The relationships between resistance and thermoelectric properties caused by impurities in metals

Y. Q. GAO, W. WANG*
Kunming Institute of Precious Metals, Kunming, Yunnan, China

A set of linear relationships between resistance and thermoelectric properties caused by impurities in metals have been derived from Matthiessen's rule and the Mott theory. These are the linear relationships between temperature coefficient of resistance and thermoelectric power or motive force, the change in resistance ratio and impurity concentration, and the change in temperature coefficient of resistance and impurity concentration etc. In terms of these linear relationships we have interpreted the empirical formulae and experimental results of platinum containing impurities in detail.

1. Introduction

It has been well known that empirical formulae were established to express the relationship between temperature coefficient of resistance and thermoelectric motive force (e.m.f.) in metals containing impurities or physical defects [1]. The temperature coefficient of resistance of platinum from 273 to 373 K can be described as

$$\alpha = 0.003922 - 0.5 \times 10^{-6}E \qquad (1)$$

where E is the e.m.f. of platinum against Pt27, which is a reference electrode in μV. 0.00392 is the temperature coefficient of resistance for Pt27. Rhys and Taimsale [2] have reported the effects of impurities with concentration up to 750 p.p.m. on the temperature coefficient and the thermoelectric power of platinum. They found a linear relationship between the change in temperature coefficient, thermoelectric power and the impurity concentration. Cochrane [3] also reported a linear relationship between tempeature coefficient and e.m.f., and the linear effects of impurities on electrical properties of platinum. He futher pointed out that the plot of effect on e.m.f. against atomic number showed periodicity.

No theoretical explanation has been given regarding either the linear relationships between temperature coefficient of resistance and thermoelectric properties or the periodicity of the effect on e.m.f. In this paper we have derived theoretically a set of equations to demonstrate these linear relationships. They are then used to interpret the empirical Equation 1 and the periodicity quantitatively.

2. Theory

2.1. Effect of impurity on the resistivity ratio and the temperature coefficient of resistance

Let us assume the validity of Matthiessen's rule. The total resistivity of a metal, ϱ, can be expressed as the sum of the residual (impurity) resistivity and thermal resistivity

$$\varrho = \varrho_x + \varrho_T \qquad (2)$$

where ϱ_x is the residual resistivity caused by the scattering of impurities and ϱ_T is due to the scattering of lattice vibration. If the impurities act independently, the total residual resistivity ϱ_x can be calculated as

$$\varrho_x = \sum_{i=1}^{n} \varrho_i = \sum_{i=1}^{n} C_i x_i \qquad (3)$$

Where ϱ_i is due to the scattering by impurity i, x_i is the atomic concentration of impurity i, C_i is the characteristic constant of resistivity caused by impurity i. When the concentration of impurity i increases from x_i to $x_i + \Delta x_i$, the change in resistivity ratio will be

$$\Delta\left(\frac{\varrho}{\varrho_0}\right)_i = \left(\frac{\varrho}{\varrho_0}\right)_{x_i+\Delta x_i} - \left(\frac{\varrho}{\varrho_0}\right)_{x_i}$$

$$= -\frac{\varrho_T - \varrho_{T_0}}{\left(\varrho_{T_0} + \sum_{i=1}^{n} C_i x_i\right)^2}(C_i \Delta x_i) \qquad (4)$$

where ϱ_0 and ϱ_{T_0} are the total resistivity and thermal resistivity at the reference temperature 273 K. ϱ and ϱ_T are the total resistivity and thermal resistivity at a specified temperature, say 373 K.

From Equation 4 we can conclude that the decrement of resistivity ratio, $(\varrho/\varrho_0)_i$, is proportional to the increment of the concentration of impurity i. The relationship between the temperature coefficients of resistivity and resistance is well documented as Equation 5

$$\alpha_\varrho = \alpha_R + \beta(1 + \Delta t \alpha_R) \qquad (5)$$

We also know

$$\frac{\varrho}{\varrho_0} = 1 + \Delta t \alpha_\varrho \qquad (6)$$

*Present address: Mechanical Engineering Department, Northeastern University, Boston, Massachusetts 02115, USA.

and

$$\frac{R}{R_0} = 1 + \Delta t \alpha_R \tag{7}$$

so that

$$\frac{R}{R_0} = \frac{1}{1 + \Delta t \beta}\left(\frac{\varrho}{\varrho_0}\right) \tag{8}$$

where α_ϱ and α_R are the temperature coefficients of resistivity and resistance respectively, the subscript 0 refers to the reference temperature, Δt is the temperature variation, β is the linear expansion coefficient. Considering a temperature range from 273 to 373 K, ϱ and R therefore stand for the resistivity and resistance at 373 K and $\Delta t = 100$ K. Combining Equations 8 and 4 we obtain

$$\Delta\left(\frac{R}{R_0}\right)_i = -\left(\frac{1}{1 + 100\beta}\right)\left[\frac{\varrho_T - \varrho_{T_0}}{\left(\varrho_{T_0} + \sum_{i=1}^{n} C_i x_i\right)^2}\right] \times (C_i \Delta x_i)$$

$$= -K_i \Delta x_i \tag{9}$$

$$K_i = \left(\frac{1}{1 + 100\beta}\right)\left[\frac{\varrho_T - \varrho_{T_0}}{\left(\varrho_{T_0} + \sum_{i=1}^{n} C_i x_i\right)^2}\right] C_i \tag{10}$$

Substituting Equation 9 into Equation 7 we get

$$\Delta(\alpha_{R_i})_i = (\alpha_R)_i - (\alpha_R)_0 = -\frac{K_i}{100}\Delta x_i \tag{11}$$

Equations 9 to 11 describe the resistance ratio change and the change in temperature coefficient of resistance, from 273 to 373 K, as a function of impurity concentration variation. When the impurity concentration increases, the temperature coefficient of resistance and resistance ratio decreases.

2.2. Effect of impurity on thermoelectric power and e.m.f. of metals

The thermoelectrric power of a metal, S, can be described by the following general equation [4]

$$S = \frac{\varrho_T S_T}{\varrho_T + \sum_{i=1}^{n} \varrho_i} + \frac{\sum_{i=1}^{n} \varrho_i (S_x)_i}{\varrho_T + \sum_{i=1}^{n} \varrho_i} \tag{12}$$

where $(S_x)_i$ is the thermoelectric power caused by impurity i in the host metal, S_T is the thermoelectric power due to the scattering by lattice vibration. At temperatures above the Debye temperature, we have [5]

$$S_T = aT \tag{13}$$

$$(S_x)_i = b_i T \tag{14}$$

$$\varrho_T = T\frac{d\varrho}{dT} = C_\varrho T \tag{15}$$

where a is the proportionality constant, b_i the temperature coefficient of thermoelectric power caused by impurity i. Combining Equations 12, 13, 14 and 15, the change of thermoelectric power ΔS_i caused by an increment of impurity concentration, Δx_i, will be

$$\Delta S_i = \frac{b_i - a}{C_\varrho}(C_i \Delta x_i) = J_i \Delta x_i \tag{16}$$

$$J_i = \frac{b_i - a}{C_\varrho} C_i \tag{17}$$

where J_i is the linear coefficient of the effect by impurity on the thermoelectric power of the metal. It is temperature independent to the first order of approximation.

We are now going to derive the relationship between the change in resistance ratio and the thermoelectric power. Combining Equations 9, 16 and 17 to eliminate $C_i \Delta x_i$

$$\Delta\left(\frac{R}{R_0}\right)_i = -\left(\frac{1}{1 + 100\beta}\right)\left[\frac{\varrho_T - \varrho_{T_0}}{\left(\varrho_{T_0} + \sum_{i=1}^{n} C_i x_i\right)^2}\right] \times \left(\frac{C_\varrho}{b_i - a}\right)\Delta S_i \tag{18}$$

Let $W = R/R_0$ and $W_i = (R/R_0)_i$, where W is the resistance ratio of the pure host metal and W_i is the resistance ratio of the metal containing impurity i. From Equation 15, $C_\varrho = (\varrho_T - \varrho_{T_0})/100$, using

$$\frac{\varrho_T - \varrho_{T_0}}{\varrho_{T_0} + \sum_{i=1}^{n} C_i x_i} = \frac{\varrho}{\varrho_0} - 1$$

and Equation 8 we can derive

$$\Delta\left(\frac{R}{R_0}\right)_i = W_i - W$$

$$= \frac{-[(1 + 100\beta)W - 1]^2}{100(1 + 100\beta)(b_i - a)}(\Delta S_i) \tag{19}$$

Equation 19 demonstrates the linear relationship between the change in resistance ratio and thermoelectric power caused by impurity in the metal. Using Equations 19 and 7, $\Delta t = 100$ K, we can get the linear relationship between the change in the temperature coefficient of resistance and the thermoelectric power.

$$\Delta(\alpha_R)_i = -\frac{\left[\frac{(1 + 100\beta)W - 1}{100}\right]^2}{(1 + 100\beta)(b_i - a)}(\Delta S_i)$$

$$= -\frac{[\alpha_{R_0}(1 + 100\beta) + \beta]^2}{(1 + 100\beta)(b_i - a)}(\Delta S_i)$$

$$\doteqdot \frac{-(\alpha_R)_0^2}{(b_i - a)}(\Delta S_i) \tag{20}$$

where $(\alpha_R)_0$ is the temperature coefficient of resistance of the pure host metal. The proportionality constant is dependent on both the characteristics of the host metal, $(\alpha_R)_0$ and a, and the temperature coefficient of thermoelectric power of impurity, b_i.

Now let us examine the relationship between the change in the temperature coefficient of resistance and the e.m.f. From Equation 16 we know that ΔS_i is temperature independent, so that

$$\Delta S_i = \frac{E_i}{t} \quad (21)$$

where E_i is the e.m.f. of the metal containing impurity i against the host metal from 273 to $(t + 273)$ K. Substituting Equation 21 into Equation 19 we have

$$\Delta\left(\frac{R}{R_0}\right) = W_i - W$$

$$= \frac{-[(1 + 100\beta)W - 1]^2}{100(1 + 100\beta)(b_i - a)}(E_i) \quad (22)$$

and

$$W_i = W - Q_i E_i \quad (23)$$

$$Q_i = \frac{[(1 + 100\beta)W - 1]^2}{100(1 + 100\beta)(b_i - a)t} \quad (24)$$

where Q_i is the proportionality constant. It not only depends on the impurity, but also depends on the host metal and temperature.

Substituting Equation 21 into Equation 20 we finally obtain

$$\Delta(\alpha_R)_i = (\alpha_R)_i - (\alpha_R)_0 = -\frac{(\alpha_R)_0^2}{(b_i - a)t}(E_i) \quad (25)$$

$$(\alpha_R)_i = (\alpha_R)_0 - Y_i E_i \quad (26)$$

$$Y_i = \frac{(\alpha_R)_0^2}{(b_i - a)t} \quad (27)$$

where Y_i is the linear coefficient of the relationship between the temperature coefficient of resistance and the e.m.f. from 273 to $(t + 273)$ K caused by impurity i.

3. Discussion

In Table I we summarize the K_i and J_i values from Rhys and Taimsale's report [2]. Substituting $\Delta x_i =$ 1 p.p.m. atomic percentage and the K_i and J_i values into Equations 9 and 16, respectively, we will be able to calculate $\Delta(R/R_0)_i$ and ΔS_i. Putting $\Delta(R/R_0)_i$ and ΔS_i into Equation 19, taking $\beta = 9 \times 10^{-6}\,\mathrm{K}^{-1}$ and $W = 1.3926$ for pure platinum, we can calculate the values of $(b_i - a)$ caused by various impurities: silicon, zinc, copper, silver, gold, palladium, nickel, rubidium, iridium, ruthenium and iron. The values of $(b_i - a)$ are listed in Table II. The thermoelectric powers are -4.45 and $-7.14\,\mu$V/K at the temperatures 273 and 373 K respectively [6]. Therefore the average value of a in this temperature region is $-0.0269\,\mu\mathrm{V/K}^2$. Then the values of b_i of various impurity could be calculated, which are also included in Table II.

The values of b_i for gold and iridium in platinum are consistent with that of dilute platinum alloys containing gold and iridium reported by Fletcher and Greig [7]. The b_i value of palladium in platinum is also consistent with Blood and Greig's result [8] qualitatively in sign but not numerically in magnitude. Maybe the concentration of palladium in the platinum alloy [8] is too large to be comparable.

From Table II we see that the b_i values caused by silicon, zinc, copper, silver and gold in platinum are negative. The elements silicon, zinc, copper, silver and gold are the simple metals. They do have free-electrons but have no vacancy in the d-electron state. The thermoelectric power under this scattering condition has to be negative despite the absolute thermoelectric powers of pure noble metals gold, silver and copper are positive. This is part of the endless confusion related to the sign of thermoelectric power. Further study is required for clarification. For most transition metal elements the b_i values are positive, with the exception of palladium, in platinum. However, both theoretical prediction and experimental data indicate a consistent negative sign for palladium in platinum. The periodicity of the effect on the e.m.f. can also be interpreted in terms of the periodic

TABLE I The effects of impurity (1 p.p.m. atomic percentage) on the resistance ratio and the thermoelectric power of platinum

Impurity	$K \times 10^6$ (1/p.p.m.)	$J \times 10^5$ (μV/K, p.p.m.)
Si	−9	9
Zn	−3.5	6
Cu	−11	5
Ag	−9	1.2
Au	−7	−7
Pd	−2.8	3.5
Ni	−3	10
Rh	−4.3	11
Ir	−16	56
Ru	−12	46
Fe	−12	49

TABLE II The values of $(b_i - a)$ and b_i caused by impurities in platinum

Impurity	$(b_i - a) \times 10^4$ (μV/K^2)	$b_i \times 10^4$(μV/K^2)	
		Calculated	Experimental
Si	157	−112	–
Zn	250	−19	–
Cu	69	−200	–
Ag	21	−248	–
Au	−158	−427	−600 [7]
Pd	187	−82	−500 [8]
Ni	479	210	–
Rh	396	127	–
Ir	540	271	350 [7]
Ru	583	314	–
Fe	623	354	–

TABLE III The linear coefficient of the relationship between the change in the temperature coefficient of resistance and e.m.f.

Impurity	$Y_i \times 10^6$(1/μV)	
	t = 1200 K	t = 1100 K
Si	0.82	0.89
Zn	0.51	0.56
Cu	1.87	2.04
Ag	6.16	6.72
Au	−0.81	−0.89
Pd	0.69	0.75
Ni	0.27	0.29
Rh	0.32	0.35
Ir	0.24	0.26
Ru	0.22	0.24
Fe	0.21	0.23

character of J_i. The e.m.f. can be calculated as

$$E_i = \int_0^t \Delta S_i \mathrm{d}t = J_i \Delta x_i t \quad (28)$$

$$J_i = \frac{b_i - a}{C_\varrho} C_i \quad (17)$$

C_i depends on the valence difference between the impurity and the host metal, Z or the effective charge, Ze [4]

$$C_i \alpha \left(\frac{Ze^2}{mv^2}\right)^2 \quad (29)$$

where e, m and v are the charge, mass and velocity of electrons, respectively. Since J_i is atomic number dependent, E_i must also bear the same periodicity of atomic number. New let us compare the empirical Equation 1 with the theoretical Equation 26. Using the values of $(b_i - a)$ in Table II and Equation 27, taking $(\alpha_R)_0 = 0.003922$, we get the values of Y_i, when $t = 1200$ and 1100 K, which are listed in Table III.

From Table III we know that the value of Y_i is impurity dependent therefore Equation 1 is only an approximate formula assuming that Y_i is equal to $0.5 \times 10^{-6}/\mu$V for all kinds of impurity. According to Corruccini [1], Equation 1 can be used for (a) pure platinum quenched at various rates and (b) annealed platinum which is contaminated by various impurties other than gold, silver and copper. This is in agreement with our results in Table III. The Y_i values of gold, silver and copper are quite different from $0.5 \times 10^{-6} \mu$V. If we take the average value of Y_i, when $t = 1200$ K, in Table III for impurities excluding gold, silver and copper, we get $0.41 \times 10^{-6}/\mu$V, which is very close to $0.5 \times 10^{-6}/\mu$V. Therefore Equation 1 can be considered as an equation for the average effect of various impurities on e.m.f. of platinum. This theory also applies to physical defects such as dislocations, vacancies etc., which can be considered as another kind of impurity other than chemical elements.

4. Conclusions

A theoretical interpretation for the empirical formula expressing the relationship between temperature coefficient of resistance and thermoelectric motive force in metals containing impurities is established. It has successfully predicted the impurity effects on resistance and thermoelectric power of platinum. Silicon, zinc, copper, silver and gold in platinum will induce negative thermoelectric power because their d-electron states are filled up. The predicted thermoelectric power values are consistent with the experimental results of gold and iridium. In the case of palladium the theory qualitatively predicts the correct sign of thermoelectric power but a numeric discrepancy exists.

The periodicity of the impurity effect on the e.m.f. of platinum is also interpreted through a relationship between C_i, which is a proportionality constant between resistance and impurity concentration, and atomic number.

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