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Modeling of Single Phase Alloy Electrical Resistivity

A Thesis

Presented To

The Faculty of the Department of Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Brian Rodrigues

May 1997

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ABSTRACT

Modeling of Single Phase Alloy Electrical Resistivity

by Brian Rodrigues

The resistivity of annealed copper-silicon and platinum-rhodium alloys was used as a basis to determine the ability of Matthiessen's rule to predict the electrical resistivity of single phase binary metallic alloys at 293 K. The electrical resistivity of Cu, Cu-3.46 a/o Si, and Cu-6.92a/o Si was found to be 1.756 $\mu\Omega$ -cm, 15.16 $\mu\Omega$ -cm, and 26.32 $\mu\Omega$ -cm, respectively. The electrical resistivity of Pt, Pt-17 a/o Rh, and Pt-22a/o Rh was found to be 10.89 $\mu\Omega$ -cm, 19.78 $\mu\Omega$ -cm, and 20.47 $\mu\Omega$ -cm, respectively. The results from this investigation, in conjunction with results previously published, show that the relationship between impurity concentration and resistivity is non-linear. For dilute concentrations the relationship between resistivity and impurity content is a second order polynomial equation, with impurity content affecting resistivity less at higher concentrations. For concentrated alloys the relationship is even more non-linear; for the Pt-Rh system it corresponded to a 4th order polynomial.

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CHAPTER 1

INTRODUCTION

Metals and alloys are currently used in numerous applications involving heat, temperature measurements, and signal and power transmissions. The applications and development of these materials requires a basic understanding of how the basic electrical properties of the host metal or solvent material are affected by the addition of impurity elements or solutes.

It is important to understand not only the electrical properties of a pure metal, but also the influence of impurities on the electrical properties. The effect of a specific solute, on the electrical properties of the host, is strongly influenced not only by the solute type and concentration, which causes distortions of the periodic crystal structure of the host, but also by the processing conditions that the material undergoes. Thermal heat treatments of the alloy during processing can have a strong effect on crystal imperfections which will affect electron scattering within the host.

The resistivity of a metal has been found to decrease linearly with decreasing temperature until it reaches a finite value. Thermal energy causes lattice atoms to oscillate about their equilibrium position causing an increase in the scattering of electron waves in the crystal. The resistivity arising from

crystal imperfections (impurities, vacancies, grain boundaries, and dislocations) are often considered to be thermally independent for purposes of determining resistivity.

The most commonly used mathematical model for determining the electrical resistivity of a metallic alloy is Matthiessen's rule. According to Matthiessen's rule the resistivity arising from independent scattering factors which are assumed to be additive in nature is given by

$$\rho = \rho_{th} + \rho_{imp} + \rho_{def} \quad [1]$$

where ρ_{th} is the thermal contribution, ρ_{imp} is the contribution from impurities, and ρ_{def} is the contribution from defects.

This study was undertaken to investigate the additivity assumption of Matthiessen's rule. Several of the models used for predicting the impurity contribution to the room temperature electrical resistivity for binary solid solution metallic alloys were first evaluated. The results from the models were compared against actual measurements taken at room temperature, for a copper-silicon and a platinum-rhodium alloy, both of which were single phase alloys.

The historical background behind the basic modeling theories is presented in Chapter 2. The alloy systems selection and historical results are presented in Chapter 3. The research objectives are contained in Chapter 4.

The experimental methodology is described in Chapter 5, followed by the experimental results in Chapter 6, and a discussion of the values and responses predicted by the various models in Chapter 7. Conclusions and recommendations for future research are presented in Chapter 8 and references are presented in Chapter 9.

CHAPTER 2

REVIEW OF EXISTING THEORIES AND MODELS

2.1 Historical Background

When an impurity atom is dissolved into a crystalline matrix, either as a substitutional or interstitial solute, a lattice distortion is produced and a stress field is generated around the atom. In the case of a substitutional solute atom, the distortion occurs whenever the solute atom is either larger or smaller than the solvent atom. Interstitial solutes cause distortions because they are usually larger than the interstitial sites they occupy. A representation of the changes in the lattice structure for both substitutional and interstitial solute atoms is presented in Figure 1.

Electron motion in a solid can be described by considering the electron to behave as a wave, rather than as a particle. In this model for electron conduction in a solid, the electron waves in a crystal lattice are scattered by the lattice atoms. Scattering is accomplished by the lattice atom absorbing the energy of the electron wave, and then re-emitting the energy of the wave. For a periodic crystal structure, it can be shown that the individual waves in the forward direction are in phase and constructively interfere (coherent scattering). In a perfect crystal, waves do not change propagation direction or

Figure 1. Effect of impurity atoms on lattice structure: 1) Interstitial impurity; substitutional impurity with 2) $r_{\text{sub}} < r_{\text{lattice}}$ and 3) $r_{\text{sub}} > r_{\text{lattice}}$.

lose energy, so there is no energy loss during electron conduction in the material.

Impurity atoms, vacancies, thermal vibrations and grain boundaries will cause localized breakdowns in the periodic structure of the crystal. In these cases the scattered waves have no phase relationships and are incoherently scattered. Electron waves propagating through the crystal will lose energy and be scattered in directions other than the forward direction. This energy loss is represented as a loss in electron conductivity, or a *resistance* to electron travel.

The addition of as small an amount as 0.06% iron is sufficient to lower the conductivity of a rolled copper rod to 90% of the International Association

of Copper Society (IACS) value. This value is also affected by heat treatment of the rod.⁽¹⁾ Some of the impurities added to the solid solution can be precipitated out of the solid solution by proper processing techniques. An example of this is the copper alloy C19400 (Cu-97.5%, Fe-2.35%, P-0.03%, Zn-0.12%). During hot rolling iron and phosphorous are taken into solution, increasing the electrical resistivity. But, with a controlled process and subsequent annealing, the iron and phosphorous can be precipitated out of solution, slightly reducing the electrical resistivity.⁽²⁾

Impurities which come out of the solid solution in the form of precipitates, compounds, or inclusions, do not affect the crystal structure in a manner sufficiently significant to decrease the conductivity. This is because once the impurities come out of solution they segregate toward the grain boundaries. This reduces the amount of distortion of the crystal lattice within each polycrystalline grain. The overall electrical conductivity is increased due to the increase in conductivity within each of the grains.

In 1862, Matthiessen and Voigt observed experimentally that the temperature coefficient of the electrical resistivity for a dilute solid solution, binary metallic alloy, was approximately equal to that for the pure metal. The resistivity of the alloy could then be described by considering that there were two dominant and independent electron scattering factors in the material: impurity scattering and phonon scattering.

Phonon scattering is considered to be due only to the scattering of the electron waves by phonons (quantized lattice vibrations) in the lattice structure of the alloy, which, for dilute alloys, is dependent on the solvent material only. Impurity scattering is caused by the additional distortion of the lattice space surrounding each of the impurity, or solute, atoms. The resistivity change created by the impurity atoms is then considered to be temperature insensitive, and concentration dependent. Matthiessen's rule, as a function of concentration (c) and temperature (T), is often written as:

$$\rho_{\text{alloy}}(c,T) = \rho_{\text{solvent}}(0,T) + \rho_{\text{impurity}}(c,0) \quad [2]$$

where $\rho_{\text{alloy}}(c,T)$ is the overall resistance of the alloy, $\rho_{\text{solvent}}(T)$ is the thermal contribution to electrical resistivity, and $\rho_{\text{impurity}}(c)$ is the impurity contribution to electrical resistivity. This rule is valid only if the resistivity due to the impurity contributions are independent of temperature, and if the time between electron collisions is isotropic.

According to Bass, et al.,⁽³⁾ at room temperature, electrical resistivity values of dilute alloys do not usually differ by more than 10% from Matthiessen's rule, which was originally established for dilute alloys, with less than 1-3 atomic per cent (a/o) impurities. However, the rule is often applied to the case of concentrated alloys, and is also used to account for all factors such as vacancies, dislocations, and grain boundaries, that may affect

the electron scattering due to atomic disorder.⁽⁴⁾ In a recent paper, for example, Drew, et al.,⁽⁵⁾ used the following expression for electrical resistivity

$$\rho_A(c,T) = \rho_S(T) + \rho_i(c) + \rho_{CW} + \rho_{GB} \quad [3]$$

where ρ_{CW} is the contribution to electrical resistivity due to cold working and ρ_{GB} is the resistivity due to scattering by the grain boundaries. For fully annealed materials it is usually assumed that $\rho_{GB} \sim 0$, and that $\rho_{CW} = 0$. Drew, et al., determined that the room temperature contributions due to ρ_{CW} and ρ_{GB} were between 0.04 to 0.10 $\mu\Omega\text{-cm}$ for α -brasses, and depended on the material and the amount of cold working.

A more general expression for the overall impurity contribution in a metallic alloy due to all possible scattering factors is given by

$$\rho_0(c) = \rho_i(c) + \rho_{CW} + \rho_{GB} + \dots = \sum_i \rho_i(c) \quad [4]$$

where each $\rho_i(c)$ is the contribution to the total electron scattering from each scattering mechanism, all of which are assumed to be temperature independent. It is generally assumed that these scattering processes are independent of each other and are additive, as expressed in [4]. $\rho_0(c)$, the *residual alloy resistivity*, is usually approximated by

$$\rho_0(c) = \rho_A(T \rightarrow 0) \quad [4a]$$

There is a large body of work devoted to determining how well Matthiessen's rule fits existing alloy systems. Deviations between Matthiessen's rule and empirical data are usually represented by an additional parameter, $\Delta(c,T)$. There are some studies which assume that Δ is also only temperature dependent. The general form of Matthiessen's rule, including $\Delta(c,T)$ then becomes

$$\rho_A(c,T) = \rho_S(T) + \rho_0(c) + \Delta(c,T) \quad [5]$$

For multiphase alloys the electrical resistivity is considered to be dependent on the resistivities of the component phases and their volume fractions. For an alloy with three phases, α , β , and γ , with resistivities ρ_α , ρ_β , ρ_γ , respectively, and component phase volume fractions of x_α , x_β , x_γ , the electrical resistivity is expressed by ⁽⁶⁾

$$\rho_{\text{alloy}} = \rho_\alpha x_\alpha + \rho_\beta x_\beta + \rho_\gamma x_\gamma \quad [6]$$

Since the original work by Matthiessen and Voigt, there have been many models proposed to predict the relationship of the impurity component of the electrical resistivity and to explain deviations from Matthiessen's model.⁽⁷⁾ Other theoretical models have been proposed, based on solid state and quantum physics, to provide better estimates of the residual resistivity term in Equation [4].

The models used to calculate the impurity component of the electrical resistivity for a disordered single phase (random) binary metallic alloy can be separated into two groups: dilute alloys (containing less than 3 a/o impurities) and concentrated alloys.

2.2 Theoretical Models (Dilute alloys)

The most common models used for calculating the impurity component of the electrical resistivity of dilute alloys are Nordheim's rule and the Linde-Norbury rule. Deviations from Matthiessen's rule for alloys that have both s and d conduction bands have been previously studied by J. Dugdale and Z. Basinski,⁽⁸⁾ who have proposed a two band model to explain these deviations. M. Cimberle, et al,⁽⁹⁾ have proposed an alternative model to the two band model to explain low temperature electrical resistivity measurements on dilute substitutional metallic alloy systems. The residual resistivity of dilute alloys has been previously calculated using phase shift methods, one of which is the Coleridge, Holzwarth and Lee (CHL) model.⁽¹⁰⁾

2.2.1 Nordheim's Rule (Dilute Case)

In the case of a dilute alloy the resistivity is often assumed to depend linearly upon the concentration of solute atoms present. In this case the residual resistivity term can be rewritten as

$$\rho_0(c) = K n_i' \quad [7]$$

where n_i' is the impurity concentration (in atomic per cent), and K is an experimentally determined value that depends both on the solute and solvent atoms.

The phonon contribution is approximated by the pure metal resistivity and is also linearly related to the temperature by

$$\rho_s(T) = K'T/\Theta_\Theta^2 \quad \text{for } 2/3\Theta_R < \Theta < 250^\circ\text{C} \quad [8]$$

where Θ_Θ is the Debye temperature. Θ_R , the characteristic temperature, and K' are empirically determined constants for the solvent atoms. According to Schröder,⁽¹¹⁾ equation [8] is true at room temperature. Matthiessen's rule can then be rewritten as

$$\rho_A(c,T) = \rho_s(0,T) + \rho_i(c,0) \quad [9]$$

$$= Kn_i' + K'T/\Theta_\Theta^2 \quad \text{for } 2/3\Theta_R < \Theta < 250^\circ\text{C} \quad [10]$$

Values for K , K' , and Θ are available for many host elements and impurities from Schröder.⁽¹²⁾

2.2.2 Linde-Norbury Equation

In 1931, according to Rossiter,⁽¹³⁾ Linde determined from experimental data that the ratio of the change in resistivity per change in atomic solute concentration ($\Delta\rho/\Delta c$) was dependent on the square of the valence differences between the solute and host atoms ($[\Delta Z]^2$). Linde's equation can be written as

$$\Delta\rho_i = [k_2 + k_1 (Z_{\text{host}} - Z_{\text{solute}})^2] \Delta C \quad [11]$$

where Z_{host} is the valence of the host atoms and Z_{solute} is the valence of the solute atoms. If the quantity $\Delta\rho_i/\Delta C$ is plotted against $(Z_{\text{host}} - Z_{\text{solute}})^2$, the result should be a line with slope k_1 and intercept k_2 , as seen in Figure 2. For a specific solvent the values of k_1 and k_2 are valid for solutes from a given row in the periodic table. The effects of each of the alloying impurities in the host matrix is additive and the total change is given by

$$\rho_i(c) = \sum \Delta\rho_i \quad [12]$$

Figure 2. Change in resistivity for one atomic per cent impurity in Cu as a function of (ΔZ^2) . (after Linde 1932).

2.2.3 Two band model

One of the models that attempts to explain $\Delta(c,T)$ in alloys that have conduction electrons in both the s and d orbitals is the two band model.^(14,15) In this model the electrons in the valence bands are viewed as two distinguishable groups of electrons, group A (s-band) and group B (d-band), which do not interactively scatter with each other. The resistivity of group A is made up of two components ρ_{A1} and ρ_{A2} . The group B resistivity is also made up of two components ρ_{B1} and ρ_{B2} . The electron groups are therefore conducting in parallel. The $\Delta(c,T)$ term in equation [4] is then replaced with

$$\Delta(c, T) = \frac{(\rho_{A1}\rho_{B2} - \rho_{A2}\rho_{B1})^2}{(\rho_{A1} + \rho_{B1})(\rho_{A2} + \rho_{B2})(\rho_{A1} + \rho_{B2} + \rho_{A1} + \rho_{B2})} \quad [13]$$

A more specific form of the two band model is described by Azarbar, et al.⁽¹⁶⁾ as follows:

$$\Delta(T) = \gamma\beta \rho_s(T) \rho_0(c) / [\gamma\rho_s(T) + \beta \rho_0(c)] \quad [14]$$

where γ and β represent the ratios of the phonon and impurity scattering between the contributing bands. Both γ and β are expected to be temperature dependent.

The predictions of the two band model can be tested by plotting $(\Delta T)^{-1}$ against $\rho_0(c)^{-1}$ at a fixed temperature. According to Equation [14] the plot should result in a straight line with a slope of β^{-1} and a y intercept of $[\gamma \rho_s(T)]^{-1}$.¹ A typical plot for this model is shown in Figure 3.⁽¹⁷⁾

Figure 3. Representative plot of $[\Delta(T)]^{-1}$ against ρ_0^{-1} for a Pt-Ti alloy at 300K.

2.2.4 The CBR model

M. Cimberle, G. Bobel, and C. Rizzuto⁽¹⁸⁾ have suggested the following empirical fit to the experimental data for $\rho_A - \rho_0$, as a function of ρ_0 .

$$\rho_A(c,T) = \rho_S(T) + \rho_i(c)$$

$$\rho_0(c) < \rho'_0(T)$$

$$\rho_A(c,T) = \rho_S(T) + \rho_i(c) + K_f(T) \log [\rho_0(c) / \rho'_0(T)] \quad \rho_0(c) > \rho'_0(T) \quad [15]$$

Cimberle, et al. have previously used this model in their studies involving various dilute metal alloys at low temperature, and copper alloy systems to temperatures as high as 300 K.

For $\rho_0(c) < \rho'_s(T)$ the temperature -dependent part of the resistivity is once again considered to be independent of $\rho_0(c)$, within experimental error, so that Matthiessen's rule is valid. For $\rho_0(c) > \rho'_s(T)$ the thermal contribution does depend on impurity concentration, such that Matthiessen's rule is no longer valid. The available data from Cimberle, et al., for various copper alloys at 298.1 K is shown in Figure 4. The dashed lines represent the fit to Equation [15].

In their paper, Cimberle et. al., indicate that their model provides a better fit than the two band model for the case of aluminum at 20 K, but that there is still some discrepancy, especially at the lower impurity levels. All of Cimberle's comparisons were done at low temperatures, typically below the Debye temperature of the pure metal.

Figure 4. $\rho_A - \rho_0$ as a function of residual resistivity, at 298.1K, for selected copper alloys.

2.2.5 Residual Resistivity (CHL Model)

Models for determining the residual resistivity in dilute alloys have been developed; these utilize the description of the scattering of electrons. A. Lodder, et al.⁽¹⁹⁾ compared several of these models, all of which were based on the phase shift method, described in quantum mechanics texts,⁽²⁰⁾ to solve for the scattering of plane waves from a spherically symmetric potential site.

The CHL model, first proposed by Coleridge, et al.⁽²¹⁾ is an advanced phase shift method which utilizes Green's function to determine the band

structure of transition metal alloys. The residual resistivity calculations using the CHL model, for various dilute copper alloys, is shown in Figure 5.

Figure 5. Residual resistivity calculations of copper with various impurities, using the CHL model. The black squares are experimentally determined values. (from Lodder, et al.)

2.3 Theoretical Models (Concentrated alloys)

The most commonly used model for concentrated alloys is Nordheim's rule.

2.3.1 Nordheim's Rule

According to Nordheim's rule, the isothermal residual resistivity as a function of the fractional atomic composition X_A and X_B , for a given series of binary A-B solid solutions is given by

$$\rho_i(c) = X_A \rho_A + X_B \rho_B + C X_A X_B \quad [16]$$

where C is an empirically determined material constant. For a binary solution, if X_B is the atomic per cent of the impurity atom present, then

$$X_A = (1 - X_B) \quad \text{where } 0 \leq X_B \leq 1 \quad [17]$$

Nordheim's equation can then be reduced to

$$\rho_i(c) = \rho_A (1 - X_B) + \rho_B X_B + C (1 - X_B) X_B \quad [18]$$

$$\rho_i(c) = -CX^2 + (\rho_B - \rho_A + C)X + \rho_A \quad [19]$$

Equation [19] then describes an inverted parabolic function as shown in Figure 6.

The maximum resistivity defined by Nordheim's equation is given by

$$\frac{\partial \rho_i}{\partial x} = -2CX_B + \rho_B - \rho_A + C = 0 \quad [20]$$

This function has a maximum when $2 C X_B = \rho_B - \rho_A + C$. If the resistivity of the two pure metals are approximately equal, then the predicted maximum resistivity of the solid solutions will occur at the point where $X_B \sim 50\%$. This

seems to make intuitive sense, since adding increased levels of B to A should cause an increase in resistivity from the pure case, yet there must be some point for increasing B in A, that the resistivity begins to converge towards the resistance for pure B.

Figure 6. Predicted response of Nordheim's equation for the residual resistivity of the Cu-Ni alloy system at 0°C, using a value of $C=200$.

It has been suggested that Nordheim's rule should only be applied to single phase disordered alloys, but that solid solutions containing transition metals do not generally obey the rule, while solid solutions where the solvent and solute atoms are in the same column of the periodic table provide good agreement with the rule.^(22, 23)

The ability of these models to predict the effect of the impurity component on the electrical resistivity, after Matthiessen's rule, according to how well each of these models predicts electrical resistivity values when applied to specific alloy systems, was investigated during the course of this research.

Chapter 3

ALLOY SELECTION

Since Matthiessen's rule normally applies only to metallic solid solutions, the alloy systems chosen for this work were also required to meet these conditions. Matthiessen's rule has been previously applied to multiphase systems, but in order to study the simplest case of Matthiessen's rule this study focused on single phase metallic alloy systems. Initial selection of the alloy systems to be investigated in this study, using the above criterion, was done using binary alloy phase diagrams⁽²⁴⁾ and alloy reference guides.^(25,26)

In order to obtain accurate measurements of the electrical resistivity of the specimens the experimental method required that the material be in the form of thin wires or strips. It was also decided that the materials to be investigated be commercially available, in either of these two forms.

The literature previously examined showed that the Cu-Si system had not been thoroughly investigated, with regards to electrical resistivity models. As can be seen from Figure 7, at 25°C, there is a single phase region in the Cu-Si phase diagram that consists of a Cu-rich α region extending to a maximum solid solubility of 8 a/o (atomic percent) Si.⁽²⁷⁾

Figure 7. Portion of the Cu -Si phase diagram.

There are two commercially available forms of Cu-Si alloy below the 8 a/o solubility limit. These are C65100 (Cu - 3 a/o Si) and C65500 (Cu - 6 a/o Si). The silicon concentration values for both of these alloys, in the form of wires, is specified in ASTM B99-86a and B99M-86a.⁽²⁸⁾

The literature previously examined also showed that the Pt-Rh system had not been thoroughly investigated, with regards to electrical resistivity models. Rhodium is completely miscible in platinum, as seen in the phase diagram in Figure 8.⁽²⁹⁾ Since Pt-Rh wires are used commercially as

thermocouples for temperature measurement, they are also available in very pure compositions in the form of wires.

Figure 8. Portion of the Pt-Rh phase diagram.

Analysis of data found in the "CRC Handbook of Electrical Resistivity of Binary Metallic Alloys" by Schröder⁽³⁰⁾ shows some discrepancies in the reported data for the copper-silicon alloy system. In addition the data presented for the platinum-rhodium alloy system does not seem to fit the behavior predicted by Matthiessen's model. It was therefore thought that it would be important to study the electrical properties of these commercially available alloys to determine how well the experimental data for these

systems fit the electrical resistivity models that currently exist. Platinum has conduction electrons in both the s- and d- bands, making it an ideal candidate to compare the two band model against other modeling systems.

3.1 Previous Studies of Electrical Resistivity

3.1.1 Cu-Si system

Previous electrical resistivity studies of the Cu-Si system for alloys extending up to 8.24 a/o Si, have been reported by Domenicali, et al.⁽³¹⁾ and is reported by Schröder, along with other data, in "The CRC Handbook of Electrical Resistivity of Binary Metallic Alloys".⁽³²⁾ Domenicali's data, as a function of temperature is presented in Figure 9, and the additional data from Schröder is presented in Figure 10.

Domenicali and Otter reported that the Cu-Si system obeyed Matthiessen's rule fairly well. They reported an increase in resistivity as a function of silicon concentration, $\partial\rho/\partial c$, of $7.2\ \mu\Omega\text{-cm}$ at -190°C , and $8.7\ \mu\Omega\text{-cm}$ at 840°C . Although this data was originally reported in the paper by Domenicali and Otter, only the experimental data was reported by Schröder. Schröder reported a $\partial\rho/\partial c$ derived from additional data of $5\ \mu\Omega\text{-cm}$ per a/o Si.

Figure 9. Electrical resistivity of Cu-Si alloys.

Figure 10. Resistivity at 273°K of Cu-Si alloys for various silicon concentrations.

3.1.2 Cu-Si Data Analysis

A plot of resistivity versus silicon concentration in copper, for different temperatures, extracted from Domenicali's data presented in Figure 9, is tabulated in Table 1, and shown in Figure 11.

Table 1. Electrical Resistivity data ($\mu\Omega\text{-cm}$) from Domenicali, et al.

atomic % Si	T = -190°C	T = 25°C	T= 840°C
0	0	1.698	7.13
2.92	10.12		18.68
4.48	14.94	16.3	24.1
5.23	16.64	18.34	26.15
6.46	19.69	21.39	30.23
8.41	22.75	24.79	35.32

Using a linear relationship between solute concentration and resistivity, for temperatures of -190°C, 25°C, and 840°C, a $\partial\rho/\partial c$ of 2.75, 2.82, and 3.36, $\mu\Omega\text{-cm}$ was determined, respectively. These values are in disagreement with those originally reported by Domenicali and Otter.

A linear fit of Schröder 's data, shown in Figure 12, indicates a $\partial\rho/\partial c$ of 4.17 $\mu\Omega\text{-cm}$. Schröder reports the value of K, for dilute alloys, for silicon in copper as being 3.1 $\mu\Omega\text{-cm a/o}$,⁽³³⁾ a value 17% higher than that calculated from Figure 11, but in close agreement with the analysis of the data from Domenicali and Otter. The error here could be due to the original

Figure 11. Resistivity of Cu-Si alloys at various temperatures from Table 1.

transcribing of data used in Figure 12, or to the number of points used in obtaining the linear estimate. The original data was not available for a more detailed analysis.

3.1.3 Pt-Rh system

Previous electrical resistivity studies of the Pt-Rh system for well annealed wire specimens, with 17, 22, and 45 a/o rhodium has been completed by Macfarlane and Collins,⁽³⁴⁾ and are also reported by Schröder.⁽³⁵⁾ The resistivity values for the annealed wires at three different temperatures are summarized in Table 2, and plotted as a function of a/o Rh in Figure 14.

Table 2. Electrical Resistivity ($\mu\Omega\text{-cm}$) data from Macfarlane, et. al.

Alloy	4.2 K	77 K	293 K
Pt-17 a/o Rh	10.1	11.9	18.8
Pt-22 a/o Rh	11.7	12.8	20.3
Pt-45 a/o Rh	12.3	13.3	18.9

Figure 12. Resistivity of Pt-Rh alloys at various temperatures.

Previous values of the electrical resistivity values for Pt-17 a/o Rh and Pt-22 a/o Rh, at 293 K, were reported by Macfarlane, et al., as being 19.0 and 19.6 $\mu\Omega\text{-cm}$ respectively.⁽³⁶⁾ Macfarlane's data agreed with these values within the experimental error reported in his paper.

Stewart and Huebener⁽³⁷⁾ studied the electrical resistivity properties and their deviations from Matthiessen's Rule, of dilute gold and platinum alloys. Their experiments included a number of annealed and then rapidly quenched pure Pt wires, in addition to one study done on a Pt-9 a/o Rh alloy. They reported for the Pt-9 a/o Rh a value of $\partial\rho/\partial c$ of $0.76\ \mu\Omega\text{-cm/a/o}$ and a residual resistivity value ρ_0 of $6.91\ \mu\Omega\text{-cm}$.

3.1.4 Analysis of the Pt-Rh system

Macfarlane and Collins's data, at room temperature, for the Pt-Rh alloys do not appear to follow the simple case of a linear relationship with solute concentration, since the value of $\partial\rho/\partial c$ is supposed to remain constant, and always positive. If the simplest form of Matthiessen's Rule were to be applicable to this system, then the resistivity should continue to linearly increase as a function of increased rhodium content.

Schröder reports a value of $0.7\ \mu\Omega\text{-cm a/o}$ for $\partial\rho/\partial c$, for rhodium in platinum at room temperature (25°C),⁽³⁸⁾ and a value of the temperature dependent resistivity of Pt as $9.81\ \mu\Omega\text{-cm}$ at 25°C . Schröder's value of $\partial\rho/\partial c$ is in close agreement with that of Macfarlane and Collins. Using Schröder's value of $\partial\rho/\partial c$, the theoretical resistivity values for the Pt-Rh alloys at 25°C were calculated for the various alloys studied by Macfarlane and Collins, and are presented in Table 3.

Table 3. Experimental vs. Theoretical resistivity values for Pt-Rh alloys.

Alloy	at. % Rh	Experimental values at 20°C $\mu\Omega\text{-cm}^{(37)}$	Calculated values at 25°C $\mu\Omega\text{-cm}$
Pt-17 a/o Rh	17	18.8	21.7
Pt-22 a/o Rh	22	20.3	25.2
Pt-45 a/o Rh	45	18.9	41.3

Chapter 4

RESEARCH OBJECTIVES

Matthiessen's rule, in its simplest form is given by

$$\rho_{\text{alloy}}(c,T) = \rho_{\text{solvent}}(0,T) + \rho_{\text{impurity}}(c,0) \quad [21]$$

and is based on the independence and additivity of the thermal factor, $\rho_{\text{solvent}}(0,T)$, and the impurity factor, $\rho_{\text{impurity}}(c,0)$. When disagreement between the theoretical model and experimental data exists an additional term $\Delta(c,T)$ is often added to the equation. There do not appear to be any significant studies evaluating the ability of Matthiessen's rule, in its simplest form, to accurately predict the electrical resistivity for single phase binary metallic alloy systems over a broad range of impurity concentrations. The principal objective in this study was to evaluate the ability of Matthiessen's rule to predict the electrical resistivity for two distinct single phase alloy systems. This study focused on the simplest case for Matthiessen's rule by studying alloy systems at a fixed temperature (20°C), and only varying the impurity concentration in each of the alloy systems investigated. Several modeling schemes exist for calculating the impurity term in Matthiessen's rule. The objectives of this investigation were as follows:

1. Comparison of several models for predicting $\rho_{\text{impurity}}(c,0)$, at room temperature, for selected alloy systems.
2. Experimental determination of resistivity for selected alloy systems.
3. Determination of effects of grain size on electrical resistivity, and comparison with values given by Drew, et al.⁽³⁹⁾
4. Comparison of experimental data with data predicted from Matthiessen's rule.
5. Suggest changes to existing models.

Chapter 5

EXPERIMENTAL METHODOLOGY

5.1 Experimental Overview

The experimental effort can be divided into 6 major categories:

1. Preparation of wire specimens for annealing and resistance measurements.
2. Annealing of wire specimens to remove any residual cold working in the material from the wire forming process.
3. Annealing and rapid quenching of the pure metal specimens to quench in defects and determine the contribution of vacancies to the electrical resistivity.
4. Determination of the electrical resistivity of the alloy and pure wire specimens, using a micro-ohmmeter and a Kelvin-type double bridge meter.
5. Chemical analysis of the copper-silicon alloy specimens to determine actual concentration of silicon and other impurities.
6. Determination of average grain sizes for each specimen, in directions both perpendicular and parallel to the wire length.

5.2. Experimental materials

The specimens of commercially available Cu-Si alloys studied, in the form of thin wires of approximately 0.889 mm diameter, were donated by John McKeone of Ansonia Copper and Brass, Inc. Ansonia does not directly make a C65500 alloy (7.16 a/o Si, 0.7a/o Mg, 0.07a/o Fe, 0.05a/o Sn), but does make a C65600 alloy, which has the same silicon composition as the C65500 alloy.⁽⁴⁰⁾ Pure copper wire (99.98%) with a wire diameter of 0.889 mm was purchased from Omega Engineering Inc.

Pure platinum (99.999%) wire and Pt-Rh alloy wires with 17, and 22 a/o Rh, were purchased from Omega Engineering, Inc. All platinum alloy samples were 0.762 mm in diameter.

A sample size of five was used for each set of annealed specimens, and a sample size of nine was used for the as-received material. All specimens were cut to a minimum length of 310 mm. This was done to ensure that all specimens met the dimensional requirements of 300 mm, as required by ASTM B193-87. The additional 10 mm length was useful for the Pt alloys because the thin wires could be easily broken in the Kelvin clips, requiring that their length be constantly checked and re-measured during the resistance measurements.

An additional 50 grams of material, from both the annealed and as received alloys of the copper silicon, was required to determine actual silicon concentration and the amount of other impurities present.

5.3 Dimensional measurements

Specimen lengths were measured using a calibrated metal ruler and a caliper. The caliper accuracy was ± 0.03 mm. Five separate measurements of the length were taken for each specimen, and the values averaged.

The cross sectional area of the specimens was determined from the average diameter of each specimen along its length. Measurements of the diameter were taken at 5 equidistant points along the wire, as shown in Figure 13, using a Normarski microscope.

Figure 13. Diagram showing approximate points along each wire specimen where diameter was measured.

The microscope was fitted with the following objective lenses: 6.5x, 10x, 20x, 40x, and 100x. The eyepiece lenses were 10x magnification. One eyepiece was fitted with a measuring reticle with a scale of 10 mm in 0.1mm increments. The magnification settings of the microscopes were calibrated with a microscope slide etched with 100 lines/mm Ronchi Rulings. Cellophane tape was used to maintain the placement of the wire specimens on the microscope stage, to avoid any specimen vibration during the measurements.

5.4 Annealing

The annealing conditions for each of the pure metals and alloys investigated are presented in Table 4. Quenching of the pure copper and

Table 4. Annealing and quenching conditions for materials investigated.

Material	Atmosphere	Time/ temperature	Quench rate/ medium
Cu	1×10^{-5} Torr	1 hour / 600 °C	10 °C/min. / Argon gas
Cu	1×10^{-5} Torr	30 minutes / 600 °C	~ 8°C/min. / Vacuum
Cu-Si	1×10^{-5} Torr	30 minutes / 600 °C	~ 8°C/min. / Vacuum
Pt	Air	1 hour / 900 °C	fast quench/ ice water 0°C
Pt	Air	1 hour / 900 °C	~ 7°C/min./ Air
Pt-Rh	Air	1 hour / 900 °C	~ 7°C/min./ Air

pure platinum specimens was done to induce vacancies in the pure specimens, to determine if Matthiessen's rule was applicable to vacancy concentrations in the same manner it is applied to impurity concentrations. Quenching of the copper alloys and platinum alloys was not attempted in order to avoid confounding the resistance contribution in these alloys due to the solute atoms, with the resistance contribution due to vacancies.

5.4.1 Apparatus

All copper specimens were annealed in a vacuum furnace, using a base pressure of $\sim 1 \times 10^{-6}$ Torr. For the slow quenching conditions, both the pure copper and copper-silicon specimens were annealed simultaneously in the same furnace. Specimens of the Cu-Si alloy used for chemical analysis were annealed at the same time as specimens used in the resistivity study. During the annealing process the different alloys were separated from each other by 1/8" alumina sheets. The furnace temperature was ramped up from room temperature to final annealing temperature at a rate of 10°C/minute.

The pure copper specimens were quenched by flowing bottled argon into the furnace until a pressure of 350 Torr was attained. It took about 30 minutes for the specimens to reach room temperature.

Annealing of the platinum alloy specimens was done in air at 760 Torr, using a CM high-temperature furnace equipped with a controller. The annealing temperature was 900°C. The furnace temperature was ramped up

from room temperature to final annealing temperature at a rate of 8°C/minute. Ramp time from room temperature was approximately 2 hours. For slow cool down the cooling rate was maintained at approximately 7 °C/minute. Fast quenching of the pure platinum specimens was done in an ice water bath at 0°C. The bath temperature was measured using a mercury thermometer.

5.5 Electrical Measurements

5.5.1 Apparatus

The electrical resistivity of the test specimens were determined at room temperature (293 K) according to ASTM B 193-87 (Standard Test Method for Resistivity of Electrical Conductor Materials).⁽⁴¹⁾ This method required an accuracy of $\pm 0.30\%$ for specimens having a resistance of $0.00001\ \Omega$ ($10\mu\Omega$) or more.

The resistance of the specimens was determined using both a Kelvin-type double bridge⁽⁴²⁾ meter and a potentiometer as required by ASTM B 193-87. For this work a Keithley Model 58 micro-ohmmeter and a Gen-Rad 1689M Digibridge[®] bridge type impedance meter were used. Each specimen in the sample group was measured five times each, on each of the two electrical measuring devices.

ASTM B 193-87 allows for use of either the micro-ohmmeter or the Kelvin type Double bridge for electrical resistance measurements. There were concerns brought up during this investigation as to the accuracy of the micro-ohmmeter for this type of resistance measurement, so both instruments were used to determine the validity of that hypothesis.

The Keithley micro-ohmmeter has a minimum range of $200\text{ m}\Omega$, with a resolution of $10\mu\Omega$, using a maximum test current of 100 mA . Both resistance measuring devices used a 4-wire resistance measurement to eliminate test lead resistance errors that occur with a 2-wire resistance measurement. The circuit diagram for resistance measurements using the micro-ohmmeter is shown in Figure 14.

Figure 14. Circuit diagram for micro-ohmmeter resistance measurements.

The Digibridge[®] uses a microprocessor to calculate the impedance from a set of 8 voltage measurements. The same set of Kelvin type probes was used with both meters, to isolate any variation between connections from the test specimens to the measuring devices. The circuit diagram for resistance measurements using the double bridge is shown in Figure 15.

Figure 15. Circuit diagram for Digibridge[®] resistance measurements.

The Keithley micro-ohmmeter was calibrated prior to performing any experiments, by John Fluke Mfg., Fremont, CA., using NIST standards for each resistance range on the meter. To eliminate any measurement

differences on the specimens due to the connecting leads from the test sample to the meters, the same set of Kelvin clip leads were used for both devices.

Resistance calibration of the double bridge meter was verified by using a set of precision resistors with values of $10.28 \mu\Omega$ and 4.013Ω , at 293K, respectively, to verify that the two meters gave the same reading for the same resistances. These resistors were checked between each meter periodically during the measurements of the alloy samples.

All measurements were done in an class 10,000 clean room at KOMAG Inc., Milpitas, CA., where the room temperature was maintained at $20^\circ\text{C} \pm 1^\circ\text{C}$, measured on an analog meter and verified using a Vaisale hand held temperature/humidity meter. Room humidity was maintained during all measurements at $55\% \pm 5\%$ and monitored with a VWR hygrometer.

5.6 Resistivity characterizations

The volume resistivity of the specimens was determined by the equation

$$\rho_v = \frac{RA}{L} \quad [22]$$

where ρ_v = volume resistivity, $\Omega \text{ mm}^2/\text{m}$

A = cross sectional area, mm^2

L = gage length, m

R = measured resistance, Ω

Resistance testing and measurements in this study were required to meet the test methods and sensitivities specified by the American Society for Testing and Materials (ASTM) designation B193-87.⁽⁴³⁾ ASTM B193-87 required a resistance measurement sensitivity of $\pm 15\%$. Using the fact that any alloying of a pure copper specimen will cause an increase in resistivity, the necessary resistance sensitivity the instrumentation was required to have was determined. A pure OFHC copper wire at 293°K should have a resistivity of $0.017241 \Omega\text{mm}^2/\text{m}$ or $1.7241 \mu\Omega\text{-cm}$.⁽⁴⁴⁾

The cross-sectional area of the copper test specimens was 0.6207 mm^2 . The expected resistance value for a copper sample 300 mm in length, the minimum length required by ASTM B193-87 standards, is then

$$R = \frac{\rho_v L}{A} = 0.017241 \Omega \text{ mm}^2/\text{m} * 300 \text{ mm}/0.6207 \text{ mm}^2 * 1\text{m}/10^3 \text{ mm}$$

$$= 8.33 \times 10^{-3} \Omega \quad [23]$$

The accuracy of the resistance measurements for both meters was $10 \mu\Omega$, which then yielded a calculated sensitivity of $\pm 0.12\%$, which was within the sensitivity limits of $\pm 0.15\%$ required by ASTM B193-87.

5.7 Chemical analysis

Since the Cu-Si samples were obtained from a commercial source, and are not normally used for their electrical properties, the alloys may contain some additional impurity elements. These elements may have large

influences on the electrical resistivity of the alloys. Phosphorous and sulfur are often added to copper to control oxidation. Chemical analysis of the specimens, to determine actual composition, was done using wet bulk chemical analysis and emission spectrographic analysis, which was performed at Metallurgical Laboratories in Concord, CA. The sensitivity for classical wet chemical analysis (gravimetric) for silicon is $\pm 3\%$ of the amount of the impurity present. The sensitivity of wet chemical analysis for sulfur and phosphorous was $\pm 0.001\%$ and $\pm 0.0005\%$, respectively. Sensitivity to other impurities provided by spectrographic analysis depended on the matrix and varied from element to element.

5.8 Microstructural Analysis

Horizontal (perpendicular) and longitudinal (lengthwise) cross section samples were prepared from one wire specimen in each of the experimental groups, to determine the average grain size of each specimen before and after annealing. All samples of the material were taken from the midpoint of the wire specimens chosen.

The specimens were cold mounted, to avoid any further heat treating effect on the material, using a Leco epoxide resin (part #811-163) and a epoxide hardener (part #811-165). The resin and hardener were mixed together using a 4:1 weight ratio of resin to hardener. Cold mounts were also made using a TAP #314 (Marine grade) epoxy and a TAP #B109 (Medium) hardener, using

the same weight ratio described above. The best results for curing in both cases came from using rubber silicone coated molds, and letting the embedded specimens air cure at room temperature under a ventilated hood for 24 hours.

Horizontal cross sections were created by suspending the wire specimens from a wooden rod placed on top of the molds. The wooden rod was held in position using a rubber band. A diagram showing the setup for the horizontal cross section sample preparation is illustrated in Figure 16.

Figure 16. Illustration of sample preparation for horizontal wire cross sectioning.

Longitudinal cross sections were prepared by laying the wire in the bottom of the mold. This was sufficient preparation for chemical etching of the copper samples, but would not provide the electrical contact to the sample surface necessary for the electrolytic etching of the platinum specimens.

Lengthwise specimens of the platinum and Pt-alloy specimens were prepared, and shaped into an L-shape, with the area closest to the center of the wire being the base of the "L". A small amount of epoxy was placed in the mold, before placing the platinum sample into the mold. A copper coated zinc disk (U.S. penny), 19 mm in diameter and 1.68 mm thick was placed on top of the wire. This was used to maintain the flatness of the specimen for polishing, and provide a means of electrical contact to the thin wire. A schematic showing the layout of the Pt wire specimen mold is shown in Figure 17.

Figure 17. Illustration of sample preparation for length-wise wire cross sectioning of Pt and Pt alloys for use with electropolishing.

After hardening, the longitudinal cross sections were removed from the molds, and a 1/8" diameter hole was drilled through the back of the sample to the surface of the copper penny to provide indirect electrical contact

with the sample. The residual epoxy in the hole was removed using a Dremel tool with a 3/16" grinding bit. Electrical contact between the back of the penny and the wire surface was verified using a hand-held digital multi-meter.

The copper specimens were rough ground using a wet 120 grit Al_2O_3 sand paper followed by wet 400 grit paper. Diamond polishing followed, using 6 micron diamond paste, followed by 1 micron alumina using a microcloth polishing cloth. Final polishing was done using 0.3 micron alumina.

Chemical etching to enhance the microstructure of the copper samples was done using a solution of 1 gram FeCl_3 , 3 ml HCl and 50 ml H_2O . samples were etched for 2 minutes and quenched in de-ionized water.

The platinum specimens were rough ground using a wet 600 grit Al_2O_3 sand paper. Diamond polishing followed, using 6 micron diamond paste, followed by 1 micron alumina using a microcloth polishing cloth. Final polishing was done using 0.3 micron alumina.

Chemical etching of the platinum specimens was attempted using a boiling aqua regia solution, but the solution temperature caused a softening of the epoxy compound destroying the integrity of the specimen surface. Electrolytic etching was attempted on a fresh set of platinum specimens using a Buehler Electromet 4 electropolisher in etch mode. The cathode was a

graphite rod threaded onto the end of a copper bar. Two different etching solutions were tried. The first was 40 g NaCl, 100 ml H₂O, and 25 ml HCl, for 1 minute at 6Vac and 0.2 A/cm². The second was concentrated HCl for 1 minute at 6Vac and 0.15 A/cm². Neither solution produced any visible grain delineation on either the horizontal or longitudinal cross sectional specimens.

The average grain size for both the horizontal and longitudinal cross sectional specimens was determined using the linear intercept (or Heyn) procedure as described in ASTM E112-88 (Standard test Methods for Determining Average Grain Size).⁽⁴⁵⁾ Where grain sizes were too large to be measured using the intercept method, the average grain size was determined by direct areal measurement of all grains contained in the micrograph, and their values averaged together. ASTM grain sizes were determined using Table 2 and Figure 6 from ASTM E112-88.

Chapter 6

EXPERIMENTAL RESULTS

6.1 Chemical analysis

Chemical analysis for the copper silicon alloys, before and after annealing are shown in Table 5. The C65100 alloy had a silicon content of 3.46 a/o, which was within 2.5% of the expected value from ASTM B99-86a. Both manganese and iron were present in amounts that may have an impact on the materials electrical properties. The C65600 alloy had a silicon content of 6.92 a/o, and a lower iron content and higher manganese content than C65100. The silicon content of C65600 was within 3.2% of the expected value.

Both alloy specimens showed a slight content decrease in copper content and a slight increase in sulfur and phosphorous content after the vacuum annealing. The measurement error for silicon concentration was $\pm 3\%$ of the relative amount present. Measurement errors for both phosphorous and sulfur were ± 0.001 a/o. The change in relative amounts of copper, sulfur and phosphorous between the annealed and unannealed specimens may be due to natural variations in the copper alloy composition

Table 5. Chemical analysis (in atomic percent) of copper-silicon alloys, as-received and after annealing.

	C65100	C65100	C65600	C65600
Element	as received	annealed	as received	annealed
Copper	96.037	96.008*	92.220	92.048*
Iron	0.201	0.201	0.077	0.076
Nickel	0.001	0.001	<0.001	<0.001
Aluminum	0.005	0.005	0.011	0.009
Lead	0.001	0.001	0.001	0.001
Tin	0.002	0.001	0.051	0.041
Manganese	0.283	0.283	0.722	0.722
Silicon	3.459	3.459	6.913	6.927
Silver	0.002	0.002	0.002	0.002
Sulfur	0.002	0.008*	0.002	0.004*
Phosphorous	0.007	0.032*	0.001	0.169*

* represents significant changes in impurity concentration after annealing.

that could possibly vary from wire specimen to wire specimen. The changes in phosphorous content can be expected to have some small effect on the electrical resistivity.

6.2 Electrical Resistivity

6.2.1 Experimental Results

All specimens were measured using both the Keithley micro-ohmmeter and the Gen-Rad Digibridge. The resistance measurements

between the two instruments was found to be consistent to within $\pm 0.4\%$, with the exception of the data for the annealed pure copper sample, which showed a difference of 2.3% between devices.

Single measurement errors for the copper alloys were on the order of $\pm 0.7\%$ of the measured values, which is less than the variation within each group. Single measurement errors for the platinum alloys was on the order of $\pm 0.2\%$ of the measured values, which is also less than the variation within each group.

All alloy samples showed the expected decrease in resistivity after annealing, with the exception of the pure copper specimen. The pure copper specimen showed an increase in resistivity after annealing, and almost no change in resistivity after annealing and rapid quenching.

6.2.2 Copper-Silicon

The electrical resistivity values for all of the copper specimens, as measured on the micro-ohmmeter and the Kelvin bridge meter, is presented in Table 6. The electrical resistivity as measured on the micro-ohmmeter for the annealed C65100 and C65600 specimens was found to be $15.0865 \mu\Omega\text{-cm}$ and $26.241 \mu\Omega\text{-cm}$, respectively. The resistance of the pure copper specimen, before annealing was $1.7302 \mu\Omega\text{-cm}$, which was within the experimental error of the expected value for OFHC copper at 293K of $1.7241 \mu\Omega\text{-cm}$. The Metals

Handbook, Desk Edition, 1985 gives a resistivity value for copper, at 20°C, of 1.6730 $\mu\Omega\text{-cm}$.⁽⁴⁶⁾

Table 6. Experimental results for the copper and copper alloy specimens.

	As received		Annealed		Anneal + rapid quench	
Sample	micro- ohmmeter ($\mu\Omega\text{-cm}$)	Double Bridge ($\mu\Omega\text{-cm}$)	micro- ohmmeter ($\mu\Omega\text{-cm}$)	Double Bridge ($\mu\Omega\text{-cm}$)	micro- ohmmeter ($\mu\Omega\text{-cm}$)	Double Bridge ($\mu\Omega\text{-cm}$)
Pure Cu	1.7302	1.7346	1.7568	1.7969	1.7321	1.7361
C65100	16.2865	16.3328	15.0865	15.1578		
C65600	28.7368	28.7693	26.2421	26.3182		

Data for the electrical resistivity of various Cu-Si alloys previously studied at 293 K by A. Norbury (Linde-Norbury Rule) and K. Kuwada⁽⁴⁷⁾ is presented in Table 7. The experimental data for the Cu-Si alloys along with the values from Norbury, et al. are presented in Figure 18.

Table 7. Cu-Si resistivity values from Norbury, et. al.

Copper alloy	Resistivity ($\mu\Omega\text{-cm}$)	Temperature (K)
Pure Cu	1.70	293
Cu-2.1a/o Si	9.5	290
Cu-3.8 a/o Si	15.24	291
Cu-5.9 a/o Si	20.80	290

Figure 18. Plot of experimental data for the Cu-Si alloys along with the values from Norbury, et al.

Both the experimental and historical data for the copper silicon alloy system, presented in Figure 18, indicate that the increase in resistivity for increasing amounts of silicon in copper, at 293K, is non-linear.

6.2.3 Pt-Rh alloys

The electrical resistivity values for the platinum specimens, as measured on the micro-ohmmeter and the Kelvin bridge meter, is presented

in Table 8. The resistance for the pure platinum specimen was 10.8942 $\mu\Omega\text{-cm}$ which was within the experimental error of previously reported values from MacFarlane, et al.⁽⁴⁸⁾ The resistance for the Pt-17 a/o Rh and Pt-22 a/o Rh was 19.7839 $\mu\Omega\text{-cm}$ and 20.4741 $\mu\Omega\text{-cm}$, respectively.

Table 8. Experimental results for Pt and Pt-Rh alloy specimens

	As received		Annealed		Anneal +	rapid quench
Sample	micro- ohmmeter ($\mu\Omega\text{-cm}$)	Double Bridge ($\mu\Omega\text{-cm}$)	micro- ohmmeter ($\mu\Omega\text{-cm}$)	Double Bridge ($\mu\Omega\text{-cm}$)	micro- ohmmeter ($\mu\Omega\text{-cm}$)	Double Bridge ($\mu\Omega\text{-cm}$)
Pure Pt	10.9409	10.9782	10.8942	10.8776	10.6181	10.6073
Pt-17a/o Rh	20.3531	20.3799	19.7839	19.8240		
Pt-22a/o Rh	21.0572	21.0810	20.4741	20.4934		

The Metals Handbook, 1985 Desk edition, gives a resistivity of platinum at 20°C of 10.6 $\mu\Omega\text{-cm}$.⁽⁴⁹⁾ Macfarlane, et. al, reported values for the resistivity at 293K of Pt-17 a/o Rh, and Pt-22 a/o Rh of 18.8 $\mu\Omega\text{-cm}$ and 20.3 $\mu\Omega\text{-cm}$ respectively,⁽⁵⁰⁾ with an uncertainty in their measurements of $\pm 5\%$. They also reported previous values from other studies for Pt-17 a/o Rh and Pt-22 a/o Rh of 19.0 $\mu\Omega\text{-cm}$ and 19.6 $\mu\Omega\text{-cm}$, respectively.

Experimental data for the platinum alloys measured, along with the previous data from Macfarlane, et al., including error bars, where available, is presented in Figure 19. The experimental and published data indicates that

over a broad impurity concentration range the resistivity increase in platinum for increasing rhodium concentrations is not only a non-linear function, as was seen in the case of the copper-silicon system, but actually decreases for extremely large concentrations of rhodium in platinum. This system seems to fit the case of Nordheim's model for concentrated alloys.

Figure 19. Plot of experimental data for the Pt-Rh alloys along with the values from Macfarlane, et al.

6.3 Error Analysis

Resistivity data for each alloy was plotted using a statistical method, known as an Evaluating the Measurement Process (EMP) study,⁽⁵¹⁾ using two sets of interrelated charts: an X-bar or Average chart, and a Range chart. The purpose of plotting the data in this manner was to independently determine the contribution to the experimental error, from both the specimens and the measurement equipment. These charts are included in Appendix A and contain data from both the micro-ohmmeter and the double bridge meter. Each point on the X-bar chart represents the average of the 5 resistivity measurements taken from each wire specimen. The range chart contains the value of the maximum measurement minus the minimum measurement for each set of 5 readings. Statistical analysis of the range charts was used to calculate the upper control limit (UCL) and lower control limit (LCL) values for the X-bar chart. These UCL and LCL values were determined separately for each measuring device, based on the formulas contained in Table 9, and A_2 was determined to be 0.577⁽⁵²⁾.

The R-bar value was used for each alloy to determine the measurement error (σ_e) separately for each resistance meter. Comparisons of measurements between instruments was done using a paired t-test for mean differences. Points that were beyond the upper control limit on the range

Table 9. Calculations for control limits for average and range charts.

Calculation	X-bar Chart	Range chart
Target value	= Average X-bar= Grand average (X-bar-bar)	=average range (R-bar)
UCL	= $\bar{X} + (A_2 * \bar{R})$	= $2.114 * \bar{R}$
LCL	= $\bar{X} - (A_2 * \bar{R})$	0

chart were eliminated from the t-test on both instruments to maintain the data pairing used in the t-test. These out of control values are indicators that there was some inconsistency in the measuring process of the specimen with that instrumentation. Possible reasons for these inconsistencies could include inconsistent probe contact with the sample, stress induced damage in the specimen during handling between measurements, and measurement errors in specimen length combined with a natural variation in alloy composition across the specimen length.

The average electrical resistivity for each alloy specimen and the probable measurement error for each instrument is presented in Table 10. The last column of Table 10 contains the significance level (P) of the paired t-test.

Analysis of the paired t-test P values can be divided into four cases:

Case 1) $P > 0.15$; Inconclusive, both instruments gave similar results.

All of the annealed platinum specimens and the as-received C65600 fell into this grouping. No significant differences were

Table 10. Summary analysis of the X and R charts in Appendix A.

	Micro-Ohmmeter		Double Bridge meter		
Alloy	average resistivity ($\mu\Omega$ -cm)	σ_e	average resistivity ($\mu\Omega$ -cm)	σ_e	P
Copper	1.7145	0.0027	1.7345	0.0183	0.1670
C65100	16.2825	0.0374	16.3237	0.1020	0.0010
C65600	28.7456	0.0243	28.7471	0.0518	0.8625
Copper annealed	1.7568	0.0190	1.7968	0.0285	0.0001
Copper annealed /quenched	1.7321	0.0014	1.7361	0.0060	0.0440
C65100 Annealed	15.0865	0.0108	15.1580	0.0126	0.0020
C65600 Annealed	26.2421	0.02998	26.3182	0.0168	0.0016
Platinum	10.9402	0.0022	10.9739	0.0010	0.0160
Pt-17a/o Rh	20.1860	0.0141	20.2227	0.0090	0.1150
PT-22a/o Rh	21.0308	0.0071	21.0488	0.0106	0.0370
Pt annealed	10.8942	0.0192	10.8776	0.0037	0.2800
Pt annealed/q uenched	10.6181	0.0157	10.6056	0.0135	0.4300
Pt-17a/o Rh annealed	19.7231	0.0259	19.7375	0.0851	0.6300
Pt-22a/o Rh annealed	20.416	0.0150	20.4824	0.0085	0.4980

distinguishable between the micro-ohmmeter and the double bridge meter measurements.

Case 2) $0.1 \leq P < 0.15$; Possible difference between instruments.

The as-received copper and as-received Pt-17a/o Rh alloys both fell into this category. Analysis of the run charts indicates that the behavior of each specimen was similar between instruments.

Case 3) $0.05 \leq P < 0.1$; Probable differences.

The annealed C65100 alloy was the only specimen in this case. While there were visible differences between the two instruments for each pair of readings, the differences appeared to be of a constant value, with the double bridge meter always reading slightly higher than the micro-ohmmeter.

Case 4) $P < 0.05$; Likely machine to machine differences.

The as-received specimens of C65100, platinum, and Pt-17a/o Rh all fell within this case. There is no known reason for these differences in the readings of the platinum alloys at this time, since the 4.014Ω calibration resistor used during the platinum alloy measurements showed a relative difference between instruments of only $\pm 0.001\Omega$.

Differences that did exist between instruments occurred in the third or fourth significant figure and were less than $\pm 0.1\%$ for a resistivity value of $10\ \mu\Omega\text{-cm}$. These differences were indicative of calibration differences between the instruments.

The small average ranges in each specimen group produced extremely tight control limits for the X-bar charts. The X-bar chart is statistically out of control for almost all of the wire specimens, with the exception of the as-received copper specimens. This is an indication that when the sample resistivity background noise was only based on repeatability there were detectable differences in the average resistivity from specimen to specimen.

In many of the X-bar control charts it is easy to group the specimens into two distinct subgroups, an indicator that there was some natural variation in resistivity from specimen to specimen. The grouping seems to follow the measurement order of the specimens in all cases, indicating that this may be due to experimental change in the measurement set-up. But the change occurs simultaneously, with respect to specimen order, for both instruments, and any natural variation in the measurement process caused by changing samples or equipment should be random.

A more likely explanation is that there is some natural variation in wire alloy composition along the wire as it is loaded onto the bulk spools, and that this variation in composition causes a variation in electrical resistance measurements. The results of the chemical analysis reported between the

annealed and as-received specimens of C65100 and C65600 may also provide data in supporting this model as the origin of the differences in resistivity between specimens.

6.4 Microstructural analysis

Micrographs of the as-received pure copper and copper -alloy specimens are presented in Figures 20 through 22. The as- received pure copper specimen, consisted of small non equiaxed grains, as shown in Figure 20a and 20b, with an ASTM micro grain size number $G = 10.6 \pm 0.2$. The as-received copper-silicon alloys both showed indications of cold work damage, as shown in Figures 21 and 22. This type of damage is consistent with damage created during the wire drawing process.

Micrographs of both the annealed and annealed and quenched pure copper specimens showed an increase in micrograin size number from $G = 10.5 \pm 0.2$, corresponding to an area of $89.1 \times 10^{-6} \text{ mm}^2$ to $G = 1.5 \pm 0.1$ (0.0456 mm^2), as shown in Figures 23 and 24. After annealing, small grains formed in both of the copper silicon alloys specimens, as shown in Figures 25 and 26. The average micrograin size number was $G=11.2 \pm 0.2$ ($73. \times 10^{-6} \text{ mm}^2$) for the C65100 alloy and $G= 8.2 \pm 0.1$ ($450. \times 10^{-6} \text{ mm}^2$) for the C65600 alloy. A summary of the grain size values is presented in Table 11.

(a)

(b)

Figure 20. Micrograph of as-received pure copper specimens: (a) horizontal at 400X; (b) longitudinal at 400X.

(a)

(b)

Figure 21. Micrograph of as-received specimens of C65100: (a) horizontal at 400X; (b) longitudinal at 400X.

(a)

(b)

Figure 22. Micrograph of as-received specimens of C65600: (a) horizontal at 400X; (b) longitudinal at 400X.

(a)

(b)

Figure 23. Micrograph of annealed pure copper specimen: (a) horizontal at 200X (b) longitudinal at 100X.

(a)

(b)

Figure 24. Micrograph of annealed and quenched pure copper specimens: (a) horizontal at 100X (b) longitudinal at 100X.

(a)

(b)

Figure 25. Micrograph of annealed C65100 specimens: (a) horizontal at 400X; (b) longitudinal at 400X.

(a)

(b)

Figure 26. Micrograph of annealed C65600 specimens: (a) horizontal at 400X;
(b) longitudinal at 400X.

Table 11. Summary of Grain Size Measurements

	As received	annealed	annealed + quenched
Sample	ASTM Micro-Grain Size Number G	ASTM Micro-Grain Size Number G	ASTM Micro-Grain Size Number G
Pure Copper	10.5 ± 0.2	1.5 ± 0.1	1.5 ± 0.1
C65100	-	11.0 ± 0.2	
C65600	-	8.2 ± 0.1	

Grain enhancement on the thin Pt alloy wire samples using either chemical or electrochemical techniques was not obtained. In both the copper and platinum samples, it was not possible to quench the annealed samples rapidly enough to induce defect formation within the specimens, as indicated by a decrease in resistivity after annealing and quenching for both pure metal samples. Calculations done using average grain size values from ASTM E112-88, based upon the experimental determination of the ASTM grain size number, show that for pure copper there was a grain size increase corresponding to 5,107% with almost no change in resistivity. The calculation of the change in grain size for the pure copper specimen, before and after annealing, is presented in Appendix B.

The C65100 alloy showed a resistivity decrease after annealing of 7.35%, or $1.20 \mu\Omega\text{-cm}$, and the C65600 alloy showed a decrease of 8.7%, or $2.49 \mu\Omega\text{-cm}$. Because of the amount of initial cold work damage in the Cu-Si alloy specimens, it was not possible to estimate the change in grain size after

annealing. The resistivity change for both of the Cu-Si alloys, due to the effect of cold working and grain size, was 1 order of magnitude larger than the value of $0.14\ \mu\Omega\text{-cm}$ predicted by Drew, et al.⁽⁵³⁾ This indicates that the processing conditions of the copper-silicon alloys will influence the final electrical properties sufficiently to affect the modeling predictions of Matthiessen's rule.

The platinum alloy specimens showed a decrease in resistivity of 3% or $0.57\ \mu\Omega\text{-cm}$, which is just slightly larger than the value predicted by Drew, et al. Further work needs to be undertaken, possibly with larger diameter Pt alloy wire samples, to study the grain structure changes after annealing, and their possible effect on sample resistivity.

The electrical resistivity of the pure copper specimens was found to increase upon annealing, contrary to expectations based upon current knowledge and theory. From the control charts in Appendix A and the chemical analysis of the as-received Cu-Si and annealed Cu-Si alloys there are indications that there are compositional variations within the alloy specimens. These variations cannot be explained at this time, but would impact the electrical properties of the alloys. It is possible that these variations also exist in the pure metal species. Due to the extremely small diameter of the specimens required for measurements such as those done during the course of this investigation, that which would otherwise be a

minor variation in the bulk could have a greater effect in thin cross sections. There is insufficient data at this time to be able to unequivocally determine the cause of increase in the resistivity of the pure copper specimens, upon annealing. The pursuit of such a study is also beyond the scope of this investigation. Further research on the electrical resistivity of individual specimens, before and after annealing, and chemical and microstructural analyses of each of the specimens will need to be performed to understand this phenomenon.

Chapter 7

EVALUATION OF THEORETICAL MODELS

7.1 Theoretical Models (Dilute alloys)

7.1.1 Nordheim's Rule (Dilute Case)

As explained in Chapter 2, for cases involving dilute alloys Matthiessen's rule can be written as

$$\rho_{\text{alloy}}(t, T) = \rho_{\text{impurity}}(c, 0) + \rho_{\text{solvent}}(0, T) \quad [24]$$

$$= Kn_i' + K'T/\Theta_{\theta}^2 \quad \text{for } 2/3\Theta_R < \Theta < 250^{\circ}\text{C} \quad [25]$$

where n_i' is the impurity concentration (in atomic per cent). Values for K , K' , and Θ from Schröder are presented in Table 8. ⁽⁵⁴⁾

Table 12. Values of K , K' and Θ for various alloys.

element	Θ (K)	K ($\mu\Omega\text{-cm}/(\text{a/o})$)	K ($\mu\Omega\text{-cm}/(\text{a/o})$)	K' ($\mu\Omega\text{-cm K}$)
		Cu	Pt	
Cu	335			
Si		3.1		530
Pt	233			
Rh	310	4.4	0.7	

7.1.1.1 Cu-Si alloys

Using the values from Table 8, the expected linear fit to the Cu-Si system at 293K is given by :

$$\rho_{\text{alloy}}(c, 293\text{K}) = \rho_{\text{impurity}}(c, 0) + \rho_{\text{solvent}}(0, 293\text{K}) \quad [26a]$$

$$= 3.1n_i + 1.384 \mu\Omega\text{-cm} \quad [26b]$$

A plot of the experimental results as a function of atomic per cent Si is presented in Figure 27. The equation describing the linear fit through these is

Figure 27. Plot of experimental Cu-Si data and a linear fit of the data.

given by

$$\rho_{\text{alloy}}(c, 293\text{K}) = 3.5542 n_i + 2.1382 \mu\Omega\text{-cm} \quad [27]$$

which appears to be close to the $\partial\rho/\partial c$ of $4.17 \mu\Omega\text{-cm}$ calculated from

Gerritsen's data.⁽⁵⁵⁾ A linear fit through Norbury's data yields

$$\rho_{\text{alloy}}(c, 293\text{K}) = 3.152 n_i + 2.354 \mu\Omega\text{-cm} \quad [28]$$

which is in closer agreement with the value reported by Schröder.

While the previous linear fits to Domenicali's data give good approximations to experimental data, Figure 28 shows that a better fit can be obtained by applying a 2nd order polynomial equation of the form $y = M_0 + M_1x + M_2x^2$ to both the experimental data and Norbury's data. The values of M_i are presented in Table 13.

Figure 28. Resistivity of experimental Cu-Si data fitted to a 2nd order polynomial.

Table 13. Polynomial factors for 2nd order equations used in Figure 28.

Equation is of the form $y = M_0 + M_1x + M_2x^2$

	Experimental data	Norbury, et al.
M ₀	1.7591	1.794
M ₁	4.2107	3.992
M ₂	-0.0948	-0.14
R ²	1.00000	.99912

A similar 2nd order polynomial fit to the data from Domenicali, et al at various temperatures is shown in Figure 29. The values of M_i are presented in Table 14.

The first order constant M_1 for all three temperatures seems to be closer to the values calculated using Gerritsen's data than the previous linear fits. M_1 is within $\pm 10\%$ for all the systems as predicted by Bass,⁽⁵⁶⁾ but there is variation in the M_2 term that is greater than 10% from room temperature.

Figure 29. Resistivity of Cu-Si alloys at various temperatures from Domenicali, et al., fitted to a 2nd order polynomial.

Table 14. Polynomial factors for 2nd order equations used in Figure 29.

Equation is of the form $y = M_0 + M_1x + M_2x^2$

	T = -190°C	T = 25°C	T = 840°C
M ₀	-0.0670	1.6794	7.1502
M ₁	4.01	3.90	4.23
M ₂	-0.015	-0.135	-0.105
R ²	.9996	.99982	.9998

There is a slight variation with temperature for both the first and second terms, indicating that perhaps there is still a temperature dependency to the concentration dependent resistance term.

7.1.1.2 Pt-Rh alloys

There is very little resistivity data for platinum-rhodium alloys with less than 10 a/o rhodium. Since the linear approximation is only meant to be applied to dilute alloys, there is no current data available to determine how well it would fit dilute Pt-Rh alloys. Applying the same set of equations from Schröder to determine a linear fit to the Pt-Rh system required using experimental data for Pt-17 a/o Rh and Pt-22 a/o Rh to try and determine a value for K' for rhodium in platinum. Using the values from Table 8 for K and Θ , and using the experimental resistivity data from this study for Pt-17 a/o Rh and Pt-22 a/o Rh, values of 1463 $\mu\Omega\text{-cm K}$ for K' and 944.96 $\mu\Omega\text{-cm K}$

for K, were calculated. This indicates that K' is not a constant but varies inversely with concentration for the Pt-Rh alloy system.

The resistivity data both from this research and from others do not indicate a linear fit. The data obtained indicates that a linear approximation will not work in the data range of the Pt-Rh alloys studied in this investigation.

7.1.2 Linde-Norbury Rule

7.1.2.1 Cu-Si alloys

If the Linde- Norbury rule is applicable to copper-silicon alloys , then it should be possible to calculate a straight line fit through the resistivity values for the following alloy systems: Cu-Al, Cu-Si, and Cu-P

Aluminum is soluble in copper at 293 K to approximately 0.5 w/o (10.6 a/o). Schröder⁽⁵⁷⁾ reports the resistivity for Cu- 2.78 a/o Al as 5.85 $\mu\Omega$ -cm.

Archbutt⁽⁵⁸⁾ reports a resistivity for a cold rolled Cu -.494 w/o P (1 a/o) of 8.59 $\mu\Omega$ -cm at 293 K. The plot of the change in resistivity per 1 a/o impurity as a function of $(\Delta Z)^2$ is shown in Figure 30.

No data for a copper 1 a/o sulfur alloy was found in the literature, but the linear fit in Figure 30 predicts a value of 10.93 $\mu\Omega$ -cm. The line fit through the data in is given by the equation:

$$y = -0.25277 + 0.44725x \quad [29]$$

Figure 30. Effect of ionic charge on the change in the resistivity of copper per 1/a/o of alloying element in annealed random, binary solid solutions at 293 K. Straight line fit through data is prediction by Linde-Norbury model.

This linear equation predicts a change in resistivity for silicon in copper of $3.77 \mu\Omega\text{-cm/a/o Si}$. This is approximately the same value predicted by the linear fit to the data using Nordheim's model for dilute alloys. Higher concentrations of aluminum in copper do lead to a higher $\Delta\rho/\Delta c$, so that the aluminum value can vary depending on the a/o ratio used for the calculation.

If the concentration of the impurity element is low the Linde- Norbury rule appears to make the same prediction as Nordheim's rule for dilute

alloys. The Linde-Norbury model is in agreement with experimental results, only as long as the change in resistivity per atomic per cent impurity remains constant. This essentially limits use of this model to a range of impurity concentrations where the resistance change is linear. Further studies need to be completed at higher concentrations of impurities to determine if the change in resistivity per atomic per cent impurity remains constant.

7.1.2.2 Pt-Rh alloys

Platinum has nine 5d electrons and one 6s electron, while rhodium has eight 4d electrons and one 5s electron; they have the same number of valence electrons ($\Delta Z = 0$). Using the Linde- Norbury rule requires the resistivity data for the following alloys Pt-Pd, Pt-Ag, Pt-Cd, Pt-In, and Pt-Sn. There was no data available in any of the reviewed literature, including Schröder, for any of the platinum alloys necessary to verify if the Linde-Norbury rule holds in this case.

7.1.3 Two Band Model

The two band model is used to determine the value of $\Delta(T)$ from equation [5]. Substituting a value of 293 K for the temperature, and assuming that $\rho_0(c) = \rho_A(T \rightarrow 0)$ can be replaced by $\rho_A(4.2 \text{ K})$, the general equation for resistivity becomes

$$\rho_A(c, 293 \text{ K}) = \rho_S(293 \text{ K}) + \rho_A(4.2 \text{ K}) + \Delta(293 \text{ K}) \quad [30]$$

7.1.3.1 Cu-Si alloys

There are no reported residual resistivity values for any of the Cu-Si alloys studied. Domenicali and Otter did study a wide range of Cu-Si alloys, but only at a temperature range of 73 K. An extrapolation of Domenicali, et al.'s data down to 4.2 K, assuming a linear extrapolation from higher temperatures, was used to determine the values for $\rho_A(4.2 \text{ K})$.

Using the experimental values for the Cu-Si alloys, along with the values for $\rho_A(4.2 \text{ K})$, a plot for $\rho_0(c)^{-1}$ and $(\Delta T)^{-1}$ was generated. The plot of these values is presented in Figure 31.

A linear fit through the data indicates $\beta = 0.094$, $\gamma = -23.1$, however there is a large amount of scatter present in the data. Using the above values for β and γ in equation [30], along with the values of ρ_A from Domenicali, and the determination of ρ_s from this investigation from equation [27], the predicted values of resistivity for the C65100 and C65600 alloys are $13.60 \mu\Omega\text{-cm}$ and $23.62 \mu\Omega\text{-cm}$, respectively. Both of these values are approximately 10% lower than the experimental results.

Figure 31. Plot of $(\Delta T)^{-1}$ in $[(\mu\Omega\text{-cm})^{-1}]$ against $\rho_0(c)^{-1}$ in $[(\mu\Omega\text{-cm})^{-1}]$ for Cu-Si alloys at 273K.

The Two Band Model was able, in this case, to provide a fit to the experimental data. The fit might be improved if more accurate values for ρ_A for both alloys were available.

7.1.3.2 Pt-Rh alloys

Using the experimental values for the Pt-Rh alloys, along with the residual resistivity data for these alloys from Macfarlane and Collins⁽⁵⁹⁾ values can be generated for $\rho_0(c)^{-1}$ and $(\Delta T)^{-1}$. The plot of these values is

presented in Figure 32. A linear fit through the data indicates $\beta = -0.197$ and $\gamma = -0.002$.

Previous studies have determined values of β and γ for Pt-Ti and Pt-V dilute alloys (0.1 a/o to 1.0 a/o impurities) as 0.22 and 0.03, respectively.⁽⁶⁰⁾ The reason for a negative β value for the Pt-Rh alloys could be due to the use

Figure 32. Plot of $(\Delta T)^{-1}$ in $[(\mu\Omega\text{-cm})^{-1}]$ against ρ_0^{-1} in $[(\mu\Omega\text{-cm})^{-1}]$ for the Pt-Rh alloys studies at 273K.

of more concentrated impurity levels, or could be due to the Rh impurity itself. No values for β and γ were found in the literature for higher concentrations of Ti or V in platinum.

Using the above values for β and γ in equation [30], along with the values of ρ_A from Macfarlane, et al, and the determination of ρ_s from this investigation, from equation [27], the predicted values of resistivity for the Pt-17a/o Rh and Pt-22 a/o Rh alloys are 21.26 $\mu\Omega\text{-cm}$ and 22.90 $\mu\Omega\text{-cm}$, respectively. Both of these values are approximately 10% higher than the experimental results.

The two band model in both alloy systems, only provided the correction factor $\Delta(c,T)$ to Matthiessen's rule. Using the correction factor in both cases the calculated resistivity was still off by $\pm 10\%$ from the experimentally determined values. The reason for this lies in the fact that $\Delta(c,T)$ can become a constant. From the equation

$$\Delta(T) = \gamma\beta \rho_s(T) \rho_0(c) / [\gamma \rho_s(T) + \beta \rho_0(c)] \quad [31]$$

if $\gamma \rho_s(T) \gg \beta \rho_0(c)$, then equation [31] reduces to

$$\Delta(T) = \beta \rho_0(c) \quad [32]$$

The resistivity value predicted by Matthiessen's rule, at each impurity level, thus increases by an amount equivalent to $\beta \rho_0(c)$. This will obviously have a larger correction effect at higher concentrations of impurities. If $\gamma \rho_s(T) \ll \beta \rho_0(c)$, then equation [31] reduces to

$$\Delta(T) = \gamma \rho_s(T) \quad [33]$$

However, $\gamma \rho_s(T)$ is a constant at a fixed alloy temperature, and therefore shifts the predictions for all concentrations by the same amount.

Since it has already been shown from both alloy systems studied that resistivity does not vary linearly with impurity concentrations, the addition of another factor to Matthiessen's rule will not be of use in improving the predictability of the rule at a fixed temperature.

7.1.4 CBR Model

The CBR model assumes that there is an impurity limit below which Matthiessen's rule is valid, and above which there is a temperature dependent contribution. A plot of $\rho_A - \rho_0$ as a function of ρ_0 should produce a linear relationship similar to that shown in Figure 6.

7.1.4.1 Cu-Si alloys

Using the data from Domenicali, et al., to determine ρ_A and ρ_0 for various Cu-Si alloys, the plot of $(\rho_A - \rho_0)$ as a function of ρ_0 is shown in Figure 33, along with the data previously reported for various Cu alloys at 298.1 K by

Figure 33. $\rho_A - \rho_0$ as a function of residual resistivity, at 298.1K, for selected copper-silicon alloys.

Cimberle, et al. Cimberle, et al. had concluded from their data that for many alloy systems at low temperatures, including the copper alloy system, there were deviations from Matthiessen's Rule above some transition resistivity,

$\rho_0'(T)$, and that these deviations increased logarithmically with ρ_0 . They had also determined that for the copper system the value of $(\rho_A - \rho_0)$ increased with $\log(\rho_0)$, but was constant with respect to temperature, up to 298.1 K.

The data presented in Figure 33 strongly disagrees with this conclusion, and points to a possible second transition temperature effect in the copper alloy system.

One possible reason for the disagreement is the effect of the concentration of impurities in the alloy systems that Cimberle, et al. studied. Cimberle, et al. provided no data on the impurity concentration ranges used in calculating their model, only the temperature ranges. It is possible that if their data was based on dilute concentrations of impurities (< 1 a/o) that the predicted response of their model could change for higher impurity concentrations. The accuracy of the results calculated from Domenicali, et al., is limited by the ability to derive an accurate value for $\rho_0 \rightarrow \rho_A(4.2 \text{ K})$ by assuming a linear extrapolation from higher temperatures.

7.1.4.2 Pt-Rh alloys

Using data from Macfarlane and Collins to determine ρ_A and ρ_0 for various Pt-Rh alloys, the plot of $(\rho_A - \rho_0)$ as a function of ρ_0 is shown in Figure 34.

Figure 34. $\rho_A - \rho_0$ as a function of residual resistivity, at 298.1K, for selected platinum-rhodium alloys.

Cimberle, et al., had obtained data for only one Pt-Rh sample at various temperatures ≤ 50.5 K, and had noted that the Pt-Rh alloy results had not followed the pattern seen in other Pt alloys they had examined. The data in Figure 34 does not seem to follow the expected responses predicted by Cimberle et al. in other alloy systems. In this case it is not certain if the effects are due to temperature, concentration of impurities, or impurity type.

Based on this data it does not appear that the CBR model accurately reflects the changes in resistivity for room temperature Cu-Si or Pt-Rh alloy systems.

7.1.5 CHL Model

7.1.5.1 Cu-Si alloys

As previously reported, there is no direct data available for determining the residual resistivity of Cu-Si alloys at 4.2 K. The CHL model predicts a residual resistivity value for silicon in copper as $4.0 \mu\Omega\text{-cm}$ per 1 a/o impurity. A. Lodder, et. al ⁽⁶¹⁾ give a value of the residual resistivity for 1 a/o Si in copper as 3.95, which is close to this value.

7.1.5.2 Pt-Rh alloys

No studies of how well the CHL model fit the residual resistivity data for a Pt-Rh alloy were found in the literature.

7.2 Theoretical Models (Concentrated alloys)

7.2.1 Nordheim's Rule (Concentrated Case)

7.2.1.1 Cu-Si alloys

There are several different reported values for the resistivity of silicon. The ASM Metals Handbook reports a value of $10 \mu\Omega\text{-cm}$ at 273 K. The CRC Handbook of Chemistry and Physics reports a resistivity of $3\sim 4 \mu\Omega\text{-cm}$ at 273K,⁽⁶²⁾ noting that the value is very sensitive to purity.

Using a value of $3.5 \mu\Omega\text{-cm}$ as the resistivity for silicon at 20°C, the best fit to the experimental data was found by using a value of Nordheim's

constant of $C = 360$. This value of C gives a good fit within the solubility range of silicon in copper, as shown in Figure 35. Additional data for various silicon concentrations in copper needs to be collected to determine the validity of the model.

Figure 35. Predicted response of Nordheim's rule for the Cu-Si data using a value of $C=360$.

7.2.1.2 Pt-Rh alloys

Resistivity at 293 K for pure platinum and pure rhodium has been previously reported as $10.6 \mu\Omega\text{-cm}$ and $4.51 \mu\Omega\text{-cm}$, respectively.⁽⁶³⁾ Figure 36 shows the experimental data, along with previously reported data⁽⁶⁴⁾ for other

Pt-Rh alloys, and expected results using Nordheim's rule for several values of Nordheim's constant C .

Figure 36. Predicted response of Nordheim's rule as applied to the experimental Pt-Rh data. Δ represent previously reported data for Pt-Rh alloys.

Based on this data the best fit to the Pt-Rh data was found for a value of $C=50$, but the fit to the data failed above 22 at% Rh. The best fit to the available Pt-Rh data for the full solid solubility range of rhodium in platinum was actually obtained through a 4th order polynomial fit, as is shown in Figure 36.

Chapter 8

CONCLUSIONS

The electrical resistivity for annealed specimens of pure copper, Cu-3.46 a/o Si, and Cu-6.92a/o Si was found to be 1.756 $\mu\Omega$ -cm, 15.16 $\mu\Omega$ -cm, and 26.32 $\mu\Omega$ -cm, respectively. The electrical resistivity for annealed specimens of pure platinum, Pt-17 a/o Rh, and Pt-22a/o Rh was found to be 10.89 $\mu\Omega$ -cm, 19.78 $\mu\Omega$ -cm, and 20.47 $\mu\Omega$ -cm, respectively. A summary of the both the experimental and previously published electrical resistivity values for all of the pure metals and alloys studied here is presented in Appendix C.

Electrical resistivity measured before and after annealing indicated that cold work damage present in the Cu-Si alloys accounted for approximately 8% of their initial resistivity measurements, a value much higher than previously reported for α -brass. Both the copper-silicon and platinum-rhodium alloys showed a nonlinear change in electrical resistivity with increasing concentrations of impurities.

In order for Matthiessen's rule to be valid, both $\rho_{\text{solvent}}(0,T)$ and $\rho_{\text{impurity}}(c,0)$ must be predictable. At a fixed temperature $\rho_{\text{solvent}}(0,T)$ becomes a constant, and the validity of Matthiessen's rule depends on the term $\rho_{\text{impurity}}(c,0)$. The model used in predicting this term must be able to predict

the resistivity contribution of the impurity atoms over the range of solid solubility in the solvent metal.

From this study it was found that Nordheim's model for concentrated alloys gave the best predictions for Cu-Si alloys up to 6.92 a/o Si, and for Pt-Rh alloys up to 22 a/o Rh. For the concentrated form of Nordheim's rule the value of C , at 293 K, in the Cu-Si and the Pt-Rh systems, was found to be 360 and 50, respectively. However, at above 22 a/o impurity content in the Pt-Rh system Nordheim's model was found to be not applicable.

The two band model provided Matthiessen's rule with a correction factor, but this still only brought calculations using Matthiessen's rule within $\pm 10\%$ of the experimental values. The $\Delta(c,T)$ factor had a large error value associated with it due to the large scatter in the data points used to calculate β and γ and the inconsistency in expected response between the Cu-Si and Pt-Rh systems. The expected response of the Pt-Rh alloy in the calculations for determining β and γ were the inverse of the reported response in both the Pt-V and Pt-Ti systems. These results may indicate that there may be some preferred situations where the two-band model is more applicable, for example at lower temperatures or more dilute impurity levels.

The experimental data for both the Cu-Si alloys and the Pt-Rh alloys did not fit the response predicted by the CBR model. In the copper system the

Cu-Si data actually indicated a possible second transition in the plot of $(\rho_A - \rho_0)$ as a function of ρ_0 .

The ability of the CHL model to predict the residual resistivity of the Pt-Rh alloy system was impossible to determine, due to the lack of resistivity data for any Pt-Rh alloys at 4.2 K. The CHL model did predict the residual resistivity for the Cu-Si system and was in agreement with previously reported results.

None of the models studied here were able to provide a complete fit of Matthiessen's rule to an alloy system where there is a broad range of impurity concentrations in solid solution with the solvent metal. Findings from this study suggest that several of these models can approximate the resistivity response due to a change in impurity concentrations, but only over limited concentration regions.

The results of this investigation, in conjunction with results previously published, shows that the relationship between impurity concentration and resistivity is non-linear. For dilute concentrations the relationship between resistivity and impurity content is a second order polynomial equation, with resistivity being affected less by impurity content at higher concentrations. At concentrations > 10 a/o the relationship is even more non-linear. The only fit to the Pt-Rh data found corresponded to a 4th order polynomial fit.

Chapter 9

RECOMMENDATIONS FOR FUTURE RESEARCH

Further studies of the resistivity of various Pt-Rh alloys, both dilute and highly concentrated are necessary to determine how well Matthiessen's rule fits the Pt-Rh system at low concentrations, and to determine a value of K' for rhodium in platinum.

Water quenching of both pure copper and pure platinum samples needs to be conducted to determine if Matthiessen's rule can predict resistivity changes as a function of vacancy concentrations.

Studies of Matthiessen's rule using the same models, at different temperatures, would indicate if there are any obvious changes in any of these model's predictions or values of their constants. Changes in these constants would indicate that $\rho_{\text{solvent}}(0,T)$ and $\rho_{\text{impurity}}(c,0)$ are not independent of each other.

There is an amazingly limited amount of resistivity data available given the enormous number of possible single phase alloy systems available to study, especially at room temperature. An investigation into a broader range of single phase alloy systems, using the same models would also be useful in determining the general applicability of the predictive models.

An investigation of how these models behave as the complexity of the system being studied is increased should also be undertaken. Do these models work within constraints determined here when applied to two phase systems?

Chapter 10

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APPENDIX A

Figure 37. X-bar and R-bar chart for electrical resistivity of pure copper (as-received).

Figure 38. X-bar and R-bar chart for electrical resistivity of Cu-3.46 a/o Si (as-received).

Figure 39. X-bar and R-bar chart for electrical resistivity of Cu-6.92 a/o Si (as-received).

Figure 40. X-bar and R-bar chart for electrical resistivity of pure copper (annealed).

Figure 41. X-bar and R-bar chart for electrical resistivity of pure copper (annealed and quenched).

Figure 42. X-bar and R-bar chart for electrical resistivity of Cu-3.26 a/o Si (annealed).

Figure 43. X-bar and R-bar chart for electrical resistivity of Cu-6.92 a/o Si (annealed).

Figure 44. X-bar and R-bar chart for electrical resistivity of pure platinum (as-received).

Figure 45. X-bar and R-bar chart for electrical resistivity of pure Pt-17a/o Rh (as-received).

Figure 46. X-bar and R-bar chart for electrical resistivity of pure Pt-22a/o Rh (as-received).

Figure 47. X-bar and R-bar chart for electrical resistivity of pure platinum (annealed).

Figure 48. X-bar and R-bar chart for electrical resistivity of pure platinum (annealed and quenched).

Figure 49. X-bar and R-bar chart for electrical resistivity of pure Pt-17a/o Rh (annealed).

Figure 50. X-bar and R-bar chart for electrical resistivity of pure Pt-22a/o Rh (annealed).

APPENDIX B

Determination of the micro-grain size number was done for all samples using the linear intercept, (or Heyn), procedure described in ASTM E112-88 (Standard Test Methods for Determining Average Grain Size). The intercept procedure calculates the number of grains intercepted by a straight line of a fixed length. This value was compared with the data in Figure 6 in ASTM E112-88 to determine the micro-grain size number G . Determination of the average grain size was done using Table 2 in ASTM E112-88. The as-received pure copper specimen had an ASTM value of $G = 10.6 \pm 0.2$ which corresponded to an average grain area of $89.1 \times 10^{-6} \text{ mm}^2$. The annealed pure copper specimen had an ASTM value of $G = 1.5 \pm 0.1$, corresponding to an area of 0.0456 mm^2 . The areal change after annealing was given by

$$100\% * (0.0456 \text{ mm}^2 - 89.1 \times 10^{-6} \text{ mm}^2) / 89.1 \times 10^{-6} \text{ mm}^2 = 5,107\%$$

APPENDIX C

Table 15. Experimental and reported results for copper and Cu-Si alloys at 293K.

metal/alloy	Experimental	Metals Handbook (Ref #46)	Norbury, et al. (Ref #47)	ASM Packaging Handbook (Ref #44)
pure copper	1.7568	1.6730	1.70	1.7241
Cu-2.1 a/o Si			9.5	
Cu-3.46	15.0865			
Cu-3.8			15.24	
Cu-5.9			20.80	
Cu-6.92	26.2421			

Table 16. Experimental and reported results for platinum and Pt-Rh alloys at 293K.

metal/alloy	Experimental	Omega Engineering (Ref #64)	Metals Handbook (Ref #46)	MacFarlane (Experimental) (Ref #34)	MacFarlane (Reported) (Ref #34)
pure platinum	10.8942	9.83	10.6		
Pt-11 a/o Rh		15.79			
Pt-17 a/o Rh	19.7839	18.45		18.8	19
Pt-22 a/o Rh	20.4741	18.95		20.3	19.6
Pt-32 a/o Rh		19.28			
Pt-45 a/o Rh		18.68		18.9	
Pt-56 a/o Rh		16.79			
pure Rh		4.29			

Reference #'s pertain to references contained in Chapter 10, References.