Influence of Cold Work on the Resistivity of Dilute Copper Alloys

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Measurements are reported of the residual electrical resistivity of a copper plus 1 atomic percent antimony alloy which had been cast and rolled. A large *increase* was observed on annealing, as noted by Kropschot, Garber, and Blatt. However, metallographic examination and the smallness of the change observed on subsequent rerolling suggest that their proposed mechanism of "migration" during cold work plays a much smaller part than lack of homogeneity in the cast alloy.

RECENTLY Kropschot, Garber, and Blatt[1] reported preliminary results of measurements of the electrical resistivity of dilute copper alloys, showing the changes in residual resistivity (measured at 4.2°K) observed on annealing cold-worked specimens of pure copper and of copper containing one atomic percent of the various solutes germanium, indium, tin, and antimony. For the alloys they observed quite large *increases* in resistivity on annealing, the increase being most pronounced for CuSb, which after casting and rolling gave a residual resistivity $\rho_0 \simeq 1.3\,\mu$ ohm-cm and on subsequent annealing gave $\rho_0 = 4.0$ to $4.3\,\mu$ ohm-cm.

For rather pure specimens of metallic elements, it is expected and indeed observed that annealing *decreases* the resistivity due to the removal of vacancies, dislocations, etc., and in many alloys a similar small decrease has been observed (see review by Gerritsen[2]). However in a few instances alloys[3] have been reported to show a contrasting small increase during annealing due, perhaps, to change in short-range order. In the case of the dilute copper alloys, Kropschot et al. suggested that the rather large change was a result of the generation of vacancies during cold work, these vacancies being sufficiently mobile at room temperature to aid the diffusion of solute atoms which would be ultimately trapped at the dislocation lines; on annealing, these atoms would be freed to distribute themselves uniformly through the solvent and enhance the resistivity.

It seemed to us improbable that changes due to this mechanism would be as large as those observed in CuSb; the density of solute atoms at the dislocations would need to be unduly high and a lack of homogeneity in the original ingot seemed a more likely explanation. Hence, we were led to re-examine the electrical resistivity of a CuSb alloy and to include observations of thermal conductivity and the effect of rerolling. If the mechanism suggested by Kropschot et al. were correct, rerolling the annealed specimen should decrease the resistivity again, while data on the lattice thermal conductivity might reveal information about the distribution of the scattering centers.

Copper plus one atomic percent antimony specimens were made by induction melting a small charge of 99.99+% pure copper ("freezing-point" copper from the National Bureau of Standards, for which annealed test strips showed a resistance ratio $\rho_0/\rho_{293} \simeq 2\times10^{-3}$) and 99.999_5% pure antimony (JM6639) sealed in an evacuated silica tube. The cylindrical ingot of about 8-mm diameter was rolled to form a bar of cross section about 16 mm² (specimen No. 1), then annealed in a clean helium atmosphere by raising the temperature to 600°C, then raised further at a rate of 50°C per day to 940°C and maintained at this temperature for about 2 days (No. 2 specimen). It was later rerolled to form a bar of about 6 mm² cross section (No. 3). On the specimens Nos. 1, 2, and 3 values of electrical resistivity at temperatures between 2°K and 300°K, and values of thermal conductivity between 2°K and 90°K were obtained by methods described previously.[4] The electrical data in Table I indicate that a substantial increase in residual resistivity occurred on annealing, as noted by Kropschot et al. but any change on subsequent rerolling was only comparable with the experimental error involved in determining the geometry and using the galvanometer amplifier. Values of ρ_0 for Nos. 2 and 3 correspond closely to the figure of $5.4\,\mu$ ohm-cm per atomic percent of antimony in copper, found by Linde (see reference 2).

The specimens were later electrolytically polished and examined under a metallographic microscope. CuSb No. 2 and No. 3 both seemed of quite uniform α phase (cubic phase) with slight evidence of "equilibrium segre-

TABLE I. Electrical resistivities of CuSb specimens in μ ohm-cm units.

	$\rho_0 \equiv \rho_{4.2}$	$\rho_{90}-\rho_0$	$\rho_{293}-\rho_0$
No. 1 (cold worked)	3.07	0.51	2.34
No. 2 (annealed)	5.29	0.38	1.88
No. 3 (cold worked)	5.23	0.40	1.96
Pure copper[a]	$\sim10^{-3}$	0.28	1.68

[a] See reference 4.

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[1] R. H. Kropschot, M. Garber, and F. J. Blatt, Phys. Rev. Letters **2**, 91 (1959).

[2] A. N. Gerritsen, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 137.

[3] J. O. Linde, Appl. Sci. Research **B4**, 73 (1956).

[4] G. K. White, *Experimental Techniques in Low-Temperature Physics* (Oxford University Press, New York, 1959), p. 157.

gation" (McLean[5]) at the grain boundaries, i.e., they showed variations in the degree of etching at the boundaries consistent with the mechanism proposed by McLean to explain embrittlement in copper-antimony alloys. By contrast, specimen No. 1 showed considerable coring of the α phase. These enriched areas of α phase and also ϵ phase[6] (hexagonal phase) regions were shown much more clearly in another specimen which was cast and inadvertently "homogenized" by heating for 48 hours at 1050°C. This latter specimen was quite brittle, the ϵ phase was distributed along grain boundaries and was surrounded by areas of enriched α phase which etched much more rapidly than the central areas of the grain.

The specimen No. 1 also showed the most pronounced departures of its electrical resistance from Matthiessen's rule, as judged by the deviations of values of $\rho_T-\rho_0$ from the value for pure copper (Table I).

Values of lattice thermal conductivity, λ_g, were deduced from the observed total thermal conductivity (e.g., see Klemens[7] and Kemp et al.[8]) and indicated apparently normal behavior, i.e., proportionality to T^2 below about 10°K with a maximum at around 40°K. For the annealed specimen, $\lambda_g \simeq 5\times10^{-4}\,T^2$w cm^{-1} deg^{-1} at low temperatures, and for the cold-worked specimens $\lambda_g \simeq 1\times10^{-4}\,T^2$. Assuming that for the latter specimens dislocations are the dominant scattering source in this region, a dislocation density of 2×10^{12} lines cm^{-2} is deduced from the theoretical phonon scattering probability.[7] Previous work[8] indicates that the number of dislocations is overestimated by a factor of 3 to 6, so that we are led to a density of about 5×10^{11} for the cold-worked CuSb specimens.

[5] D. McLean, *Grain Boundaries in Metals* (Oxford University Press, New York, 1957), p. 140.
[6] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958).
[7] P. G. Klemens, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 1.
[8] W. R. G. Kemp, P. G. Klemens, and R. J. Tainsh. Phil. Mag. 4, 845 (1959); J. N. Lomer and H. M. Rosenberg, Phil. Mag. 4, 467 (1959).

Summarizing our evidence,

(i) rerolling produced no significant change in electrical resistivity;

(ii) metallographic examination indicated that our specimens were inhomogeneous before they were annealed; the observed departures from Matthiessen's rule support this;

(iii) the known α-phase solubility limit[6] (about 5 atomic percent antimony at 640°C and 2 atomic percent at room temperature) and complex phase diagram make it not unlikely that most specimens are similarly inhomogeneous until they are carefully heat treated;

(iv) heat conductivity observations suggest that the density of dislocations is not unduly large in the cold-worked specimens and it therefore seems improbable that a majority of impurity atoms (nearly 5×10^{20} per cm^3 for antimony) could be trapped at these lines.

Therefore we believe that the suggested large-scale migration of solute atoms to dislocations on cold working does not occur, but that specimens as cast and first rolled are probably inhomogeneous and hence scatter the charge carriers less effectively than later when they are annealed to become relatively homogeneous. Of course, this does not rule out the possibility that *small* decreases in resistivity may occur in some alloys during cold work, by the mechanism proposed by Kropschot et al.

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