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Ductile Superconducting Copper-Base Alloys

Abstract. *A new class of ductile superconductors has been prepared by casting and appropriate heat treatments. These alloys superconduct between 4° and 18°K and contain at least 90 atom percent copper and a superconducting phase such as Nb_3Sn or niobium. They can be processed into wires by conventional metallurgical techniques.*

Ductile superconducting materials are essential in many engineering applications, such as superconducting magnets, power transmission lines, motors, and generators (*1*). The superconducting materials used in these applications should have a reasonably high transition temperature, a high critical field, and a high critical current density. They should be easy to manufacture and inexpensive. Furthermore, they should exhibit high thermal stability under the influence of high magnetic field and current density. I report here a new class of ductile superconducting alloys, the members of which are composed primarily of a ductile metal such as Cu with a small amount of some superconducting element such as Nb or Sn. These alloys can be cast into ingots and processed by conventional metallurgical techniques. Typical examples are $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ and $Cu_{90}V_{7.5}Si_{2.5}$ (the subscripts represent atom percentages). These ductile alloys are superconducting at a temperature between 4° and 18°K (the superconducting temperature depends on the alloy composition and the heat treatment). Preliminary experiments indicate that they are high-field superconductors and can be manufactured into wires (~0.2 mm in diameter) or sheets (0.2 mm thick) on a mass production scale and at a cost comparable to that of ordinary copper wires.

The alloys were prepared by the induction melting of the appropriate quantities of the constituents in a water-cooled silver boat (*2*) in an argon atmosphere. The alloys were melted several times and were then cooled at a rate of about 100°C/sec in the silver boat. The as-cast ingot is ductile enough to be rolled into wires with a cross section of 1 by 1 mm. For some of the alloys, an appropriate heat treatment is necessary to increase and sharpen the superconducting transition temperature. The heat treatment varies from alloy to alloy, and usually consists of annealing in a vacuum at a temperature between 500° and 900°C for from a few hours to a few days. For example, the alloy $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ with a superconducting transition temperature (T_c) of about 12°K was annealed at 600°C for 2.5 days or at 800°C for 5 hours. I determined the T_c by measuring the electrical resistivity as a function of temperature with a standard four-probe technique. The criterion for superconductivity is that the potential drop across a 15-mm length of a specimen 0.5 by 0.5 mm is less than 10^{-8} volt at a current of 100 ma. This corresponds to an upper bound in resistivity of about 10^{-10} ohm-cm. Typical results of the resistivity measurements on two Cu-Nb-Sn alloys are shown in Fig. 1. It is apparent that the resistive superconducting transition is affected by rolling, annealing, and the addition of a small amount of P. On the basis of these results, the following statements can be made:

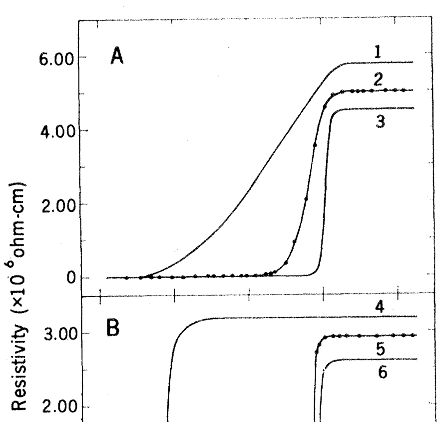

Fig. 1. Electrical resistivity as a function of temperature for two alloys of different compositions: (A) alloy $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ as cast (curve 1), rolled (curve 2), and doped with less than 0.1 atom percent P and then rolled (curve 3) (all alloys were annealed at 800°C for 5 hours); (B) alloy $Cu_{93.5}Nb_{5.0}Sn_{1.5}$ as rolled (curve 4), and then annealed at 800°C for 2 hours (curve 5) and 6 hours (curve 6).

1) A resistive superconducting state has been observed in all the new alloys.

2) If the alloy is first rolled and then annealed, the superconducting transition is sharpened. For instance, the resistivity of the $Cu_{93.0}$-$Nb_{5.0}Sn_{2.0}$ alloy cast and then annealed at 800°C for 5 hours starts to decrease at 17.5°K, and a complete superconducting state is reached at about 5°K (Fig. 1, curve 1). The rolled sample heat-treated in the same manner becomes superconducting around 12°K (Fig. 1, curve 2).

3) The addition of a small amount of P (< 0.1 atom percent) results in an increase in T_c and a sharper transition. As shown in Fig. 1, curve 3, the T_c of the $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ alloy containing less than 0.1 atom percent of P is increased to 15.5°K and the transition is only 1.5°K wide.

4) The effect of annealing at a given temperature for different lengths of time is shown in Fig. 1, curves 4–6, for the $Cu_{93.5}Nb_{5.0}Sn_{1.5}$ alloy. The as-rolled sample superconducts at 6.5°K. The superconducting transition temperature of the same alloy can be increased to 12°K by annealing at 800°C for 2 hours and to 15°K by annealing at 800°C for 6 hours. Moreover, the ratio of Nb to Sn does not always

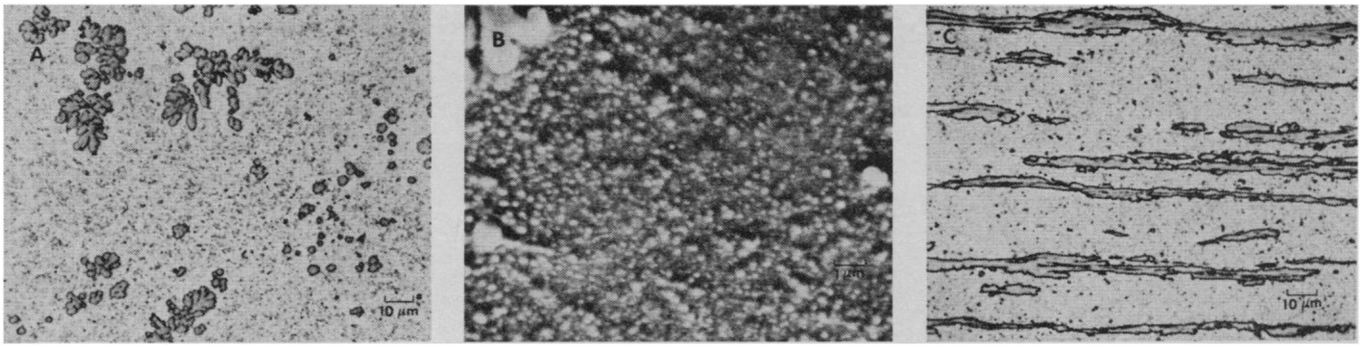

Fig. 2. (A) Photomicrograph of the $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ alloy cast and annealed at 800°C for 5 hours. (B) Scanning electron micrograph of the sample shown in (A). (C) Photomicrograph of the $Cu_{93.0}N_{5.0}Sn_{2.0}$ alloy rolled and annealed at 800°C for 5 hours. A small amount of P (< 0.1 atom percent) was added to this alloy.

correspond to that found in the compound Nb_3Sn and can be varied within certain limits without destroying the superconducting transition.

In an effort to understand the results described above, I carried out x-ray diffraction measurements and a microstructure study. The x-ray diffraction patterns of all the alloys show a predominant face-centered cubic Cu-rich phase ($a = 3.630 \pm 0.005$ Å), a lesser body-centered cubic Nb phase ($a = 3.30 \pm 0.01$ Å), and a Nb_3Sn phase ("βW" or A-15 structure, $a = 5.29 \pm 0.01$ Å). The Nb_3Sn phase is barely detectable in the as-rolled samples. The annealing of rolled alloys results in a decrease in the intensity of the Nb diffraction pattern and an increase in the intensity of the Nb_3Sn phase. In short, the "βW" compound Nb_3Sn is formed in the Cu matrix through a selective diffusion process during annealing.

The microstructures of these alloys (Fig. 2, A–C) bear a close resemblance to those of Cu-Nb (*3, 4*) and Cu-Nb-Al (*4*) alloys. Therefore, it can be concluded, as in (*3, 4*), that the Nb precipitates in the samples which are not cold-worked are distributed randomly in the Cu matrix in two forms: (i) the dendritic particles (average size, 20 μm) are formed at high temperature when the bulk of the alloy is still in the liquid state (Fig. 2A) and (ii) the fine particles of Nb (average particle size, ~ 1500 Å) are formed by precipitation in the solid state. The distance between neighboring precipitates ranges from almost zero to ~ 5000 Å. The Nb_3Sn phase formed during annealing is probably located on the boundary between the Nb and Cu phases. Rolling elongates and aligns the Nb particles in the rolling direction. In the rolled sample, as shown in Fig. 2C, these particles are deformed to needle-like filaments and are practically continuous.

In view of the structural findings, the results of the resistivity measurements can be understood as follows. The superconducting state of the cast $Cu_{93.0}Nb_{5.0}Sn_{2.0}$ alloy annealed at 800°C for 5 hours can be attributed to the proximity effect (*5*) of the superconducting particles whose closest interparticle distances are compatible with the coherence length (ξ_N) in the Cu matrix. In order for the proximity effect to be a plausible mechanism for the observed superconductivity, the average interparticle distances must be short enough to form a superconducting path through the proximity effect. A lower bound of ξ_N can be estimated from the value of the resistivity at a temperature just above the onset of superconductivity. In this alloy ξ_N is of the order of 1000 Å at 4.2°K (*6*). Therefore, the average interparticle distances shown in Fig. 2, A and B, are short enough so that the proximity effect is a satisfactory explanation. The unusually broad superconducting transition (~ 12°K wide) indicated by resistivity measurements is consistent with a wide distribution of precipitate sizes and the interparticle distances.

In the rolled and annealed samples, the superconducting filaments are continuous. Therefore, the filamentary effect becomes important, T_c is increased, and the transition is sharpened. It is not well understood how the presence of a small amount of P improves the superconducting properties. One possible explanation is that P acts as a deoxidizer and prevents an oxide layer from forming around the precipitates, thus enhancing the diffusion of Nb and Sn.

In preliminary experiments the critical current density (J_c) of these new alloys at zero magnetic field and their transverse critical field at low current density (~ 30 amp/cm^2) were measured. It was found that J_c is of the order of 10^3 to 10^4 amp/cm^2. Since J_c is a structure-sensitive property, a systematic study of the heat treatment variables, the amount of cold rolling, and the amounts of impurities added may make it possible to increase J_c to 10^6 amp/cm^2 or even higher. Furthermore, the effect of high magnetic fields on J_c requires a detailed study. The critical field measurements indicate that, at 4.2°K, the resistive superconducting state is not affected by a transverse magnetic field of ~ 50 kilogauss. In view of the findings in Cu-Nb alloys (*4*), the critical field of this new class of alloys should be at least equal to that of Nb_3Sn (that is, ~ 200 kilogauss). Because of the high proportion of Cu relative to the superconducting phase, and because of the excellent bond between these two phases, the alloys described in this report are expected to have a high degree of thermal and mechanical stability at high current density and high field. In addition, the estimated cost of wires made from these alloys should be about two orders of magnitude less than that of the composite superconductors now on the market.

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6. The details of this kind of estimate are discussed in (*4*).
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