Materials Transactions, JIM, Vol. 38, No. 8 (1997), pp. 714 to 718

Precise Purity-Evaluation of High-Purity Copper by Residual Resistivity Ratio

Kouji Mimura*, Yukio Ishikawa*, Minoru Isshiki*
and Masanori Kato**

**Institute for Advanced Materials Processing, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-77, Japan*
***Nikko Kinzoku Co. Ltd., Toranomon 2-10-1, Minato-ku, Tokyo 105, Japan*

To evaluate the purity of high-purity copper with high accuracy by the residual resistivity ratio (*RRR*), the optimum annealing condition before the *RRR* measurement and the diameter dependence (size effect) of *RRR* for high-purity copper (5N and 6N grade copper) wires, 0.2–2 mm in diameter, annealed under the optimum condition have been investigated.

The most suitable annealing temperature and period were determined to be 923 K and more than 14.4 ks (4 h), respectively. For the size effect on *RRR*, the relationship between RRR_W (*RRR* measured for a copper wire with diameter d), RRR_B (*RRR* of the bulk copper) and the specimen diameter d (mm) was found as follows:

$$RRR_W^{-1}=RRR_B^{-1}+(3.8\times10^{-5})\cdot d^{-1}$$

The product of $\rho\cdot\lambda=6.5\times10^{-16}\,\Omega\mathrm{m}^2$ for copper was also obtained from the slope of the above equation. Furthermore, it became clear that the difference in RRR_W is dependent on the specimen diameter and increases with purity of the specimen. Therefore, the influence of the size dependence on *RRR* must be considered carefully whenever to evaluate and to compare the purity of high-purity metals by *RRR*.

(Received March 10, 1997)

Keywords: *copper, high-purity metals, residual resistivity ratio, size effect, vacuum annealing, evaluation of purity*

I. Introduction

In the study on purification of metals, the evaluation of their purity is an important subject. Since the accuracy of chemical analyses decreases as the trace impurity levels become lower, the residual resistivity ratio has widely been used to estimate quantitatively the purity of high-purity metals. However, in estimating the metal-purity with high accuracy by the residual resistivity ratio, there are some points to be considered.

The residual resistivity ratio (*RRR*) is expressed by eq. (1), as the ratio of the resistivity $\rho_{298\,\mathrm{K}}$ (or electrical resistance $R_{298\,\mathrm{K}}$) at room temperature like 298 K to the residual resistivity $\rho_{4.2\,\mathrm{K}}$ (or residual resistance $R_{4.2\,\mathrm{K}}$) at 4.2 K. The resistance R (Ω) of a given sample wire with the cross-sectional area S (m^2) and the length l (m) between the potential contacts is related to the resistivity ρ (Ωm) by $R=\rho(l/S)$. Since the change of (l/S) with temperature from 298 to 4.2 K is negligibly small and then the influence of the sample dimensions on the ratio of $R_{298\,\mathrm{K}}/R_{4.2\,\mathrm{K}}$ can be cancelled, $R_{298\,\mathrm{K}}/R_{4.2\,\mathrm{K}}$ is almost equivalent to $\rho_{298\,\mathrm{K}}/\rho_{4.2\,\mathrm{K}}$ as shown in eq. (1).

$$RRR=\frac{\rho_{298\,\mathrm{K}}}{\rho_{4.2\,\mathrm{K}}}\simeq\frac{R_{298\,\mathrm{K}}}{R_{4.2\,\mathrm{K}}}. \qquad (1)$$

In general, the resistivity $\rho(T)$ at temperature T is given by eq. (2), where ρ_0 is the residual resistivity independent of temperature, and ρ_T caused by electron-phonon scattering is dependent on temperature. At room temperature, ρ_T is dominant in $\rho(T)$ because of ρ_T being much larger than ρ_0. On the other hand, $\rho(T)$ is dominated by ρ_0 at 4.2 K because of ρ_T becoming much smaller than ρ_0.

$$\rho(T)=\rho_0+\rho_T \qquad (2)$$

$$\rho_0=\rho_{\mathrm{imp}}+\rho_d. \qquad (3)$$

The residual resistivity ρ_0 can be expressed as the sum of ρ_d, arising from electron scattering by physical defects such as boundary, dislocation and surface, and ρ_{imp} by solute impurities, as shown in eq. (3). For well-annealed metals, ρ_0 depends predominantly on ρ_{imp} due to $\rho_{\mathrm{imp}}\gg\rho_d$. An improvement of metal-purity with decreasing solute impurity level results in the decrease of ρ_{imp} and $\rho_{4.2\,\mathrm{K}}$ and then in the increase of *RRR*, when ρ_d has been lowered sufficiently.

Consequently one of the factors to obtain *RRR* values with accuracy is to anneal the thin wire specimens under a suitable condition before the *RRR* measurement, in order to reduce the influence of ρ_d on ρ_0 as much as possible. However, the influence of the annealing condition on *RRR* values has not been investigated well. The optimum annealing condition must be then discussed and normalized for the *RRR* measurement of each metal.

Another point is the size effect on *RRR*. For the *RRR* measurement of high-purity metals, the thinner wires should be required to get the correct residual resistivity ρ_0 at 4.2 K, because ρ_0 decreases with increasing purity of the specimen. In this case, the contribution of a surface scattering of conduction electrons on ρ_0 should not be disregarded. Although several fundamental studies(1)-(6) for the effect of specimen size on the electrical resistivity at 4.2 K of copper thin wires have been reported, no concrete studies about the influence of the size effect on the evaluation of high-purity copper by means of *RRR* values have been carried out yet. It is often difficult, therefore, to compare the purity of a copper with that of another copper using the reported *RRR* values exactly.

In the present work the optimum annealing condition and the diameter dependence (size effect) of *RRR* of high-purity copper wires have been investigated quantitatively.

II. Diameter Dependence (Size Effect) of the Residual Resistivity Ratio

According to Nordhiem(7), the diameter dependence of the electrical resistivity of cylindrical wires with diffuse surface scattering of conduction electrons can be described by the following relation:

$$\rho_W=\rho_B\left(1+\frac{\lambda_B}{d}\right) \tag{4}$$

where ρ_W and ρ_B are the resistivities of a thin wire with diameter d and of the bulk material, respectively, and λ_B is the bulk mean free path of conduction electrons. For the case of partial specular surface scattering of conduction electrons, a modified Nordheim formula, as shown in eq. (5), has been proposed by Dingle(8).

$$\rho_W=\rho_B\left[1+C(1-P)\frac{\lambda_B}{d}\right]. \tag{5}$$

Here P is the specularity parameter ($0\leq P\leq 1$) and C is a fitting parameter. As an example, $P=0.45$, i.e. 45% of conduction electrons at the surface were reflected specularly, was found by Mende and Thummes(4) from the resistivity measurements of copper whiskers with microscopically smooth and optically high reflecting surfaces. By contrast, since the surface smoothness of the polycrystalline copper wires studied in this work must be inferior to that of the whisker, the influence of specular surface scattering on *RRR* is expected to be negligibly small.

At 4.2 K, eq. (4) is rewritten as eq. (6).

$$\rho_{W,4.2\,K}=\rho_{B,4.2\,K}\left(1+\frac{\lambda_{B,4.2\,K}}{d}\right). \tag{6}$$

It is presumed that $\rho_{W,298\,K}=\rho_{B,298\,K}$, which is reasonably from eq. (4) because of the very small mean free path at room temperature ($\lambda_{298\,K}$ of copper is approximately 40 nm(4) to 42 nm(9)), so that dividing both sides of eq. (6) by $\rho_{W,298\,K}$ and $\rho_{B,298\,K}$ respectively gives eq. (7):

$$\frac{\rho_{W,4.2\,K}}{\rho_{W,298\,K}}=\frac{\rho_{B,4.2\,K}}{\rho_{B,298\,K}}\left(1+\frac{\lambda_{B,4.2\,K}}{d}\right). \tag{7}$$

Since $\rho_{298\,K}/\rho_{4.2\,K}$ means *RRR*, eq. (7) is transformed to

$$RRR_W^{-1}=RRR_B^{-1}+(RRR_B^{-1}\cdot\lambda_{B,4.2\,K})\cdot d^{-1}. \tag{8}$$

Here RRR_W and RRR_B are the *RRR* values of the specimen wire with diameter d and the bulk material, respectively. From eq. (8), by plotting the RRR_W^{-1} values against d^{-1}, the diameter dependence of *RRR* is presented by a straight line with the slope of $RRR_B^{-1}\cdot\lambda_{B,4.2\,K}$ (i,e. $\rho_{B,4.2\,K}\cdot\lambda_{B,4.2\,K}/\rho_{B,298\,K}$). Also, the RRR_B can be obtained by extrapolating the straight line to $d^{-1}=0$.

III. Experimental Details

1. Sample preparation

High-purity copper wires, 2 mm in diameter, with purities of 5N(>99.999%) and 6N (>99.9999%) grades, supplied by Nikko-Kinzoku Co. Ltd. were used as the starting material. The impurity contents of the two wires analyzed using GDMS are shown in Table 1. Wire samples 0.2–2 mm in diameter were prepared by drawing the wires and then cut to the length of about 120 mm. After

Table 1 Impurity contents of 5N and 6N grade copper samples by GDMS analysis.

Element	Impurity Conc. (mass ppm)	
	5N-Cu	6N-Cu
Na	0.006	0.038
Mg	<0.012	0.001
Al	0.36	0.006
Si	0.335	0.05
P	<0.009	<0.003
S	0.062	0.01
Cl	0.016	0.013
K	0.093	0.009
Ca	<0.45	<0.023
Ti	0.12	<0.027
V	<0.009	<0.001
Cr	<0.011	<0.002
Mn	<0.01	<0.001
Fe	<0.01	0.006
Co	<0.009	<0.001
Ni	0.006	<0.002
Zn	<0.08	<0.15
Ga	<0.015	<0.007
Ge	<0.046	<0.024
As	0.01	0.006
Se	0.25	<0.037
Br	0.018	<0.035
Zr	<0.08	0.045
Nb	0.53	0.001
Mo	<0.06	0.005
Ag	0.008	0.113
Cd	<0.08	<0.04
Sn	<0.11	0.024
Sb	<0.016	<0.008
Te	<0.13	<0.06
W	<0.032	<0.004
Pb	<0.04	0.005
Bi	0.009	<0.003
Th	<0.005	<0.001
Cu (mass%)	>99.9997	>99.99992

wiredrawing, the samples were electropolished by 20–30 µm at each polishing, in a 24%phosphoric acid-24% ethanol-5%propanol aqueous electrolyte so as to eliminate the contaminated surface-layer, and rinsed with deionized water using an ultrasonic cleaner.

The diameter of each specimen was measured by a micrometer along the longitudinal direction of the wire. The deviation from the mean diameter was less than 0.002 mm.

2. Annealing in high vacuum

The annealing equipment is depicted in Fig. 1. The quartz sample tube (ID 3 mm × 150 mm) including a sample wire was placed in the quartz furnace tube (ID 27 mm × 500 mm). The quartz tubes had been thoroughly cleaned in a 5%HF solution and rinsed with deionized water by an ultrasonic cleaner.

After placing the sample in the furnace tube, the apparatus was evacuated down to nearly 1×10^{-6} Pa by a system of sputter-ion and turbo-molecular pumps and then the sample was heated up to the given temperature in a infrared heating furnace.

The optimum annealing condition to get the highest *RRR* values was examined by measuring the annealing time dependence of *RRR* at 873, 923 and 973 K, using the 6N grade copper wire 0.5 mm in diameter. Then the influence of the size effect on *RRR* was investigated by measuring the *RRR* of the copper wires 0.2–2 mm in diameter annealed under the obtained optimum annealing condition.

3. Measurement of the residual resistivity ratio

The electrical resistances were determined at room temperature and at liquid helium temperature (4.2 K) by a standard four-wire dc method. The mean voltage drop, with sensitivity of 10 nV, across the specimen wire was measured for each direction of direct current flow (max 2A) passing through it. For the measurement at room temperature, the specimen wire was dipped in deionized water and its temperature was measured by a Pt-resistance thermometer with accuracy of ±0.1 K. The resistance at 298 K was obtained by a correction calculation using the temperature dependence coefficient of copper resistivity, 4.3×10^{-11} Ωm/K.

IV. Results and Discussion

1. Optimum vacuum annealing of copper thin wires

Figure 2 shows change in *RRR* of 6N copper wires with 0.5 mm in diameter as a function of the annealing time at 873, 923 and 973 K. The *RRR* value of the wire without annealing was about 650 to 800.

The *RRR* attained about 4000 at 3.6 ks (1 h) and then gradually increased to around 5300 at 86.4 ks (24 h) at the annealing temperature of 873 K. On the other hand, at 923 K, the *RRR* reached quickly approximately 5300 at 14.4 ks (4 h) and then held as nearly constant with the time. At the higher temperature of 973 K, the *RRR* increased to about 5100 at 3.6 ks (1 h). After that, it gradually decreased to less than 5000. The decrease in *RRR* was attributed to contaminations of the specimens from the quartz tube or the annealing atmosphere above 973 K. Consequently, the most suitable temperature and period for the annealing of copper wires were concluded to be 923 K and more than 14.4 ks (4 h). So, for the examination of the size effect on *RRR*, copper wires 0.2–2 mm in diameter were uniformly annealed in a high vacuum for 86.4 ks (24 h) at 923 K.

2. Diameter dependence of the residual resistivity ratio of copper thin wires

Figure 3 shows the reciprocal residual resistivity ratio for 5N and 6N grade copper wires well-annealed under the optimum condition as a function of the inverse sample diameter, d^{-1} (mm^{-1}). The data can be interpreted according to eq. (8) and the linear relationships between RRR_W^{-1} and d^{-1} are represented by eq. (9) for 5N and eq. (10) for 6N, respectively, calculated by the least squares

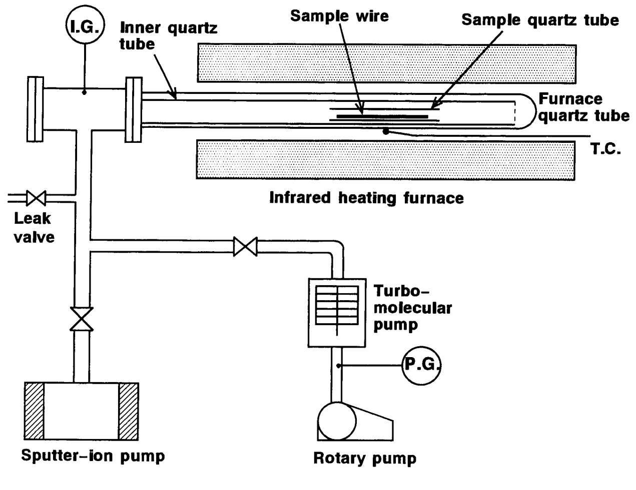

Fig. 1 Schematic drawing of a vacuum annealing apparatus for copper wire specimens.

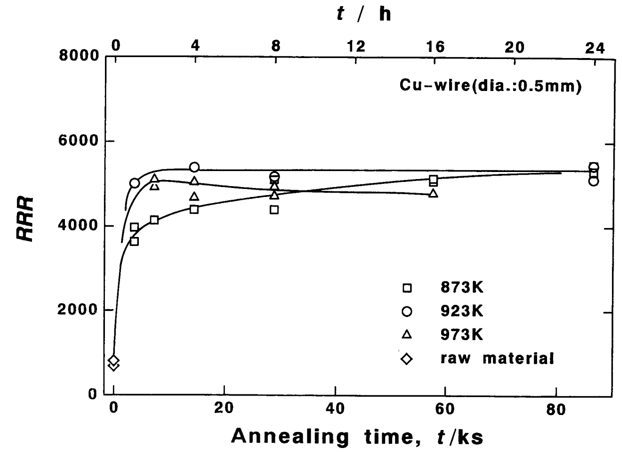

Fig. 2 Changes in *RRR* values of 6N copper wires 0.5 mm in diameter as a function of the annealling time at 873, 923 and 973 K.

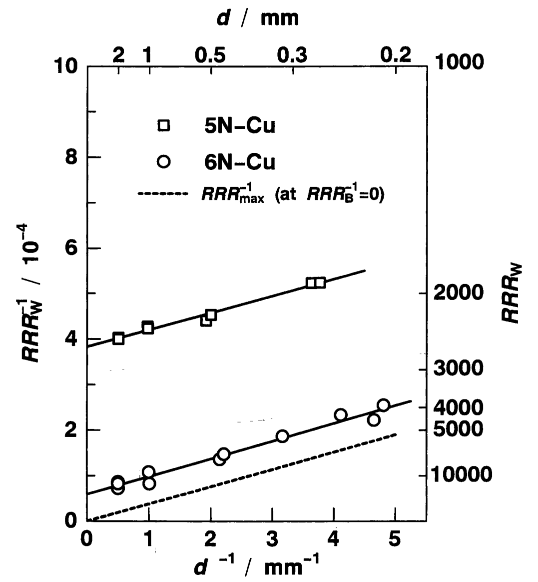

Fig. 3 Reciprocal residual resistivity ratio of 5N and 6N copper wires as a function of the inverse diameter. The dashed straight line is according to eq. (12), derived from the calculated maximum RRR_W (RRR_{max}) on the assumption of $RRR_B^{-1} \simeq 0$ ($RRR_B \simeq \infty$).

method.

$$RRR_W^{-1} = 3.83 \times 10^{-4} + (3.77 \times 10^{-5}) \cdot d^{-1} \tag{9}$$

$$RRR_W^{-1} = 5.92 \times 10^{-5} + (3.84 \times 10^{-5}) \cdot d^{-1}. \tag{10}$$

Since there is little difference in the slope of both straight lines, it is recognized that the appearance of the size effect on RRR_W according to eq. (8) is independent of the purity of the specimens. Therefore, the relationship between RRR_W^{-1}, RRR_B^{-1} and d^{-1} for the case of high purity copper can be generally represented by eq. (11), using the mean value of the slope 3.8×10^{-5} (mm).

$$RRR_W^{-1} = RRR_B^{-1} + (3.8 \times 10^{-5}) \cdot d^{-1} \tag{11}$$

In addition, the bulk residual resistivity ratios (RRR_B) of 5N and 6N copper are obtained to be approximately 2610 and 16900, respectively, from the intersection with the ordinate ($d^{-1} = 0$) of both straight lines.

We obtain the dashed straight line shown in Fig. 3 according to eq. (12) which is derived from eq. (11) under the assumption of RRR_B^{-1} to be nearly zero. Since $RRR_B^{-1} = 0$ corresponds to $RRR_B \simeq \infty$,

$$RRR_{max}^{-1} = (3.8 \times 10^{-5}) \cdot d^{-1} \tag{12}$$

this line indicates a relation between the reciprocal of the maximum RRR_W values (RRR_{max}), which is dependent only on the surface scattering of conduction electrons, and the inverse specimen diameter, d^{-1} (mm^{-1}).

As mentioned previously, the slope of eq. (11) is related to ρ and λ as shown in eq. (13).

$$\frac{\rho_{B,4.2\,K}\lambda_{B,4.2\,K}}{\rho_{B,298\,K}} = 3.8 \times 10^{-5}\ \text{(mm)}. \tag{13}$$

Since the room temperature resistivity of copper is $\rho_{298\,K} = 1.69 \times 10^{-16}\ \Omega m$, the product of $\rho \cdot \lambda$ at 4.2 K is obtained as eq. (14). This value of $\rho \cdot \lambda = 6.5 \times 10^{-16}\ \Omega m^2$ is in good agreement with the

$$\rho_{B,4.2\,K}\lambda_{B,4.2\,K} = 6.5 \times 10^{-16}\ \Omega m^2 \tag{14}$$

values from measurements of the diameter dependence (size effect) of copper thin wires, about 0.005 to 0.35 mm in diameter, with RRR_B of between about 200 and less than 3000 by Mende *et al.*(2), Arbuzov *et al.*(5) and Peterseim *et al.*(6) Then, it is clear that the diameter dependence of *RRR* represented by eq. (11) is applicable continuously to copper thin wires of less than 0.2 mm diameter with purities of 4N to 6N or higher.

On the other hand, according to the quasi-free electron model of metals(4)(9), the product $\rho \cdot \lambda$ is represented by

$$\rho\lambda = \frac{m_e v_f}{e^2 n}. \tag{15}$$

Here m_e is the electron mass (9.11×10^{-31} kg), v_f the electron velocity at the Fermi level (1.574×10^6 m/s for copper), e the electron charge (1.602×10^{-19} C), n the free electron density (approximately $8.5 \times 10^{28}\ m^{-3}$ for copper assuming one free electron per copper atom). As is well known, m_e, v_f, e and n for a given metal are constant and generally independent of temperature, so that $\rho \cdot \lambda$ results in a temperature independent constant. From eq. (15), a theoretical value of $\rho \cdot \lambda$ for copper is calculated to be

$$\rho\lambda = 6.6 \times 10^{-16}\ \Omega m^2 \tag{16}$$

Since this value is almost equal to that of eq. (14), it is recognized that assumptions such as one free electron per copper atom and the surface specular reflection of conduction electrons being negligible ($p = 0$) for polycrystalline copper wires are the reasonable ones.

3. Evaluation of metal-purity by the residual resistivity ratio

In Fig. 4, the residual resistivity ratios of 5N and 6N copper wires are plotted against the specimen diameter on a linear scale. On the other hand, the dotted line shows the calculated one, according to eq. (11), which corresponds to a purer copper having $RRR_W = 10000$ at $d = 0.5$ mm. The respective RRR_B value is indicated on the right side of each line.

The dashed straight line in the figure indicates the calculated maximum RRR_W values (RRR_{max}) at the respective specimen diameter d (mm), according to eq. (17) deduced from eq. (12).

$$RRR_{max} = (2.63 \times 10^4) \cdot d. \tag{17}$$

From this relation between the specimen diameter and the RRR_{max}, which is thought to be an ideal *RRR* value caused only by the diffuse surface scattering of conduction electrons, it is recognized that no matter how pure a copper specimen wire might be, its RRR_W at $d = 0.5$ mm, for example, does not exceed about 13200.

As seen in Fig. 4, the 5N copper wires do not exhibit practically so much differences in RRR_W with the specimen diameter in the range of 0.2 to 2 mm. On the other hand, it is clear that difference in RRR_W of 6N copper is

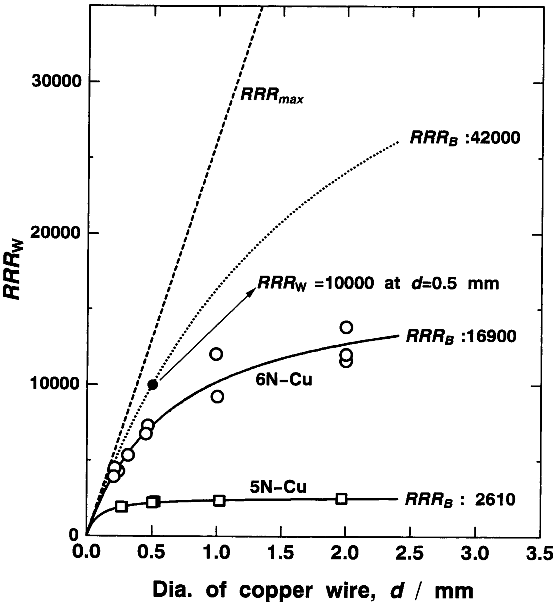

Fig. 4 Residual resistivity ratio of 5N and 6N copper wires as a function of the specimen wire diameter d. The dotted line shows the calculated RRR_W for the copper wire having $RRR_W = 10000$ at $d = 0.5$ mm. The dashed straight line indicates the calculated maximum RRR_W (RRR_{max}), according to eq. (17).

strongly dependent on the specimen diameter between 0.2 and 2 mm and then the difference enlarges with increasing specimen purity. For example, the RRR of 6N copper increases from about 7200 at $d=0.5$ mm to above 12000 at $d=2$ mm, and to 16900 as the RRR_B, which is more than double the value obtained at $d=0.5$ mm. Also, in the case of $RRR_W = 10000$ at $d=0.5$ mm, the RRR_B will be more than 4 times the value at $d=0.5$ mm. Therefore, when we evaluate the purity of a high purity metal and compare its purity with that reported in the literature by the use of RRR, the influence of the size dependence on them must be considered carefully and the specimen diameter and the RRR_B values must be discussed.

V. Conclusion

The diameter dependence (size effect) of the residual resistivity ratio (RRR) of the well-annealed high-purity copper (5N and 6N grade copper) wires 0.2–2 mm in diameter and the optimum annealing conditions of the specimen wire before the RRR measurement have been studied. The most suitable annealing temperature and period were determined to be 923 K and more than 14.4 ks, respectively.

For the size effect on the RRR, the relationship between RRR_W (RRR measured for high-purity copper wire with diameter d), RRR_B (RRR of the bulk copper) and the specimen diameter d (mm) was given as follows:

$$RRR_W^{-1} = RRR_B^{-1} + (3.8 \times 10^{-5}) \cdot d^{-1}.$$

The product of $\rho \cdot \lambda = 6.5 \times 10^{-16}\ \Omega\mathrm{m}^2$, obtained from the slope of the above equation, was in good agreement with a theoretical value of that calculated from the free electron model for copper with one free electron per atom.

Also, it has been found that difference in RRR_W of the high-purity metals is dependent largely on the specimen diameter. Therefore, the influence of the size dependence on RRR must be considered very carefully whenever to evaluate and to compare the purity of high-purity metals by RRR values.

REFERENCES

(1) J. E. A. Alderson and C. H. Hurd: Phil. Mag., **24** (1971), 1239.
(2) H. H. Mende and U. Neitz: Solid State Communications, **13** (1973), 1635.
(3) W. Vieweger and H. Wever: Z. Metallk., **66** (1975), 639.
(4) H. H. Mende and G. Thummes: Appl. Phys., **6** (1975), 93.
(5) V. L. Arbuzov, S. Ye. Danilov, S. M. Klotsman and V. N. Matveyev: Phys. Met. Metall., **45** (1978), 46; Fiz. metal metalloved., **45** (1978), 507.
(6) J. Peterseim, G. Thummes and H. H. Mende: Z. Metallk., **70** (1979), 266.
(7) L. Nordheim: *Act. Sci. et Ind.*, No. 131, Herman, Paris (1934).
(8) R. B. Dingle: Proc. Roy. Soc., **A201** (1950), 545.
(9) C. Kittel: *Introduction to solid state physics*, 3rd Edition, John Willey & Sons, (1967), p. 215.