Residual resistivity and aging-clustering effects of Cu-rich Cu-Ni alloys

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The residual resistivities of copper-nickel alloys with nickel concentrations ranging from 20 ppm to 44 at.% and the observation of Ni-cluster growth at room temperature on one sample are reported. From samples arc-melted over a Cu hearth, wires 1 mm in diameter were drawn, annealed at 800 °C for 3 days, and quenched in ice water. Pieces of wire adjacent to the samples were used for chemical analysis on the 3–44-at.% samples and parts of the samples were used for spectrophotometric analysis on the dilute alloys. Results show that the resistivity at 4.2 °K over the concentration range studied is given by $\rho - \rho_{Cu}(4.2\,°K) = 1.112x$ ($\mu\Omega$ cm/at.% Ni), where x is the nickel concentration in at.%. By chance the electrical resistivity from 1.3 to 300 °K of samples of $Cu_{1-x}Ni_x$ ($x = 0.32$ and 0.44) were remeasured after they had been on the shelf at room temperature for 3 years. The new results showed that the electrical resistivity of the $x = 0.44$ sample had changed quite markedly. The sample was then reannealed at 800 °C and quenched in ice water, and the resistivity was measured for the third time. The sample again took on nearly the same character it had originally displayed. The nature of the change of resistivity with shelf time suggests that Ni-cluster growth at room temperature occurred.

I. INTRODUCTION

In the recent past, we have investigated resistivity minima in dilute alloys of Fe, Mn, and Cr in Cu-Ni alloy hosts.[1–4] Since this work required that we measure the electrical resistivity of the Cu-Ni host alloys at low temperatures, we became interested in the properties and history of the Cu-Ni alloy system. In this paper we report on the concentration dependence of the residual resistivity and on aging and clustering effects at room temperature. Continued high interest in Cu-Ni alloys has prompted us to prepare this paper. It is our hope that it will be of help to others who get involved in Cu-Ni sample preparation and research.

Of the large number of publications on Cu-Ni only a few closely related to the present work will be cited. Early work by Krupkowski[5] came to our attention in a paper by Coles.[6] Other early work was done by Linde,[7] who carried out studies down to nitrogen temperatures on samples containing up to 3 at.% Ni. Martin[8] has shown that there is a cluster problem related to the size of the sample being quenched. His work prompted us to use small wire samples to avoid this difficulty. A large and useful list of references related to s- and d-band effects and on clustering in these alloys may be found in the work of Seib and Spicer.[9] More directly concerned in the present work are resistivity studies by Houghton *et al.*[10] who looked at Ni-clustering effects on the electrical resistivity of Cu-Ni alloys in the 35–50-at.%-Ni regime. Other related work is reported by Skoskiewicz and Baranowski[11] and Crangle and Butcher.[12]

II. SAMPLE PREPARATION

Our samples were prepared from a 99.999%-pure copper rod and from a 99.999%-pure nickel bar obtained from American Smelting and Refining Co. As seen below, the copper contained 7 ppm Ni as the impurity of highest concentration, so we believe that the rod purity was probably overstated. The first step consisted of electron-beam melting the copper and nickel prior to forming the alloys. This procedure helped to remove volatile impurities. After this, weighed amounts of copper and nickel were arc melted together some six or seven times over a water-cooled copper hearth. The sample was inverted between arc-melting operations to maximize the mixing. The samples forthcoming were in the form of short bars (fingers) and these were swaged and then drawn through tungsten-carbide dies to give wires 1 mm in diameter,

For the residual-resistivity work reported here samples 5 in. long were cut and annealed inside highly evacuated quartz ampoules. After the annealing procedure the samples were immediately quenched in ice water. The annealing time was generally 3 days and the temperature 800 °C. A set of experiments to establish annealing times and temperatures showed that wide latitude is possible and is discussed later.

Sample composition was determined by two different procedures depending on the nickel content. Pieces of wire adjacent to the samples were used for chemical analysis on the 3–44-at.% samples, and parts of the samples themselves were used for

spectrophotometric analysis of the dilute alloys. The chemical analysis gave the concentration to within about $\frac{1}{2}\%$ of the concentration. The spectrophotometric method was good to about 2 ppm nickel in the very dilute (< 100 ppm) range and about $\frac{1}{2}\%$ in the intermediate range.

The residual electrical resistivity was measured by the standard four-probe method with a spacing of 8 cm for the voltage probes. The latter consisted of knife edges mounted rigidly using stycast (an insulating material) in holes drilled in a Cu bar. A spring arrangement held the probes of this bar against the sample in the sample holder. The latter was designed as a simple dip probe which could be inserted into a standard 50-1 liquid-helium storage Dewar whose 1-in.-diam neck provided access. Thus the residual (4.2°K) resistivity was measured with the samples immersed in liquid helium. The potentiometer-photocell amplifier used for the voltage measurement had a resolution of ±5 nV. The electrical current was less than 200 mA, except in the case of the pure copper (for which 350 mA was used) and was stable to 1 part in 10^5.

The geometric factor a/l was determined from some 20 measurements of the diameter along the wire sample and some 20 measurements of the spacing between the knife edges of the voltage probes described above.

III. RESULTS AND DISCUSSION

The residual resistivity versus Ni concentration for a number of samples ranging up to 44 at.% Ni is shown in Fig. 1. Our results show a linear dependence of ρ_0 on the Ni concentration up to 44 at.% Ni. This should be compared with the results of

FIG. 2. Residual resistivity of Cu-Ni alloys vs Ni concentration in the dilute regime.

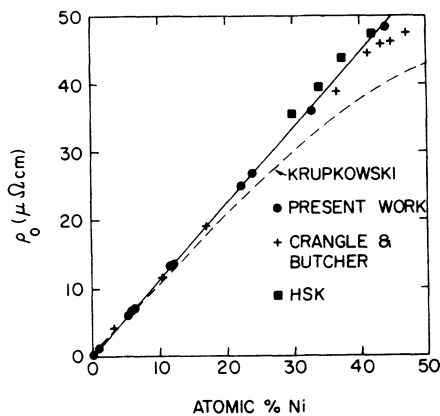FIG. 1. Residual resistivity of Cu-Ni alloys vs at.% Ni. The dashed curve is the work of Krupkowski (Ref. 5) (see text) and the HSK points come from Houghton, Sarachik, and Kouvel (Ref. 10). The results of Crangle and Butcher (Ref. 12) are also shown.
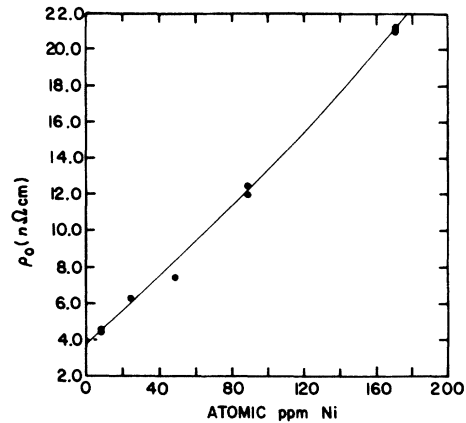
Krupkowski, [5] which have a different dependence as shown. Since his data were taken at 373°K, we have subtracted an estimated ρ (373°K) for each alloy using a working base line drawn from ρ_{Cu} (373°K) to ρ_{Ni} (373°K) as a basis for the estimate. The validity of this procedure is debatable. It is believed that part of the difference between Krupkowski's results and ours may come about from this procedure, as well as from differences in sample preparation and possibly from the purity of the starting materials. The residual (4.2°K) resistivities of Houghton et al.[10] (HSK in the figure) fall close to our line. The data of Crangle and Butcher[12] fall below our line at the higher concentrations. The work of Skoskiewicz and Baranowski[11] was on foils, so their data are not suitable for our plot. Linde's low-concentration results[7] (not shown) are close to ours. It should be remarked that at high Ni concentrations the rapid variation of ρ with temperature could lead to some spread in selecting the ρ_0. A least-squares fit of a line to our data up to and including the 24-at.%-Ni sample gives

$$\rho_0 - \rho_{Cu} \ (4.2°K) = 1.112x \ (\mu\Omega \ cm/at.\% \ Ni), \quad (1)$$

where x is the Ni concentration in at.%.

In the very dilute regime the quality of the base copper is highly significant, and this can be seen in Fig. 2, which shows the residual resistivity versus Ni concentration for samples containing up to 200 ppm nickel. Here the behavior is strongly influenced by the impurities other than nickel which make some curvature appear. The 7 ppm Ni in our base copper helped give us an extra point on this graph.

The effects of annealing time and temperature were investigated on samples with 0, 6, 12, and 22 at.% Ni. Annealing temperatures ranging from

660 to 1000 °C were equally effective. The times at these temperatures ranged from 1 h to 3 days, with imperceptible effects on the residual resistivity. It is believed that the small diameter of the samples made this result possible.

The possibility of a Kondo effect in the very dilute samples (50 and 100 ppm Ni) was investigated, but no resistivity minimum was observed. At high Ni concentrations (30–50 at.% Ni) there is a resistivity minimum which has been attributed to spin on Ni clusters by Houghton *et al*.[10] and by Crangle and Butcher.[12]

Theoretical work by Nordheim[13] predicts a parabolic form for the residual resistivity versus composition for simple s-band metals. Mott[14] considered both s and d bands and obtained a more complicated dependence on concentration.

It is believed that Ni clusters contribute to the residual-resistivity behavior found for this alloy system. In order to treat the problem semiquantitatively we assume the Nordheim[13] relationship $\rho_0 = Ax(1 - x)$, where x is the Ni concentration. We determine A by setting

$$\left.\frac{d\rho_0}{dx}\right|_{x\to 0}$$

equal to the experimental slope of ρ_0 versus x of Eq. (1). We seek an additive term to compensate for the parabolic form of Nordheim. We treat the problem in a manner suggested by Bennett *et al*.[15] when they describe the magnetic moment of an iron atom having n nickel nearest neighbors as

$$\mu_n = (2.85 + 0.6n)\mu_B , \qquad (2)$$

where μ_B is the Bohr magneton. We replace the iron atom by a nickel atom and get a magnetic moment of

$$\mu_n = 0.6(n + 1)\mu_B \qquad (3)$$

for a "small" cluster of n nickel atoms surrounding the central nickel atom. Next we invoke the scattering of conduction electrons by magnetic impurities described by deGennes and Friedel[16] for incoherent scattering and obtain the magnetic scattering contribution $\Delta\rho \propto xS(S + 1)$. We let $S(S + 1)$ $\sim \mu_n^2$; then the additional scattering due to clustered magnetic moments treated statistically is given by

$$\rho_{mag} = Bx \sum_{n=1}^{12} P_n(x)\mu_n^2 ,$$

where the $P_n(x)$ is a binomial distribution function which weights the μ_n according to the statistical likelihood of the existence of a cluster of size n. Thus we expect

$$\rho_0 = Ax(1 - x) + Bx \sum_{n=1}^{12} P_n(x)[0.6(n + 1)]^2. \qquad (4)$$

When this approach is used and B is properly chosen, a good fit to the experimental behavior is obtained for $0 < x < 0.45$.

The cluster effect on the residual resistivity made us curious about the resistivity minimum exhibited by Cu-Ni at the higher concentrations. From the graphs of ρ versus T published by Houghton *et al*.[10] we obtained the depth of the minimum versus Ni concentration, and noticed that if we neglected the phonon aspect of the problem, i.e., if we assumed that the phonon effect was essentially unchanged over the concentration range $0.3 < x < 0.45$, we could apply to this system the original Kondo[17] expression for spin-flip scattering:

$$\Delta\rho(T) = cR_u(\pi\rho_1 J)^2 S(S + 1)[1 + 4\rho_0 J\ln(T/T_0)]. \qquad (5)$$

Here c is the atomic concentration of magnetic impurities, R_u is the unitarity limit of the resistivity, which is a constant for a given host, ρ_1 is the density of the conduction-electron states at the Fermi level for one direction of the spin, J is the strength of the s-d exchange interaction which is negative, S is the spin on the impurity, and T_0 is a characteristic temperature. This suggests that for clusters we should have the depth of the minimum proportional to the product of the cluster concentration and the appropriate spin function for each cluster size. We propose that the depth should be given by

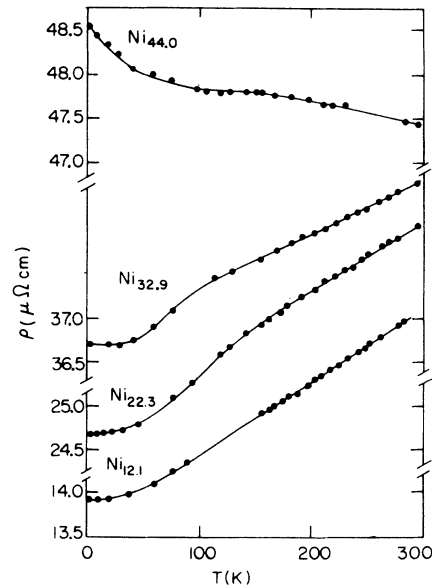$$\delta(x) = kx \sum_{n\geqslant 6}^{12} \binom{12}{n} x^n (1 - x)^{12-n} S_n(S_n + 1), \qquad (6)$$

FIG. 3. Electrical resistivity vs temperature for Cu-Ni alloys.
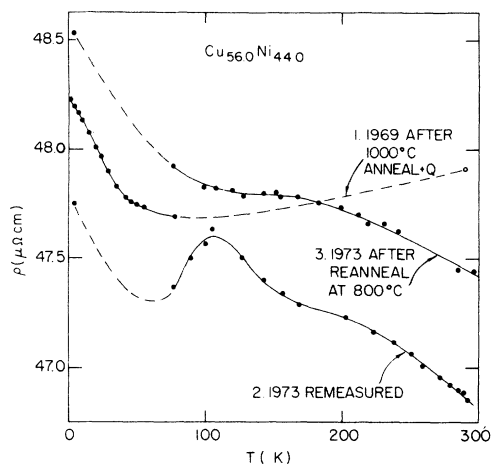
FIG. 4. Electrical resistivity vs temperature for the $Cu_{0.56}Ni_{0.44}$ sample (i) as measured originally after 3-day 1000 °C anneal and quench in ice water, (ii) as measured a second time after some 3 years on the shelf at room temperature, (iii) as measured for the third time after a reanneal for 3 days at 800 °C and quench in ice water. The dashed portions of the curves indicate regions where data points were not taken.

where S_n is expected to grow with cluster size as $\frac{1}{6}(n - 6)$, and k is a constant which we use to match the experimental result at $x = 0.42$. This spin behavior is suggested by Bennett et al.[15] A remarkably good fit to the experimental results was obtained. This may be fortuitous in view of the high temperatures of the minima.

While engaged in the above-described work we noticed that our resistivity-vs-temperature results shown in Fig. 3 were somewhat at variance with the results of Houghton et al.[10] for our 44-at.%-Ni sample. This prompted us to remeasure the resistivity of this sample and of the 32-at.%-Ni sample, which by the time of this second mea-

surement had been on the shelf for 3 years. The results of the remeasurement for the 32-at.%-Ni sample were very close to the original results, but for the 44-at.%-Ni sample they were quite different from the old results, as can be seen in Fig. 4. A peak or bump at 120 °K was found which was not seen in the previous results. In view of the fact that Ni clusters have been reported at the root of a number of effects in this concentration range[9,10,12,15] we attributed the newly found peak to slow Ni-cluster growth at room temperature. In order to establish this more convincingly we decided (after considerable thought about losing a rather unique specimen) to reanneal the sample for three days at 800 °C, quench in ice water and measure the resistivity for the third time.

The results are also shown in Fig. 4. The peak at 120 °K is gone. We conclude that the annealing and quenching has restored the statistically expected Ni clusters and that the 120 °K peak was a consequence of abnormal Ni-cluster growth during the 3 years on the shelf. It should be noted here that in the case of other alloys of Cu it has been found by Beck[18] that cluster formation occurs in Cu-Fe, Cu-Mn, etc. In these studies the migration of the transition elements into clusters was expedited by exposure to elevated temperatures.

It was mentioned earlier that this particular sample had originally been quenched from 1000 °C. This would be significant if, as we believe, the migration at room temperature of Ni atoms to form clusters is aided by vacancies (this would be one of the thermodynamic driving forces); then the 1000 °C annealing temperature may have helped us make this interesting observation.

ACKNOWLEDGMENTS

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