diagram. The data points are from [3].

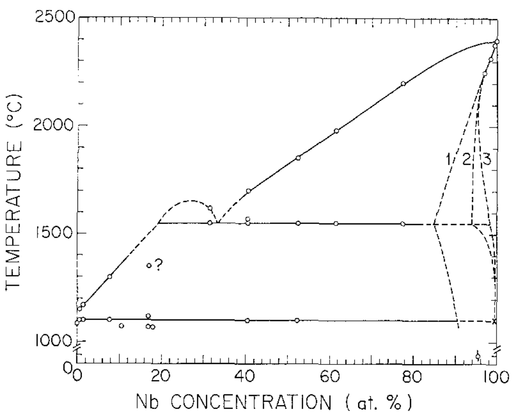

Figure 11 Cu-Nb phase diagram .The data points shown by (○) are from [3]. Three possible phase boundary lines are shown on the Nb rich side of the diagram and are explained in the text.

It is clear from the results presented in the previous section that any possible mechanism responsible for the superconducting properties observed in the Cu-Nb alloys, should account for the very large superconducting volume fraction for alloys containing less than 1.5 at. % Nb. In addition, the mechanism should also explain the disappearance of resistivity in $Cu_{99.8}Nb_{0.2}$ and $Cu_{99.5}Nb_{0.5}$ alloys below 3K. Four possible mechanisms to explain these experimental results are discussed.

1. The superconductivity observed may be due to the Nb dissolved in Cu (i.e. α solid solution). In view of the small solubility of Nb in Cu, it is unreasonable to expect this to be the cause of superconductivity. Furthermore, this mechanism cannot explain why an alloy like $Cu_{97.0}Nb_{3.0}$ would not be superconducting to at least the same extent as $Cu_{99.5}Nb_{0.5}$. Another evidence which is against this mechanism is that $Cu_{99.8}Nb_{0.2}$ alloy rapidly quenched from the liquid state [7] at a rate of $\sim 10^5$°C sec^{-1} remains normal at 1.5K.

2. The niobium may form a layer on the surface of the copper-rich grains. To be superconducting at $\sim$ 4K, the layer has to be about 100Å thick [8, 9]. If a typical grain size of 20 μm is assumed, then a simple calculation indicates that the amount of Nb needed to build such a layer is at least a few per cent. In addition, part of the Nb is already present as precipitates and there is simply not enough Nb to form such a superconducting layer in the dilute alloys $Cu_{99.8}Nb_{0.2}$ and $Cu_{99.5}Nb_{0.5}$. The Nb layer formed on grains can then be ruled out as a mechanism for superconductivity.

3. The Nb may form filaments and hence provide a continuous superconducting path. This is unlikely because first, there is no metallographic evidence for the existence of filaments, and second, the filaments mechanism would not explain the large superconducting volume observed.

4. The proximity effect of the discrete Nb particles embedded in the Cu matrix gives rise to the superconductivity observed. The metallographic results (as shown in Fig. 9b) definitely confirm the existence of discrete particles, and these particles can be identified as essentially Nb particles according to the phase diagram. It is reasonable to assume that there is a distribution of particle sizes ranging from the relatively large size visible in Figs. 9a and b (lesss than 1 μm) to submicroscopic size not observed with light microscopy. In addition, there is a distribution of interparticle distances ranging from zero to few μm. In view of the probable distribution of the superconducting Nb particles just described, it is clear that the infinite conductivity observed in $Cu_{99.8}Nb_{0.2}$ and $Cu_{99.5}Nb_{0.5}$ alloys can result from the leakage of Cooper pairs in Nb particles in the Cu-matrix. The average interparticle distance must be comparable with the coherence length (of the order of 1000Å) so that the Cooper pairs form a continuous path for superconduct-

ivity. The mechanism of proximity effect also explains the large superconducting volume as suggested by the inductance bridge measurements. The very wide superconducting transition shown in both the resistivity and the inductance measurements is consistent with the effect of a distribution of particle sizes as well as inter-particle distances. The larger Nb particles contained in alloys $Cu_{97.0}Nb_{3.0}$ and $Cu_{95.0}Nb_{5.0}$ are typically 10 μm in diameter. It is expected that these Nb particles supercoduct at about the same temperature as bulk Nb [8, 10]. The interparticle distances (about 10 to 30 μm) are of the order of 100 times a typical coherence length. This definitely precludes the possibility of forming a superconducting path through the proximity effect of these particles. The effect of these superconducting particles (for $T < 9$ K) on the resistivity of the bulk alloy can be understood by considering the resistivity of an ideal system consisting of small, well-separated spheres of second phase (i.e. Nb) uniformly embedded in a metallic matrix (i.e. Cu). The resistivity of the alloy can be written approximately as [11]:

$$\rho_{\text{alloy}} = \frac{\rho_{\text{Cu}}[1 - f(\rho_{\text{Cu}} - \rho_{\text{Nb}})/(\rho_{\text{Cu}} + 2\rho_{\text{Nb}})]}{1 + 2f[(\rho_{\text{Cu}} - \rho_{\text{Nb}})/(\rho_{\text{Cu}} + 2\rho_{\text{Nb}})]} \tag{1}$$

where ρ_{Cu}, and ρ_{Nb} are the resistivities of the matrix Cu and the second phase Nb, and f is the volume fraction of the second phase. In the limiting case, when the particles become superconducting below the transition temperature, i.e. $\rho_{\text{Nb}} = 0$, Equation 1 can be approximated by the following expression:

$$\rho_{\text{alloy}} \cong \rho_{\text{Cu}}(1 - 3f). \tag{2}$$

As shown in Fig. 8, the superconducting volume fraction of $Cu_{97.0}Nb_{3.0}$ near 9K is about 3% (i.e. $f = 0.03$). Then, the resistivity at about 9K would be reduced by a factor of $3f \cong 9\%$ which is about the right order of magnitude as indicated by the resistivity measurements (Fig. 4). Similarly for the case of $Nb_{5.0}Cu_{95.0}$, f is about 0.06 at 8.5K, and the resistivity should decrease by $\sim 3f = 18\%$ according to Equation 2. This is again approximately in agreement with the results of resistivity measurements (Fig. 8). In view of the approximations made in the above discussion, a quantitative agreement is not expected. This kind of analysis does indicate that if the superconducting particles are distributed far apart (i.e. interparticle distance is larger than the coherence length) the effect of the particles would reduce the resistivity according to Equation 2. This conclusively demonstrates the need for a mechanism such as the proximity effect to explain the superconductivity of the alloys $Cu_{99.8}Nb_{0.2}$ and $Cu_{99.5}Nb_{0.5}$. In terms of this mechanism, the effect of annealing on the superconducting properties as shown in Figs. 3, 4, 7 and 8 can be understood as follows. Annealing at 800°C for ~ 2 days results in recrystallization, a relatively larger mean free path which can enhance the proximity effect. For alloys containing less than 1 at.% Nb, supersaturated α solid solution retained by cooling from the liquid state could precipitate more fine Nb particles during annealing. This effect also can lead to a sharper superconducting transition and a larger superconducting volume. On the other hand, it is possible that prolonged annealing at 800°C or higher can cause the very fine Nb precipitation to coalesce and grow in size. This effect would tend to increase the superconducting transition temperature of the individual Nb particles. If the interparticle distances become significantly large as a result of coalescing, the proximity effect would be reduced. Diffusion between Nb and Cu during annealing could reduce the proximity effect. Judging from the results, this effect is not significant probably because of the near zero solubility of Cu and Nb at 800°C. From Figs. 9c and d, it can be seen that the size of the large Nb particles is reduced and the number of smaller Nb particles is increased after annealing. These smaller particles probably do not contribute significantly to the superconductivity because of their relatively large interparticle distances (typically $\sim$ 5000Å). The reduction in size of the larger Nb particles as a result of annealing is consistent with the observation that in the annealed samples the magnitude of the first resistivity drop at $\sim$ 9°K is reduced.

Superconducting proximity effect has been studied in the form of superimposed films of a superconductor and a normal conductor [12]. Previous work indicates that spurious effects can result from an insulating oxide layer or poor electrical contact between the superconducting and normal films. The present alloys should be free from these difficulties.

The magnetic properties of the Cu-Nb alloys have not been studied in this work. The magnetic properties of a superconductor film are greatly modified by the proximity effect of normal metal [12], and similar effects can be expected in the present alloys. In these alloys, it should be of interest to find out how a distribution of superconducting particle sizes and interparticle distances will modify the magnetic properties. A measurement of critical field as a function of temperature should be particularly interesting in view of a recent unusual prediction that some system consisting of superconducting spheres dispersed through a metal matrix may exhibit multiple transition temperatures [13]. Such an effect, if it exists, should have been observed in the measurements of superconducting volume fraction by the inductance bridge technique. A close examination of the experimental results obtained in this investigation have failed to show any evidence of this effect.

Near the transition temperature, the specific heat of superconducting particles distributed in a metal is certainly affected by the proximity effect. As pointed out by Fulde and Moormann [14], the specific heat jump is a sensitive measure of the proximity effect. Therefore, a comparison between the specific heat of Cu-Nb alloys and that of bulk Nb should yield some valuable information concerning the proximity effect. A programme of measuring the magnetic properties and the specific heat of Cu-Nb alloys is in progress.

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References

1. N. KURTI and F. SIMON, *Pric. Roy. Soc. (London)* **A151** (1935) 610.
2. R. H. BORCHERTS and A. H. SILVER, Bulletin of the *Amer. Phys. Soc.* **13** (1968) 379. To the knowledge of the authors, the detailed results of this work have not been published.
3. I. A. POPOV and N. V. SHIRYAEVA, *Russ. J. Inorg. Chem.* **6** (1961) 1184.
4. R. P. ELLIOTT, "Constitution of Binary Alloys", First Supplement (McGraw-Hill, New York, 1965) p. 253.
5. B. B. ARGENT and R. E. GOOSEY, private communication to G. L. Miller, "Tantalum and Niobium' (Academic Press, New York, 1959) pp. 566-67.
6. R. KIEFFER and H. NOWOTNY, *Metall.* **17** (1963) 669.
7. P. DUWEZ and R. H. WILLENS, *Trans. AIME* **227** (1962) 362.
8. C. J. KIRCHER, *Phys. Rev.* **168** (1968) 437.
9. P. HILSCH, *Z. Physik* **167** (1962) 511.
10. H. E. CLINE, B. P. STRAUSS, R. M. ROSE, and J. WULFF, *J. Appl. Phys.* **37** (1966) 5.
11. J. C. MAXWELL, "A Treatise on Electricity and Magnetism" 3rd Edn. (Dover Publications, New York, 1954).
12. G. DEUTSCHER and P. G. DE GENNES, Chapter 17, "Proximity Effects in Superconductivity", Vol. 2, ed. by R. D. Parks (Dekker, New York, 1970) p. 1005.
13. WILLIAM SILVERT and AMRENDRA SINGH, *Phys. Rev. Letters* **28** (1972) 222.
14. P. FULDE and W. MOORMANN, *Physik Kondensierten Materie* **6** (1967) 403.

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