The Electrical Resistivity of Cu-Ni Alloys and Matthiessen's Rule*

Yoshio SHIBUYA

The Research Institute for Iron, Steel and Other Metals

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Synopsis

The electrical resistivity of copper-nickel alloys has been measured at the temperature-range from ordinary to liquid nitrogen temperature and the validity of Matthiessen's rule concerning the alloys having the compositions approaching copper has been examined. The results obtained are as follows. (1) Both resistivity vs. composition curves obtained at 23°C and −183°C are approximately parabolic. (2) It has been ascertained that Matthiessen's rule does not hold in the case of Cu-Ni alloys adjacent to copper, i.e. $d\rho/dt$ is not constant with the change of nickel-concentration but changes linearly with it. (3) A plausible explanation based upon the conduction theory of electricity in metals has been given for the deviation from Matthiessen's rule.

I. Introduction

The physical properties of Cu-Ni alloys have been measured by many researchers. One of the reasons may be that they are very useful alloys. Another reason may be, apart from the practical application, that though the alloys, the nickel-concentration of which exceeds 40 per cent are ferromagnetic, they are very adequate as materials for the experimental investigation, because they form an unbroken series of solid solutions and the physical interpretation of experimental results can be comparatively simplified.

The measurement of electrical resistivity of these alloys has been performed by many investigators, for instance, Chevenard[1], Krupkowsky and de Haas[2], and Svensson[3]. The electrical resistivity of Cu-Ni alloys in a limited range of concentration has been measured by Nobury and Kuwada[4] and Linde[5]. Therefore the question about the electrical conductivity of these alloys seems no longer to afford any scope for discussion and it may be like putting a fifth wheel to a coach to publish one more paper on the electrical resistivity of these alloys. The present research was undertaken, however, for the purpose of examining the validity of Matthiessen's rule for the electrical resistivity of these alloys adjacent to copper which had not been done yet completely and of explaining the deviation from the said rule from the theoretical point of view.

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* The 750th report of the Research Institute for Iron, Steel and Other Metals.
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(1) P. Chevenard, Journal Inst. Met., **36** (1936), 39.
(2) A. Krupkowsky and W.J. de Haas, Comm. Leiden, **194a** (1930).
(3) B. Svensson, Ann. d. Phys., **25** (1936), 263.
(4) A.L. Nobury and K. Kuwada, Phil. Mag., **4** (1928), 1338.
(5) J.O. Linde, Ann. d. Phys., **15** (1932), 219.

The fact that the increase in the resistance of a metal due to a small concentration of another metal in solid solution is in general independent of temperature was first shown by Matthiessen. Thenceforth this is well-known as Matthiessen's rule. Matthiessen's rule asserts that the electrical resistivity of an alloy specimen is given by:

$$\rho = \rho_0 + \rho_T,$$

where ρ_0 is the residual resistivity which is equal to the resistivity of the alloy at the absolute zero of temperature and is independent of temperature, and ρ_T is the temperature-dependent resistivity of an ideal, pure metal. Namely the relation of resistivity against the temperature of dilute solid solutions should be displaced upwards by the amount appropriate for the specified concentration above that of a pure specimen. As the consequence of the rule we should expect the same value of temperature-variation of the resistivity irrespective of the concentration, that is, $d\rho/dt$ should be constant. The said rule obtained empirically is, of course, not rigorous. From the theoretical point of view(6), Matthiessen's rule is satisfied, provided that:

(1) The effective number of free electrons is unaltered by the addition of foreign atoms.

(2) The thermal vibrations of the foreign atoms give the same scattering as those of the atoms of the solvent metal. Neither of these conditions, however, will be fulfilled exactly and we should expect a deviation from the rule.

We measured the electrical resistivity of Cu-Ni alloys at the temperatures between room and liquid nitrogen temperature, and plotted $d\rho/dt$ for alloys of small nickel concentration against the alloy concentration. We gave a plausible explanation for the deviation from Matthiessen's rule.

In Sec. 2 a brief account is given of the experimental procedure and specimens. Experimental results are described in Sec. 3 and a theoretical consideration on the results, together with the existing theory of the deviation from Matthiessen's rule, is discussed in Sec. 4.

II. Experimental procedure and specimens

The experimental procedure we adopted was an usual one; the potential drop, measured with a precision-potentiometer, between two knife-edges pressed to a specimen with light pressure was compared with that between two terminals of a standard resistance of 1/1000 ohms. The distance between two knife-edges was 44.9 m/m at 20°C. For the purpose of eliminating errors due to thermo-electromotive forces, the electric current through the specimen and the standard resistance was reversed and the measurement was done again. Two measured values of potential drops thus obtained were averaged and the average value was used to find the resistivity of the specimen.

The schematic diagram of experimental apparatus is shown in Fig. 1. A vacuum

(6) N.F. Mott, The Theory of Properties of Metals and Alloys, (1936), 288.

chamber V, dipped in a liquid-nitrogen Dewar vessel N is evacuated to a considerable vacuum with the use of a rotary vacuum pump. The temperature of the specimen is maintained to the desired value above the liquid nitrogen temperature by adjusting properly the current through the heater H, wound with constantan wire on a copper cylinder C which enclosed the specimen-holder D. The copper cylinder C has two caps, C_1 upper and C_2 lower, which serve for the uniformity of temperature around the specimen. The temperature of the specimen is measured by the use of two copper-constantan thermocouples T_1 and T_2 attached to the specimen S at the points near upper and lower ends. The average value of two temperatures is adopted as the temperature of the specimen S.

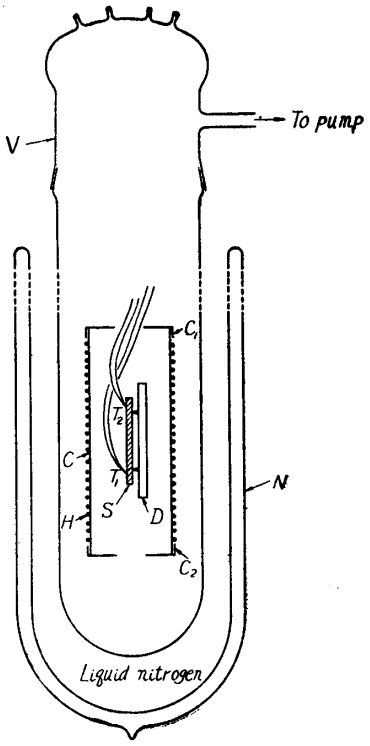

Fig. 1. Schematic diagram of the specimen-chamber

The Ni-Cu ingots were got by melting in an induction furnace electrolytic nickel and copper charged to the required proportion in a crucible. For the purpose of measuring the thermal resistivity as well as the electrical conductivity, the dimension of alloy specimens was standardized to the diameter of 4 mm and the length of 60 mm. The specimens of the specified shape were made from the ingot by forging followed by machining. Although the specified dimension is not a desirable one for the measurement of the electrical resistivity, we did not experience particular inconvenience. The specimens prepared to size were annealed at 900°C (Ni-side)~800°C (Cu-side) for

Table 1. Composition of Alloys in Weight Percent.*

No. of specimen		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Charge	Cu	100	99	98	96	95	90	85
	Ni	0	1	2	4	5	10	15
Analysis	Cu	ballance	bal.	bal.	bal.	bal.	bal.	bal.
	Ni	0	0.95	1.26	2.31	4.71	9.91	14.86
	Mn	0.001	0.02	0.004	0.004	0.02	0.02	0.02
	Fe	0.002	0.02	0.012	0.014	0.02(	0.03	0.02
	Co	trace		tra.	tra.			

No. of specimen		No. 8	No. 9	No. 10	No. 11	No. 12	No. 13	No. 14	No. 15
Charge	Cu	80	70	50	30	20	15	10	5
	Ni	20	30	50	70	80	85	90	95
Analysis	Cu	bal.	bal.	bal.	bal.	bal.	bal.	bal.	bal.
	Ni	19.83	29.89	49.75	69.56	78.20	86.14	90.98	95.35
	Mn	0.04	0.03	0.05	0.05	0.05	0.10	0.13	0.26
	Fe	0.02	0.03	0.03	0.03	0.05	0.05	0.04	0.03
	Co								

* The two groups of specimens, i.e. the first group (Nos. 1, 3 and 4) and the second one (the rest) were prepared at different times.

6 hours in high vacuum.

The result of the chemical analysis of impurities contained in the alloys is shown in Table 1.

III. Experimental result

The relations between the electrical resistivity and the composition of Cu-Ni alloys at 23°C and −183°C are shown in Fig. 2. The measured value of the resistance was converted to the resistivity after making allowance for the thermal contraction.

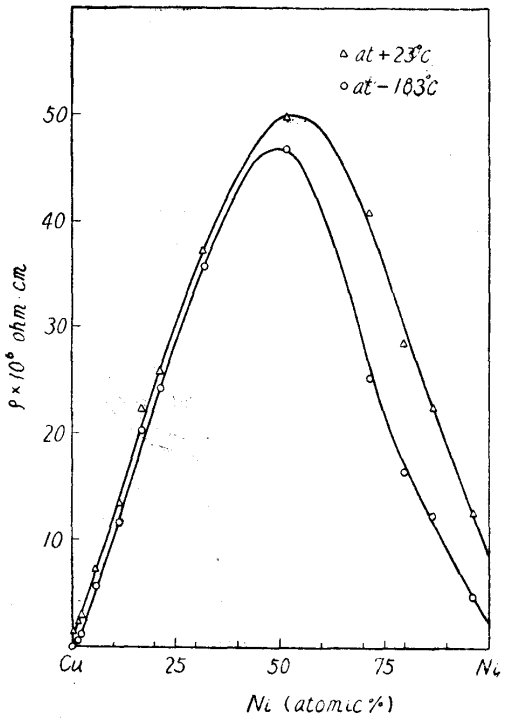

Fig. 2. Resistivity of Cu–Ni alloys which form an unbroken series of solid solutions.

According to the results obtained by Svensson[3] and by Krupkowsky and de Haas[2], the maximum of resistivity seems to displace to Cu-side with the decrease of temperature. Our result does not show such a clear displacement and the position of maximum seems to appear at about the composition of 50 per cent Cu.* It would be due to the scanty of measured points around 50 per cent Cu. In order to clarify this point it will be necessary to plot the ressstivity-curve with a large number of measured points around the composition in question.

The temperature-dependence of resistivity of alloys having small concentration of nickel is shown in Fig. 3. The average $d\rho/dt$ increases with the increase of nickel content. This is shown in Fig. 4. If Mattiessen's rule holds good, $d\rho/dt$ for the specimen of small nickel content should be independent of the nickel concentration. A theoretical explanation for this discrepancy will be given in the following section.

IV. Theoretical consideration

According to the conduction theory of electricity in metals[6], we may write for the resistivity of alloys of small concentration,

$$\rho = \rho_0 + \rho_T, \qquad (1)$$

where

$$\rho_0 = \frac{m}{Ne^2}\frac{1}{\tau_0}, \quad \rho_T = \frac{m}{Ne^2}\frac{1}{\tau_T}.$$

In above *Eq.* (1) ρ_0 is equal to the resistivity of the alloy at the absolute zero of temperature, and is independent of temperature; ρ_T will be approximately proportional to the temperature except at very low temperatures, as for a pure

* Compositions are expressed in atomic percentages throughout, unless a special notice is given.

metal. Furthermore e and m are the electronic charge and the mass of an electron respectively and N the effective number of electrons per unit volume. $\frac{1}{\tau_0}$ is the number of times pei second that an electron is scattered by a foreign atom, and $\frac{1}{\tau_T}$ the number of times per second that it is deflected owing to the thermal vibration of the atoms. Matthiessen's rule is not satisfied unless the two conditions described in the introduction is fulfilled exactly.

Grüneisen[7] discovered for the first time that the apparent residual resistance of different pure copper specimens increased with the temperature and concluded that Matthiessen's rule did not hold in this case. The theoretical treatment of the deviation from Matthiessen's rule was taken up first by Dube[8], whose result was, however, incorrect. Sondheimer and Wilson[9] discussed also this problem. Afterwards Kohler[10] worked out a general theory of the electrical resistivity of metals with the help of variation method and extended his calculation to the deviation from Matthiessen's rule. According to his result,

$$\rho \geqq \rho_0 + \rho_T \qquad \text{or} \qquad \rho = \rho_0 + \rho_T + \Delta \ ,$$

where

$$\Delta = \beta \cdot \gamma \frac{\rho_0 \rho_T}{\beta \rho_0 + \gamma \rho_T} \ ,$$

in which β and γ are positive numbers. At sufficiently low temperatures, where the ideal resistivity ρ_T is small compared with the residual one ρ_0, the deviation Δ tends to zero. On the ther hand, at high temperatures, where ρ_T is no longer very small, Δ increases with the increase of temperatures. In the extreme case that ρ_T is large compared with ρ_0, we expect a temperature-independent deviation. His result shows a good agreement with the experimental one.

In the present consideration, however, we start with the use of *Eq.* (1) and assume that $\frac{1}{\tau_T}$ in the second term which is the number of times per second that an electron is deflected by the thermal vibrations of the atoms is not altered by the addition of nickel atoms*. Although the first term changes with the addition of nickel atoms, it is independent of temperature and does not affect $d\rho/dt$. Then if ρ_T for a pure metal is a linear function of the temperature, the gradient $d\rho/dt$ for an alloy will be altered in accordance with the change in N which depends on the quantity of nickel atoms added to copper. The result obtained shows that the resistivity between -195.8°C and 23.0°C of copper-nickel alloys up to

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(7) E. Grüneisen, Ann. Phys., **16** (1933), 538.
(8) G.P. Dube, Proc. Cambr. Philos. Soc., **34** (1938), 559.
(9) E.H. Sondheimer and A.H. Wilson, Proc. Roy. Soc. London, **A190** (1947), 435.
(10) M. Kohler, Zeit. f. Phys., **126** (1949), 495.

* $\frac{1}{\tau_T}$, being a function of the ion-mass M and the characteristic temperature Θ of the metal, will be changed by the addition of foreign atoms. Assuming that both the average ion-mass M and the average Θ of an alloy change linearly with the concentration x of nickel, the change in $\frac{1}{\tau_T}$ will not exceed $0.3x$ and may be negligible compared with the change in the effective number of electrons per unit volume, N, as shown later.

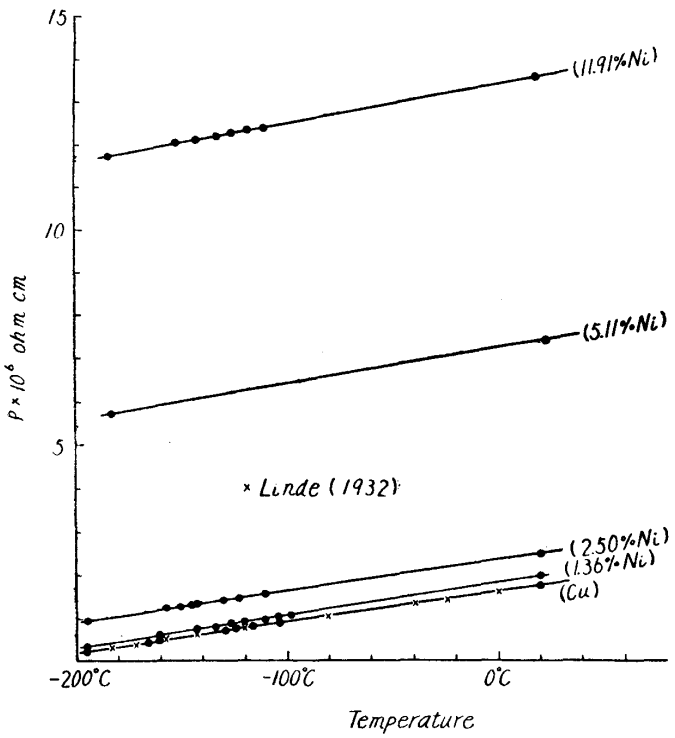

Fig. 3. Resistivity-temperature relations of Cu-Ni alloys having the composition adjacent to copper: the figures show the atomic percentages of nickel. To avoid confusion the relation for the alloy of 1.03% Ni was omitted in the figure. The straight line for the alloy of 5.11% Ni was determined with two measured values.

11.91 per cent nickel is quite approximately a linear function of the temperature.* (Fig. 3)

According to both experimental results on the magnetism by Alder and theoretical considerations by Mott[11], Hirone[12] and Niessen[13], it was beileved earlier that N_{od}, the number of holes per atom in the 3d band at the absolute zero of temperature was 0.6 for pure nickel and N_{od} decreased with the addition of copper atoms and became null at the composition of 60 per cent copper; N_{os}, the number of electrons per atom in the 4s band at the absolute zero of temperature would decrease linearly from unity with the addition of nickel atoms, i. e., the decrease of N_{os} would be one per cent with the addition of one per cent nickel. Afterwards Wohlfarth[14], taking correctly the two bands into consideration, worked out more reasonably the collective electron treatment of ferromagnetism and extended the calculation to finite temperatures. According to his calculation N_s, the number of electrons in the 4s band of Cu-Ni alloy having the composition less than about 10 per cent nickel does not differ noticeably from N_{os} even at 1000°K. The decrease of N_s in this composition range is the same as in earlier theories, that is, one per cent with the addition of one per cent nickel.

It may be, therefore, legitimate to assume that the effective number N of electrons per unit volume in Cu-Ni alloys having the composition up to about 10

(11) N. F. Mott, Proc. Phys. Soc., **47** (1935), 571.
(12) T. Hirone, Sci. Rep. Tohoku Univ., **27** (1938), 101.
(13) K. F. Niessen, Physica, **6** (1939), 1011.
(14) E. P. Wohlfarth, Proc. Roy. Soc., Lond. **A195** (1949), 434.

* The temperature-dependence of the resistivity of copper-nickel alloys in the whole range of composition shows diverse features according to the composition. For instance, one of them shows a behaviour practically independent of temperature between 0° and 400°C, i. e. its $d\rho/dt$ is nearly zero. This alloy is the well-known constantan (Cu 60 per cent, Ni 40 per cent (in weight)). The temperature-dependence of the resistivity of Cu-Ni alloys which contain less than 11.91 per cent Ni between the specified range of temperature is, however, approximately quite linear.

per cent nickel decreases linearly with the increase of nickel content and that the addition of x per cent nickel causes the decrease in N of x per cent. Then we should expect that $d\rho/dt$ of these alloys increases linearly from that of pure copper with the increase in the concentration of nickel and the increasing rate is x per cent with the addition of x per cent nickel. Fig. 4 shows the relation between the average $d\rho/dt$ and the concentration of nickel x obtained experimentally together with thus theoretically estimated one(broken line). Assuming the existence of a linear relationship between $d\rho/dt$ and x, we determined the full line from the experimental data by the method of least square. Thus our result is in agreement with that due to Grüneisen in that the apparent residual resistance of specimens of different concentration of impurity increases with the temperature.

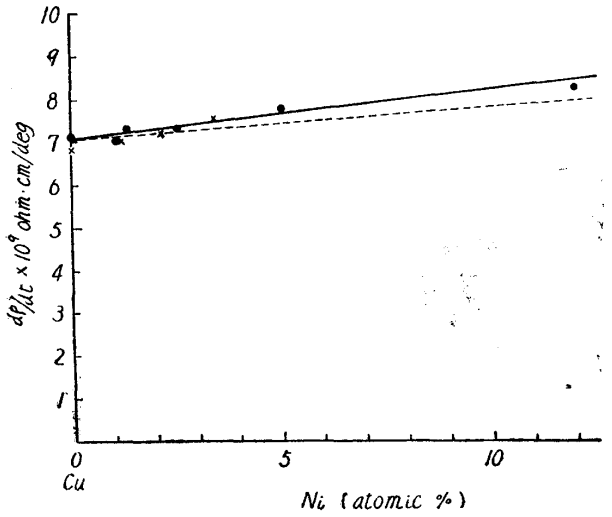

Fig. 4. Change in the mean value of $d\rho/dt$ with composition for Cu-Ni alloys adjacent to copper. × was determined by the author from the data due to Linde.[5]

If Matthiessen's rule does hold good, we should expect that $d\rho/dt$ is constant irrespective of x. That means that $d\rho/dt$ is a horizontal line parallel to the abscissa. Thus it was verified that Matthiessen's rule did not hold in the case of Cu-Ni alloys of small nickel concentration. Recently, however, a simple band model and a collective electron treatment for the alloy system copper-nickel seem to face a crisis, because they fail to account for the physical properties, such as Hall coefficients, magnetic properties and electronic specific heats, met with when the copper content exceeds 60 per cent. In order to account for these properties Goldman[15] has resorted to the idea of statistical fluctuation in local concentration of nickel atom. A tentative explanation was given also by Coles[16]. Nevertheless it seems to us that a conclusive treatment has not been yet presented. As a simple band model and a collective electron treatment seem, however, very successful in dealing with the ferromagnetic properties of copper-nickel alloys, we did not abandon them and showed that the deviation from the said rule could be explained in some degree by resorting to the usual model and treatment in which we took into consideration the change in the effective number of conduction electrons due to the addition of nickel atoms.

In conclusion, the author wishes to express his deep appreciation to Prof. T. Fukuroi for his encouragement and discussions throughout the work; to Mr. T.

(15) J. E. Goldman, Phys. Rev., **82** (1951), 339 (A).
(16) B. R. Coles, Proc. Phys. Soc., **B65** (1952), 221.

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