THE REVERSION KINETICS OF PRE-PRECIPITATES
IN AN ALUMINUM - COPPER ALLOY

by

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ABSTRACT
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Submitted to the Department of Metallurgy and Materials Science on January 14, 1972 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The kinetics of reversion of Guinier-Preston zones in an Aluminum - 3.85 wt.pct. Copper alloy have been investigated using electrical resistivity measurements. Since the initial stages of reversion have never been examined in earlier work and since the currently accepted mechanisms for reversion predict as yet unobserved, kinetic regimes, capacitor discharge pulse heating techniques were used to study the reversion of alloys aged to the slow reaction. A sensitive resistivity measuring instrument, based on a Kelvin Double Bridge, was used to observe small resistivity changes only half a millisecond after the specimen had been pulsed to the reversion temperature. The necessary design requirements to achieve this resolution were discussed in detail.

A second pulse heating circuit was also incorporated so that the time and temperature dependencies of the instantaneous activation energy for reversion could be obtained using the 'change of slope' method, and the results generated enabled the kinetic stages to be readily distinguished.

Specimens quenched with cold Ethanol and liquid Nitrogen after reversion treatments were shown to undergo significant plastic deformation, in spite of using the customary precautions, so the reageing studies could not be used to shed light on the reversion mechanisms.

The isothermal resistivity decay during reversion and the experimentally determined instantaneous activation energies, revealed that there was a sharp discontinuity in kinetic behaviour at 200°C. Above this temperature, an extensive, diffusion controlled dissolution reaction with an activation energy for solute diffusion of 0.63 ev., preceded the previously investigated 1.0 and 1.3 ev. stages, but below this temperature, the fast reversion reaction did not take place. A mechanism based on the 'vacancy pump' concept was proposed as the currently accepted mechanisms for reversion did not predict the observed kinetic characteristics. This alternative model implied that the GP zones in well-aged Aluminum - Copper alloys are stabilized by vacancies and that the properties of pre-precipitates in general, should be investigated with this in mind.

In order to predict the kinetics of reversion of alloys containing disc-like zones, a finite difference method was developed for the dissolution of spherically symmetric precipitates in a finite array. A perturbation solution for spherical precipitates in an infinite matrix was also derived and shown to be preferred to other approximate solutions.

Title: Associate Professor of Metallurgy.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>i</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>ii</td>
</tr>
<tr>
<td>List of Illustrations</td>
<td>vii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xi</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>xii</td>
</tr>
<tr>
<td><strong>I. INTRODUCTION</strong></td>
<td></td>
</tr>
<tr>
<td>1. The Thermodynamics of Reversion</td>
<td>2</td>
</tr>
<tr>
<td>2. The Kinetics of Reversion</td>
<td>3</td>
</tr>
<tr>
<td>3. Overall Description of Thesis</td>
<td>7</td>
</tr>
<tr>
<td><strong>II. EXPERIMENTAL APPARATUS</strong></td>
<td>9</td>
</tr>
<tr>
<td>1. The Capacitor Discharge Pulse Heater</td>
<td>9</td>
</tr>
<tr>
<td>1. Quenching Methods</td>
<td>10</td>
</tr>
<tr>
<td>2. Temperature Measurements</td>
<td>11</td>
</tr>
<tr>
<td>3. Temperature Measurement Sensitivity and Accuracy</td>
<td>13</td>
</tr>
<tr>
<td>4. Noise Rejection</td>
<td>14</td>
</tr>
<tr>
<td>2. Electrical Resistivity Measurements</td>
<td>15</td>
</tr>
<tr>
<td>1. Accuracy and Sensitivity of Kelvin Bridge</td>
<td>18</td>
</tr>
<tr>
<td>2. Noise Rejection Characteristics of Kelvin Bridge</td>
<td>22</td>
</tr>
<tr>
<td>3. Repeatability</td>
<td>23</td>
</tr>
<tr>
<td>3. The Kelvin Double Bridge</td>
<td>24</td>
</tr>
<tr>
<td>1. Circuit and Components</td>
<td>24</td>
</tr>
<tr>
<td>2. Layout and Design</td>
<td>26</td>
</tr>
<tr>
<td>3. Kelvin Bridge Performance</td>
<td>27</td>
</tr>
<tr>
<td>4. Procedures</td>
<td>29</td>
</tr>
<tr>
<td>4. Specimen Preparation</td>
<td>31</td>
</tr>
</tbody>
</table>
III. THE DISSOLUTION OF SPHERICALLY SYMMETRIC PRECIPITATES 34

1. Numerical Analysis 34
   1. Formulation of the Problem 35
   2. The Finite Difference Expressions 38

2. Mathematical Analysis 40
   1. Auxiliary Equations 40
   2. Interface Motion Along Co-ordinate Axes 41
   3. Concentration at Nodes near the Interface 42
   4. Evaluation of Expansion Coefficients 42

3. Computation Procedures 44

4. Stability and Accuracy 45
   1. Analytic Results 45
   2. Computed Results 48

5. Conclusions 52

IV. A REVIEW OF DISSOLUTION THEORY 53

1. Isolated Particles in an Infinite Matrix 54

2. Perturbation Solution for the Dissolution of Spherical
   Precipitates in an Infinite Matrix 57

3. Uniform Precipitate Arrays 61
   1. Analytic Methods 61
   2. Finite Difference Methods 63

4. The Dissolution Kinetics of Idealised GP Zones 63

5. Conclusions 67

V. A REVIEW OF PROPERTY CHANGES OBSERVED UPON AGEING AND
REVERTING ALUMINUM - COPPER ALLOYS 68

1. Property Changes on Ageing 68
2. Property Changes during Reversion

3. Interpretation of Resistivity Changes Due to GP Zones
   1. Intrinsic Resistivity Contribution
   2. Thermal Resistivity Contribution

VI. EXPERIMENTAL RESULTS

1. Resistivity Measurements Made during Reversion
   1. Fast Reversion Reaction
   2. Slow Reversion Reaction

2. Double Pulse Heat Treatments during Reversion
   1. Instantaneous Activation Energy for Reversion
   2. Estimate of the Percentage Change in Resistivity Produced by the Fast Reversion Reaction

3. The Reageing of Partially Reverted Specimens

4. Resistivity Measurements Made in Liquid Nitrogen after Reversion at 215°C.

5. Conclusions

VII. ANALYSIS OF EXPERIMENTAL RESULTS

1. Fast Reversion Reaction
   1. Initial Rate, Resistance Decay, and the Fast Reaction Completion Time
   2. Rate of Resistance Decay at Longer Times

2. Slow Reversion Reaction
   1. Activation Energy of the Slow Reversion Reaction
   3. The Origins of the Resistivity Changes during Reversion

4. Comparisons of the Slow Reversion Reactions above and below 200°C.
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5. Summary of Experimental Results</td>
<td>123</td>
</tr>
<tr>
<td>VIII. INTERPRETATION OF RESULTS</td>
<td>125</td>
</tr>
<tr>
<td>1. Inapplicability of the 'Vacancy Cluster' and 'GP Zone' Mechanisms</td>
<td>126</td>
</tr>
<tr>
<td>2. Interpretation of Reversion Kinetics Based on the Slow Reaction</td>
<td>130</td>
</tr>
<tr>
<td>'Vacancy Pump' Model</td>
<td></td>
</tr>
<tr>
<td>1. Formulation of the Model</td>
<td>130</td>
</tr>
<tr>
<td>2. Comparison of Predicted and Experimentally Determined Activation</td>
<td>132</td>
</tr>
<tr>
<td>Energies</td>
<td></td>
</tr>
<tr>
<td>3. Completion Time of the Fast Reaction Fraction</td>
<td>134</td>
</tr>
<tr>
<td>3. Reageing after Reversion Treatments above 200°C.</td>
<td>138</td>
</tr>
<tr>
<td>4. The Origin of Specimen Strains during Pulse Heating and Quenching</td>
<td>138</td>
</tr>
<tr>
<td>IX. SUMMARY AND CONCLUSIONS</td>
<td>141</td>
</tr>
<tr>
<td>X. SUGGESTIONS FOR FUTURE WORK</td>
<td>145</td>
</tr>
<tr>
<td>APPENDIX A. Description of Pulse Heater, Circuit and Components</td>
<td>146</td>
</tr>
<tr>
<td>1. Power Supplies</td>
<td>146</td>
</tr>
<tr>
<td>2. Capacitor Bank and Discharge Assembly</td>
<td>148</td>
</tr>
<tr>
<td>3. Specimen and DC Heating Current Assembly</td>
<td>148</td>
</tr>
<tr>
<td>4. Capacitor Discharge Control</td>
<td>149</td>
</tr>
<tr>
<td>5. Quench Control</td>
<td>159</td>
</tr>
<tr>
<td>6. Direct Heating Current Control</td>
<td>149</td>
</tr>
<tr>
<td>APPENDIX B. Common Mode Rejection (CMR) Derivations</td>
<td>150</td>
</tr>
<tr>
<td>1. Two-wire Thermocouple</td>
<td>150</td>
</tr>
<tr>
<td>2. Three-wire Thermocouple</td>
<td>150</td>
</tr>
</tbody>
</table>
## LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Number</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>II.1.</td>
<td>Wheatstone Bridge circuit used to nullify DC heating current induced voltage with a Three-wire Thermocouple.</td>
<td>12</td>
</tr>
<tr>
<td>II.2.</td>
<td>Kelvin Double Bridge Circuit.</td>
<td>17</td>
</tr>
<tr>
<td>II.3.</td>
<td>Kelvin Double Bridge output voltage as a function of the fractional change in specimen resistance, $\delta$.</td>
<td>19</td>
</tr>
<tr>
<td>II.4.</td>
<td>Kelvin Double Bridge, showing component values and dummy arm used for standardising the bridge.</td>
<td>25</td>
</tr>
<tr>
<td>II.5.</td>
<td>Isothermal ageing of an Aluminum = 4 wt. pct. Copper alloy at 70°C.</td>
<td>32</td>
</tr>
<tr>
<td>III.1.</td>
<td>Polar Co-ordinate scheme used.</td>
<td>37</td>
</tr>
<tr>
<td>III.2.</td>
<td>Finite array element.</td>
<td>37</td>
</tr>
<tr>
<td>III.3.</td>
<td>Polar grid superimposed on the spherical finite array element.</td>
<td>39</td>
</tr>
<tr>
<td>III.4.</td>
<td>Computation time and dimensionless time increment needed to obtain a stable solution for the volume change on dissolution, as a function of the required volume change.</td>
<td>49</td>
</tr>
<tr>
<td>III.5.</td>
<td>Accuracy and stability analysis for the limiting case of a spherical CuAl$_2$ precipitate in Al-4 wt. pct. Cu at 520°C.</td>
<td>50</td>
</tr>
<tr>
<td>III.6.</td>
<td>A comparison of analytical finite difference solutions with the experimental observations of Baty et al(48) for CuAl$_2$ precipitates in an Al-4 wt. pct. Cu alloy.</td>
<td>51</td>
</tr>
</tbody>
</table>
IV.1. A comparison of the precipitate dissolution kinetics as predicted by numerical methods, and analytical solutions assuming a stationary interface and a perturbation expansion.

IV.2. Dissolution of spherical CuAl₂ precipitates in Al-4 wt.pct. Cu: a comparison of the finite difference solutions of Tanzilli and Heckel (49) and of this investigation.

IV.3. Dissolution of ellipsoidal GP zones in an Al-4 wt.pct. Cu alloy at 200°C and 250°C, assuming an aspect ratio of 0.25.

V.1. Resistivity changes observed during the ageing of Aluminum - 4 wt.pct. Copper alloys.

V.2. Mechanical properties as observed at room temperature after reversion at various temperatures.

V.3. Resistivity changes observed during the reversion of Aluminum - 4 wt.pct. Copper alloys at various indicated reversion temperatures.

V.4. A comparison of two recent theories due to Griffin and Jones (70) and Hillel (71), for the intrinsic resistivity contribution of a zone in Aluminum-Copper.

V.5. Schematic resistivity changes during ageing.

V.6. Schematic resistivity changes during reversion.

VI.1. Thermocouple and Kelvin Double Bridge voltage output oscillographs for the reversion of an Al = 4 wt.pct. Copper alloy.

VI.12. Experimental values for the function versus the rever-
VI.13. Thermal coefficient of resistivity data of Table VI.4 plot.

VI.14. Resistivity changes observed during the reageing of an Aluminum - 3.85wt.pct. Copper alloy at 28°C after various reversion heat treatments.


VII.1. A comparison of the projected oscilloscope traces for the fast reversion reaction and the least squares', fifth order fitted polynomial.

VII.2. The temperature dependence of the true fast reversion reaction fraction, $X_f$, and the fast reaction completion time, $t_{cf}$.

VII.3. The temperature dependence of the initial rate of decay of the fast reaction fraction, $x_f$.

VII.4 Logarithm of the rate of change of the fast reaction fraction at various indicated reversion temperatures.

VII.7. Temperature dependence of the gradient of the linear stages of the log $x_f$ versus time plots at different reversion temperatures.

VIII.1. The coherent metastable GP zone solvus curve as determined by various investigators, for Aluminum - Copper alloys.

VIII.2. Extrapolation of the initial rates of resistivity change to temperatures below 200°C.
VIII.3. Variation of GP zone size with Ageing time for Al

  = 4 wt.pct.Cu.  

A.1. Capacitor Discharge Pulse Heater Assembly diagram  

B.1. A Two-wire thermocouple in series with an amplifier  

B.2. A Three-wire thermocouple in series with an amplifier 

  showing the double earthing problem  

B.3. Circuit for a three-wire thermocouple in series with 

  an amplifier  

B.4. Partial circuit diagram following a Wye-Delta 

  Transformation  

B.5. A Kelvin Double Bridge in series with an amplifier; 

  circuit diagram following two Delta-Wye Transform- 

  ations  

B.6. Circuit of Figure B.6. following a third Delta 

  -Wye Transformation  

F.1. Schematic diagram showing specimen resistivity 

  changes during the fast and slow reversion reactions 

  at two temperatures
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Number</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.1</td>
<td>Summary of results given by the stationary interface approximation for dissolution.</td>
<td>55</td>
</tr>
<tr>
<td>IV.2</td>
<td>Parameters describing the rate of change of the average matrix concentration, ( \bar{c} ), for precipitates in uniform arrays.</td>
<td>62</td>
</tr>
<tr>
<td>V.1</td>
<td>Preageing heat treatments for the alloys (Al≈4wt.pct. Cu) of Figure V.1.</td>
<td>71</td>
</tr>
<tr>
<td>V.2</td>
<td>Pre-reversion heat treatments for the alloys (Al≈4wt. pct. Cu) of Figure V.3.</td>
<td>71</td>
</tr>
<tr>
<td>VI.1 -VI.3</td>
<td>Instantaneous activation energy as determined by the 'change of slope' method.</td>
<td>92, 93</td>
</tr>
<tr>
<td>VI.4</td>
<td>Thermal coefficient of resistivity for Aluminum - Copper alloys- in the range, 100 - 300°C.</td>
<td>97</td>
</tr>
<tr>
<td>VII.1</td>
<td>Normalisation parameters for log ( \dot{x}_f ) versus time ( t ), curves for the fast reversion reaction.</td>
<td>114</td>
</tr>
<tr>
<td>VII.2</td>
<td>Estimates of ( t^* ), the time in seconds for the onset of linear log ( \dot{x}_f ) versus time behaviour for dissolving GP zones in an Al-3.84 wt.pct.Cu alloy at 200°C.</td>
<td>117</td>
</tr>
<tr>
<td>VII.3</td>
<td>Normalisation parameters for log ( \dot{x} ) versus time ( t ), curves for the fast and slow reactions of Figure VII.8.</td>
<td>117</td>
</tr>
</tbody>
</table>
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The term "reversion", first proposed by Gayler (1) for the very rapid fall in strength on heating aged Aluminum - Copper alloys for short times at high temperatures below the equilibrium solvus, in principle can be applied to the dissolution of any non-equilibrium precipitate to give a uniform solid solution. However, since the diffusional precipitation of non-equilibrium incoherent precipitates is extremely unlikely, the term has come to imply the dissolution of coherent or partially coherent non-equilibrium precipitates. Furthermore, a very vaguely defined precipitate is usually involved since even the resolution of simple solute clusters causes property reversions to homogeneous solid solution values.

In this thesis attention will be focused on those systems, notably Aluminum - Copper, in which solute clusters, or Guinier-Preston zones, seem to nucleate, grow and subsequently coarsen, in contrast to the other limiting case where clusters form by spinodal decomposition, as in the Aluminum - Zinc system. The complex issues raised in attempting to distinguish these mechanisms will fortunately be of little concern as only the later stages of zone coarsening and the early stages of reversion will be considered in detail. However, it should be appreciated that, in relation to the amount of research that has been devoted to examining the evolution of pre-equilibrium precipitate structures, the inverse process, that of their degeneration, has only recently been given detailed attention in a few isolated cases, and it has been shown that the dissolution behaviour gives valuable information about the evolution process.
It is convenient to introduce the thermodynamic and kinetic aspects of reversion separately and this will serve to demonstrate the controversial issues.

I.1. The Thermodynamics of Reversion.

The concept of a metastable phase diagram for non-equilibrium precipitates has been widely used in explaining reversion behaviour. Such a diagram has, to some extent, been theoretically justified by Cahn (2) who analysed the solvus for spherical coherent precipitates. Subsequently de Fontaine (3) used the same formalism to show that all zones must dissolve completely if the appropriate alloy is rapidly heated from some low temperature to a temperature above the solvus. This has been experimentally confirmed by Niklewski et al (4) who demonstrated that the zones in an Aluminum - Zinc alloy completely dissolved above the coherent solvus calculated by Lasek (5) using Cahn's theory. De Fontaine's work also justifies the classic technique, developed by Beton and Rollason (6), for determining the coherent solvus, wherein the aged alloy is held at high temperatures and the room temperature hardness is determined as a function of the holding time. Above some critical temperature the hardness will fall to a minimum, temperature independent value and this is the solvus temperature. However, the solvus curves for many systems are inaccurately known as for example, in Aluminum - Copper where Petov (7) gives a curve that is about 20°C above that determined by Beton and Rollason (6). Different ageing treatments may produce these discrepancies so Kelly and Nicholson (8) refer to the metastable GP zone solvus as the minimum temperature of reversion for various alloy compositions.
Since this thesis will be primarily concerned with the kinetics of reversion, further discussion of the thermodynamic aspects will be deferred. However, the experimental technique used did show a marked discontinuity in reversion kinetics at 200 Degrees Centigrade as opposed to the continuous behaviour predicted by de Fontaine and it is suggested that defects associated with the zones cause the zones to be stabilised.

1.2. The Kinetics of Reversion.

There have been very few investigations that considered the property changes during reversion in sufficient detail to enable the kinetic mechanisms to be determined. Broadly speaking, these studies can be divided into those relating to alloys that decompose spinodally and in which possible defect structure does not lead to long time anomalous ageing kinetics, and into those in which there is an enhanced solute diffusivity to all ageing times. The emphasis on these systems has derived solely from the lack of understanding of the precipitate evolution behaviour and not from a fundamental interest in the reversion kinetics per se.

Of the former, the Aluminum - Zinc system has been shown to decompose spinodally (9,10) and subsequently coarsen (11). Vacancies, either quenched-in or induced by plastic deformation, enhance the kinetics by increasing the solute diffusivity (12,13). There is no retention of quenched-in vacancies at long times (14). Because of the low temperature coherent solvus, reversion kinetics can be followed accurately after several seconds using conventional heat treating methods and Graf (15) and Herman (12), using hardness measurements, and Moringa et al (16), using small angle scattering data, found the activation energy for reversion to be that for solute diffusion in an
equilibrium concentration of vacancies. Nagata et al (17) gives a similar result for Copper - 3 wt. pct. Titanium using resistivity measurements. Moreover, Morinaga et al show that the dissolution process is the inverse of the formation process since the zones initially have discrete interfaces which become diffuse during reversion.

No such well established results exist however for the reversion kinetics of the second type of system of which the Aluminum - Copper and the Aluminum - Silver systems are typical. Upon ageing alloys of these systems an initial fast reaction with an activation energy of about .5 ev. occurs (14,18-22), due to the enhanced solute mobility during the annealing out of quenched-in vacancies. The subsequent slow reaction proceeds for many days at room temperature with rates greatly in excess of those predicted assuming an equilibrium concentration of vacancies. Several mechanisms have been proposed for this behaviour and of those, a mechanism involving an excess vacancy concentration in equilibrium with vacancy aggregates has been favoured by most investigators (20,22,23).

Identical conclusions with regard to vacancy aggregates, have been reached for the reversion mechanisms in these systems since alloys aged to the slow reaction, reverted with a time dependent activation energy that increased from 1.0 ev. to 1.3 ev. (25,26), while alloys reverted from the fast reaction stage required an activation energy of .5 ev (25). In both cases the earliest observations were made after half a second and while this is probably not crucial for alloys reverted from the fast reaction, it is significant for alloys reverted at later stages because the vacancy aggregate mechanism predicts an initial reversion stage with an activation energy of .5 ev. followed by the 1.0 and 1.3 ev. stages. Clearly the rapid heating capabilities
of a capacitor discharge pulse heater would enable the early stages of reversion to be monitored if a sensitive measuring system was incorporated. Such an instrument was developed which enabled the resistivity changes of the reverting specimen to be measured .5 msec. after pulsing to the reversion temperature. Attention was focused primarily on Aluminum - 3.85 wt. pct. Copper alloys aged to the slow reaction with heat treatments identical to those used by Shimizu and Kimura (25) in the most definitive study of reversion kinetics in Aluminum - Copper type systems to date.

A further feature of the rapid heating characteristics of the pulse heater is the inherently greater accuracy possible when the 'change of slope' method is used to determine the activation energies of kinetic processes. This method is based on the generalisation of a relationship given by Hillert (27) that effectively defines an activation energy in which the rate of change of an observable property p, is given by:

\[ \frac{1}{p} \cdot \frac{\partial p}{\partial t} = G(p,T) = G_0(p,T) \exp \left( \frac{Q(p)}{k_g T} \right) \]

where \( k_g \) is the gas constant. This expression is to be preferred to other alternative definitions since it gives an activation based on the correct dimensions of time \(^{-1}\). If the temperature is instantaneously changed from \( T_1 \) to \( T_2 \) when \( p = p_1 \) then we have:

\[ \log_e \left( \frac{\frac{\partial p}{\partial t} \bigg|_{T_1}}{\frac{\partial p}{\partial t} \bigg|_{T_2}} \right) = \log_e \left( \frac{G_0(p_1,T_1)}{G_0(p_1,T_2)} \right) - \frac{Q(p_1)}{k_g} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

where it is assumed that the same thermally activated process is occurring at all temperatures between \( T_1 \) and \( T_2 \). If it is further
assumed that the temperature dependence of the rate of property change over a sufficiently small temperature range is described by the Boltzmann factor then the function $G_0$ is independent of $T$ and we have the classic equation for the 'change of slope' method:

$$
\log_e \left( \frac{\frac{\partial p}{\partial t}|_{T_1}}{\frac{\partial p}{\partial t}|_{T_2}} \right) = - \frac{Q(p_1)}{kT} \frac{\Delta T}{T_1T_2}
$$

(1.1)

The assumption that $G_0$ is not a function of $T$ can be given some physical significance in a few simple cases as for example, in the annealing of single vacancies to sinks where it corresponds to a temperature independent sink density. In most complex situations no such physical interpretation can be invoked and the normal procedure has been to determine the activation energy at a particular stage as a function of the temperature interval $\Delta T$, and to extrapolate to zero $\Delta T$ so that the intercept gives the true activation energy $Q(p_1)$ (20). This procedure has never been justified and it would be interesting to model a few processes along the lines presented by Burton and Lazarus (28) who developed a simple computer model for a defect annihilation reaction and investigated the outcome of an instantaneous temperature increase.

The main advantage of using a pulse heater is that a truly instantaneous temperature rise is possible and continuous property changes can be recorded. Hence severe errors using discrete data points are avoided. This is important because Burton and Lazarus have shown that the instantaneous activation energy obtained by the change of slope technique is a characteristic quantity while the extrapolated apparent activation energy is not. For their model, the
latter varies with the sink density suggesting that an extrapolation
of the instantaneous energy to zero $\Delta T$ probably represents the most
fundamental observable parameter using the slope change method. This
approach was used to a limited extent in this investigation but since
it was found that the instantaneous activation energy was not a function
of $\Delta T$ (to within the experimental limits), the majority of the double-
pulse experiments involved only the reversion-time dependence of the
activation energy, without the $\Delta T$ dependence and subsequent extrapolation
to zero $\Delta T$.


In the first part of the thesis, the pulse heater will be
described and the resistivity measuring system will be analysed in
some detail. Following a discussion of the applicability of
dissolution theory to reversion and the development of some new results,
in particular a numerical method for handling the dissolution of
spherically symmetric precipitates of revolution in a finite matrix and
a perturbation method for spherical precipitates in an infinite matrix,
the correlation of property changes with alloy structure will be
critically examined, with special reference to resistivity changes.

Then the experimental observations of the reversion and reaging kinetics
of an Aluminum - 3.85 wt. pct. Copper alloy will be given and subsequently
analysed in the light of the various models proposed for the reversion
kinetics. It will be shown that two distinct reactions occur during the
early stages of reversion above 200°C with activation energies of about
.6 ev. and 1.0 ev. while only one reaction takes place below this
temperature. The results of the double pulsing experiments and other
subsidiary experiments will then be incorporated to substantiate the
proposal that extensive ageing at low temperatures causes a significant fraction of the zones to become stabilised by vacancies and that the vacancy 'pump' model (29) as amended by Herman (30) accounts for the kinetics of the slow reaction on ageing and of reversion. It is appreciated however that the mathematical formulation and the experimental confirmation of the theoretical predictions of the model leave much to be desired (31), but it is felt that the concept is valid and applicable.

Although the idea that vacancies can be associated with zones is not new (30,32,33) and has in fact recently been shown to be the case for coherent Cobalt precipitates in a Copper – Cobalt alloy using an atomistic computer model (34), there has to date been no conclusive evidence that vacancies can stabilize coherent precipitates and it is suggested that pulse heating methods are well suited to the study of this situation. Finally, some remarks relating to the technologically important problems relating to the development of subsequent precipitates from GP zones are made in view of the possible defect structure associated with the zones.
II. EXPERIMENTAL APPARATUS

II.1. The Capacitor Discharge Pulse Heater.

The capacitor discharge pulse heater was based on that originally developed by Karlyn (35) and Parker (36). The most significant changes included the incorporation of electronic timing circuits, spark gap triggers in place of mechanical relays, circuitry to enable a direct current to maintain the specimen at temperature and a second capacitor bank. This last feature was recently used by Emmer-Szerbesko (37).

A schematic circuit diagram of the pulse heater is given in Appendix A. Briefly the following sequence occurred in a typical double pulse heating experiment. While the two capacitor banks were being charged a direct current obtained from a 12 Volt lead-acid accumulator was switched on. This heating current by-passed the specimen through a lead of resistance approximately equal to that of the specimen. Initiation of the current about thirty seconds before the first pulse was necessary because a constant current power supply was not employed since it would introduce noise and contribute to voltage transient generation. Pre-initiation of the current allowed for the discharge characteristics of the accumulator and the heating up of the regulating circuit.

When the capacitors were fully charged the DC heating current by-pass relay was closed. Fixed to this relay was an adjustable micro-switch which activated a delay relay that acted as a pair of points in an automotive high tension circuit, thus causing a spark to be generated between the spark gap trigger electrodes. With careful adjustment,
discharge of the first capacitor bank occurred soon after the by-pass relay contacts had ceased bouncing. No serious problems were encountered using spark gap triggers in spite of the relatively low capacitor charging voltages employed.

The firing switch also activated two electronic timing units. The first of these triggered the spark gap of the second capacitor bank while the other switched off the DC heating current and latched open a valve that released a pressure driven quenching fluid. It was found to be unnecessary to uncouple the DC heating circuit during the second pulse.

The voltage developed in a coil wrapped around the positive lead to the first capacitor bank, upon the discharge of this bank, triggered an oscilloscope that monitored specimen resistance and temperature changes.

The specimens were mounted in well cleaned, Copper blocks that were nine centimeters apart and enclosed in a draught-proof Perspex cabinet. Draughts, unless excluded, caused appreciable specimen temperature fluctuations. The mounting blocks could be loosened so that the expansion and contraction strains on pulsing and quenching would not generate excessive plastic deformation.

II.1.1. Quenching Methods.

Water or cold ethanol was squirted onto the specimen by pressuring a flexible plastic bottle. To obtain cold ethanol, commercial denatured alcohol was first cooled in an ice bucket and then passed through a dry ice/acetone bath that was placed close to the specimen. Just before each experiment, the ethanol was allowed to flow, thus ensuring that the feed piping was cold.
The specimen was contained inside a half inch in diameter, cylindrical boat and was sprayed by three nozzles thereby achieving reasonable cooling rates (minimum rate above 50°C was 1000°C/sec.) over the entire specimen. Moreover, the cylindrical boat enabled the specimen to be held at low temperatures if the flow of cold ethanol was continued.

The boat fitted very tightly between the mounting blocks so that heat losses through specimen contact with the blocks were not altered significantly. Narrow slits in the end faces of the boat ensured containment of the quenching fluid.

II.1.2. Temperature Measurement.

The temperature at the mid-point of the specimen was measured by recording on an oscilloscope, the output from a three-wire Alumel-Cromel-Alumel (.002 inches in diameter) thermocouple that was spot welded to form an intrinsic junction at the specimen surface. The three-wire arrangement permitted nullification of the potential difference generated by the DC heating current across the thermocouple, by incorporating the thermocouple leads into a Wheatstone Bridge as described by Haworth and Gordon Parr (38) and shown in Figure II.1.

It was found to be convenient to have a reversing switch in the bridge circuit so that the ratio of the arms could be extended over a wide range. The bridge output was fed into a dual-beam oscilloscope via a diode clipper (36) that served to protect the oscilloscope from high voltage transients.

In order to establish the null point before each experiment, a low DC current was passed through the specimen and the bridge was adjusted so that no detectable inbalance was observed on reversing the current.
Figure II.1. Wheatstone Bridge circuit used to nullify DC heating current induced voltage with a 'three-wire' thermocouple.
An oscilloscope sensitivity of 50μV/cm. was used so that a 10μV imbalance was detectable. Since the output voltage of the Wheatstone Bridge $V_2$, is given by (39):

$$V_2 = \frac{V_1 \delta}{4}$$

where $V_1$ is the applied voltage and $\delta$ the fractional resistance deviation from balance, then when the normal DC heating current is passed, which is equivalent to raising $V_1$ by a factor of 10, the output for a low temperature imbalance of 10μV is 100μV corresponding to 2°C for an Alumel-Cromel thermocouple and hence the temperature is accurate to within 2°C.

II.1.3. Temperature Measurement Sensitivity and Accuracy.

In order to have a sensitivity appropriate to this accuracy of 1%, the temperature was recorded using a .5mv/cm. scale. Since most experiments gave outputs greater than the displayable range for this sensitivity, the room temperature thermocouple output could not be used as a base. Instead the output from a Honeywell Potentiometer, Model 2745, was used and to minimise the effects of amplifier drift and line voltage variations, the base was recorded immediately before the first pulse and the firing switch in fact triggered this operation.

Although this procedure introduced more sources of error, it was judged to be necessary because in some of the experiments, temperature changes rather than absolute temperatures were of more importance. In particular, for the double pulse experiments the activation energy is given by Equation 1.1 and the main source of error is in $\Delta T$, the temperature difference between the two pulses. Since it was prohibitively difficult to adjust the DC heating current after the second pulse,
\( \Delta T \) was usually only a few degrees Centigrade and the second pulse temperature stayed to within 1°C for 0.5 seconds. A \( \Delta T \) of 10°C gives a thermocouple output of 0.5mV, which can be observed to within 4% using a 0.5mV/cm. voltage sensitivity.

In general it was possible to maintain the specimen temperature to within 2°C over about 5 seconds in a single pulse experiment, but thereafter significant specimen resistance changes caused the joule heating effect of the DC current to be reduced appreciably.

II.1.4. Noise Rejection.

The Common Mode Rejection (CMR) of a device measures its ability to provide a signal that is independent of any input applied equally to both inputs and is a useful design factor. In Appendix B it is shown that for an isolated, balanced, differential amplifier in series with a two-wire thermocouple attached to a grounded specimen then the CMR is given by:

\[
\text{CMR (2-wire)} = \frac{R_a}{R_1 - R_2}
\]

where \( R_a \) is the amplifier input resistance and \( R_1 \) and \( R_2 \) the source resistances of the thermocouple. A high CMR is obtained by equalising \( R_1 \) and \( R_2 \), a point that is often not appreciated.

More relevant to this investigation is the case of the three-wire thermocouple and in Appendix B it is shown that the CMR is given by:

\[
\text{CMR (3-wire)} = \frac{R_a}{R_1 - R_2 + \frac{(R_6 - R_8)(R_7 + R_5)}{(R_5 + R_6)}}
\]

where \( R_7 \), \( R_8 \) are the interprobe resistances and \( R_5 \), \( R_6 \) are the balancing bridge resistances. Moreover, since the bridge will be balanced to
compensate for the superimposed voltage due to the DC heating current and since the Peltier Effects at the thermocouple/specimen interfaces must be minimised by ensuring that a low current passes through the bridge resistors, it is also proved in Appendix B that:

\[
\text{CMR (3-wire)} = \frac{\frac{4R_a}{4(R_1-R_2) + 2(R_6-R_8)(1-\frac{\Delta w}{w})}}{w}
\]

with the restriction that:

\[
2(1 - \frac{\Delta w}{w})(R_6 - R_8) >> 0
\]

where \(\Delta w/w\) is the fractional error in positioning the thermocouple probes and is assumed to be small (less than 10%). It is clear that the Peltier Effect restriction condition reduces considerably the available CMR and typically this would be by a factor of 50 to 1000. Moreover, the source resistance imbalance now becomes of secondary importance and the CMR will be at least 1000 times smaller than for a two-wire case. Finally, the probes need only be positioned to within 10% which is an important practical consideration.

II.2. Electrical Resistivity Measurements.

In order to accurately observe the small resistivity changes occurring during reversion (about a 4% difference between the as-aged and the fully reverted states), a sensitive measuring system is required that records millivolt voltage changes over millisecond time ranges in a high voltage environment. Difficulties are to be expected as shown by Ayers (40) who attempted to study the kinetics of the massive transformation in Copper alloys using a pulse heater and a potentiometric system for monitoring resistivity changes. In spite of the larger
resistivity changes involved (about 10%), Ayers' early time observations were seriously distorted by voltage transients so that an accurate kinetic analysis was impossible. Ground loops in the rather complex circuitry comprising the pulse heater, the oscilloscope and a differentiator/integrator unit were probably responsible. In this investigation a simpler approach was adopted and efforts were taken to ensure that a noise free, basic signal was obtained, unmodified by electronic devices such as integrators. To some extent the methods employed parallel those of Nolfi et al (41) who followed dissolution kinetics in Iron-Carbon alloys using a Kelvin Double Bridge to measure resistivity changes. However a noise-free environment and long heat treatments were involved.

A Kelvin Double Bridge was also thought to be appropriate in this investigation since the specimen can have a resistance comparable to those of the leads; large currents can be passed through the specimen while only small currents need pass through the bridge; when correctly designed and operated the Kelvin bridge gives an accurate and sensitive measurement of the specimen resistance change.

The circuit is given in Figure II.2 where \( R_1, R_2, S_1, S_2 \) are the arm resistances, \( R_x, R_s \) and \( R \) the specimen, standard and link resistances respectively. An applied voltage \( V_1 \) is developed with a battery of voltage \( V_o \) and a regulating resistance \( R_o \) and the output voltage is \( V_2 \). In general the resistances can be conveniently written as:

\[
\begin{align*}
R_2 &= R_1 (1 \pm \alpha) \\
R_x &= R_s (1 \pm \delta) \\
S_2 &= S_1 (1 \pm \beta) \\
S_1 &= R_1 (1 \pm \gamma)
\end{align*}
\]
Figure II.2. Kelvin Double Bridge Circuit.
In particular, $\delta$ is the fractional difference of the specimen resistance. The problem is to determine suitable values for the bridge parameters so that the following factors are optimised:

a) sensitivity  
b) linearity  
c) accuracy  
d) noise rejection  
e) repeatability

Each of these factors shall be considered in some detail and an appropriate bridge circuit derived.

II.2.1. Accuracy and Sensitivity of Kelvin Bridge.

The quantity $\delta$ as a function of the output voltage is shown schematically in Figure II.3. Since the coefficients $\alpha, \beta, \gamma$ and $R_k$ are non-zero there will be a finite value of $\delta$, called $\delta_0$, required to give a null point. Departures from this null point will be assigned to $\delta_x$, a change in specimen resistance. The error in assuming that $\delta_x$ is proportional to $V_2$ will be given by $\delta_x$ and will be determined by $\delta_0$ and the bridge parameters. In Appendix C it is shown that for a constant $V_1$:

$$\frac{\Delta \delta_x}{\delta_x} = \frac{-\delta_x}{2[(2+\alpha) + \frac{R_k R_l (2+2\gamma+\alpha)}{R_s [R_k + R_l (1+\gamma)(2+\beta)]}]}, \tag{2.1}$$

and that:

$$\delta_0 = \alpha - \frac{R_k R_l (\beta-\alpha)}{R_s [R_k + R_l (1+\gamma)(2+\beta)]}, \tag{2.2}$$
Figure II.3. Kelvin Double Bridge output voltage as a function of the fractional change in specimen resistance, $\delta$. 
Considering each of the bridge variables:

i) Link Resistance.

The ratio of the output voltage for \( R_x = 0 \) and \( R_x = \infty \) is given by:

\[
\frac{V_2(R_x = 0)}{V_2(R_x = \infty)} = \frac{2R_S}{(R_o + 2R_S)} \left[ (2+\alpha) + \frac{R_1}{R_S} (2+2\gamma+\alpha) \right]
\]

Typically \( R_1 > R_o > R_S \) giving the ratio to be about 10. Hence the sensitivity of the bridge decreases as \( R_x \) increases.

The ratio of the fractional error in \( \delta_x \) for \( R_x = 0 \) and \( R_x = \infty \) is:

\[
\frac{\Delta \delta_x / \delta_x (R_x = 0)}{\Delta \delta_x / \delta_x (R_x = \infty)} = 1 + \frac{R_1}{2R_S} (2+\gamma)
\]

Typically this gives a ratio of about 1000 indicating that the fractional error increases dramatically as \( R_x \) decreases.

It is also seen that to minimise the effects of the link resistance on the sensitivity the ratio of \( R_1 \) to \( R_S \) should be large and that a large \( R_x \) resistance gives improved accuracy while a small one ensures sensitivity.

ii) Arm Resistance Differences.

Considering Equation 2.2 it is seen that \( \delta_o \) is reduced by making \((\alpha-\beta)\) and \( \alpha \) small. Equation 2.1 shows that for a small link resistance:

\[
\frac{\Delta \delta_x}{\delta_x} = \frac{-\delta_x}{2[2+\alpha + \frac{R_x}{R_S} (2+2\gamma+\alpha)]}
\]

\[
= \frac{-\delta_x}{2(2+\alpha) + \frac{R_x}{R_S} (2 + \alpha - \beta)} \quad \text{(2.3)}
\]
Thus the ratio of the arm resistances reflected by large values for $\alpha$ and $\beta$ are not important provided these coefficients are less than 0.1. Also the ratio of link to specimen resistances should be large.

iii) Applied Voltage.

The applied voltage is simple:

$$V_L = \frac{V_0 \left(R_s(2 + \delta) + R_L\right)}{R_0 + R_s(2 + \delta) + R_L + R_o}$$

(2.4)

If $R_o \gg (R + 2R_s)$ then the effect of variations in $V_o$ is small and typically the fractional error due to Lead - acid accumulator voltage variations on drawing about 10 Amperes for 5 seconds is obtained by combining Equations 2.3 and 2.4 to give a fractional error in $\delta$ of

.05$\Delta V_o$ percent where $\Delta V_o$ is the voltage variation of the accumulator giving an error of approximately .5% for a 12V supply.

iv) Arm Resistance $R_1$, and Link Resistance $R_L$.

Providing the link resistance is small, $R_1$ has little effect on either the sensitivity or the accuracy. This is demonstrated by considering Equation (2.1) where the fractional error is seen to be independent of $R_1$ if $R_s > R$. Secondly, the output voltage is given by:

$$V_2 = \frac{V'_1 R''_1}{R''_1(2+\delta_o) + R''_L} \left[1 - \frac{1}{2} \cdot \frac{R_L - R''_L}{R''_L(2+\delta_o) + R''_L} \right] \delta \times \delta \times$$

where,

$$R''_L = R_s \left(1 + \frac{R_L}{R_1(1+\gamma)(2+\beta)}\right)$$

$$R_{L\alpha} = \frac{R_L(\beta-\alpha)}{(2+\beta)(1+\gamma)}$$

$$V'_1 = \frac{V}{2+\alpha}$$
To a good approximation, the output voltage is independent of $R_1$.

Hence $R_1$ is not a critical parameter with regards to the output characteristics of the bridge and this is important since it can be chosen to be large enough to avoid having large currents passing through the bridge, thus avoiding joule heating of the bridge arms.

II.2.2. Noise Rejection Characteristics of a Kelvin Bridge.

In Appendix B the Common Mode Rejection is calculated for a Kelvin Double Bridge in which the specimen and the output voltage measuring device are earthed. Assuming $R_a >> R_3 >> R_2 = R_1 >> R_o > R_s > R$

where $R_a$ is the input resistance of the measuring device which is effectively a balanced, isolated differential amplifier, and $R_3$ is the resistance of one lead from the bridge to the amplifier while the other is of resistance $R_3(1 \pm \varepsilon)$, then:

$$CMR = \frac{R_a}{R_1\left[\frac{a-b}{2} - 2\gamma\right] + 2\varepsilon R_3}$$

Several significant conclusions can be drawn from the examination of this expression. First, the ratio of the oscilloscope differential amplifier input resistance to the bridge arm resistance must be large. Second, more attention should be paid to minimising $\gamma$ and third, the CMR is independent of $\delta$ and will thus be the same when the specimen is at both room and elevated temperatures. If the Kelvin Bridge is adjusted at room temperature for a maximum CMR then this CMR will be maintained throughout the experiment. Moreover, it is better to adjust $\delta$ in order to establish a preset imbalance so that upon pulsing to temperature the bridge is balanced. This contrasts with the more normal procedure in which one of the arm resistances is varied. Finally, the leads from the bridge to the oscilloscope should be balanced and of
low resistance.

Careful design, layout and construction also determined the noise rejection performance of the bridge and these aspects will be considered later.

II.2.3. Repeatability.

It was mentioned above that the bridge was initially unbalanced at room temperature so that upon pulsing to temperature it becomes balanced due to the resistance change of the specimen with temperature. Optimally, during a particular heat treatment the bridge should deviate by equal amounts, both positive and negative, about the null point. The problem is to determine to what accuracy the bridge must be preset in order to repeatably position the oscilloscope trace on the finite screen with a high sensitivity voltage scale.

The total change in $\delta_x$ is about 0.04 so the sum of the thermal resistivity change due to a pulse heating temperature change $\Delta T$, and the preset inbalance must equal 0.04:

$$\delta_x^p + \delta_x^t = 0.04$$

where $\delta_x^t = \omega \cdot \Delta T$, $\omega$ being the thermal coefficient of resistivity. An error in $\delta_x$ of 10% can be tolerated and from Equation 2.5 the output voltage at room temperature is given approximately by:

$$V_2 = \frac{V_1}{2 + \delta_x^o} \frac{x}{\delta_x^o} = \frac{V}{2 + \delta_x^o} (.04 - \omega \cdot \Delta T)$$

and it must be measured to within 10%. $\delta_x^o$ is given by:

$$\delta_x^o = \alpha - \frac{R_x}{R_s} (\beta - \alpha)$$

For repeatability $\delta_x^o$ should be small or constant and thus $\alpha, \beta, R$, and $R_s$ must be carefully adjusted. In this investigation $R_x$ was kept
constant as was $R_s$ by ensuring that the probes were spot welded to the specimen exactly 6.5 cms. apart. A simple jig was constructed to hold the specimen in a narrow groove and a pair of fine lines exactly 6.5 cms. apart was marked off. Also, $\alpha$ was made equal to $\beta$ in a procedure that will be described. Typical values for $k$, $T$, $V_1$ and $\delta_o$ meant that on passing a low current of about 0.5 Amperes at room temperature, an output voltage of 10mV must be measured to within 10% in order to accurately preset the bridge. This is readily accomplished.

II.3. The Kelvin Double Bridge.

II.3.1. Circuit and Components.

The Kelvin Double Bridge circuit given in Figure II.4 was assembled. A 12V DC Lead - acid accumulator provided a bridge current of up to 25 Amperes that was regulated with a bank of 1 Ohm, 100 Watt resistors and a 5 Ohm, 750 Watt variable resistor. The variable arm resistances $R_2$ and $S_2$ were 50 Ohm, 10 turn, 5 Watt potentiometers, with 25K Ohm potentiometers in parallel for fine adjustment. The standard resistance was a short piece of thick (20 Gauge) Nichrome V resistance wire mounted in brass blocks that could be finely trimmed. The output from the bridge was fed into an Analog Devices instrumentation amplifier (Model 602J). This is a high CMR, balanced input, low drift differential amplifier with single ended input, variable gain and good linearity up to a gain of 1000 times. The high gains were used when the bridge was being adjusted but during an experiment a gain of only 80 times was found to be adequate.

Since the response time of an Alumel-Cromel intrinsic thermocouple with a wire diameter of .002 ins. is about 1.0 msec. (36), the very short time output from the bridge should not be used in the absence
Figure II.4. Kelvin Double Bridge, showing component values and dummy arm used for standardising the bridge.
of the accompanying temperature trace. Thus filtering of the output would not affect the resolution of the instrument provided frequencies contributing significantly to the signal after a time of about 0.5 msec. are not removed. On this basis a low-pass band five stage filter was constructed, with a pass band attenuation of .01 db. for frequencies equivalent to times of less than .5 msec., a selectivity factor of 0.3 and a stop band attenuation of 70 db. (42). Finally the output was fed into a dual beam, differential input oscilloscope (Tektronix Model 564).

Preamplification and filtering was considered to be valuable because the amplifier and filter could be located inside the bridge cabinet, thereby ensuring minimum noise pick-up when the oscilloscope was conveniently positioned some yards away to protect its operator from possible high voltage shocks. Secondly a less sophisticated oscilloscope could be employed and thirdly, the signal-to-noise ratio could be improved.

II.3.2. Layout and Design.

The most effective methods of achieving low noise pick-up are:

i) the avoidance of open circuit loops which provide magnetic flux linkage with stray magnetic fields. This entailed using twisted coaxial leads in critical circuitry and having the standard resistance mounted immediately underneath the specimen.

ii) the use of a single common ground with all earth connections made directly to this point.

iii) the enclosure of critical circuitry within two layers of isolated conductors so that cancelling electric fields can be developed inside each conductor thereby producing a very efficient shielding.
This was effected by having all components mounted inside Aluminum chassis boxes that were kept inside steel cabinets.

iv) the routing of leads in the plane of magnetic flux lines.

This applies particularly to the thermocouple and Kelvin Bridge probes and to the leads from the capacitor banks to the specimen.

Most of these features are illustrated schematically in Figure II.5.

The importance of eliminating the effects caused by the bouncing of the DC heating current by-pass relay contacts cannot be over-emphasized since a 20 msec. voltage transient appeared as a bridge output if measurements were made before the bouncing had terminated. At the early stages of this investigation this problem was not fully appreciated and hence some of the long time, multiple sweep oscillographs that are reproduced in a later chapter show this initial transient. If however, the by-pass relay is closed some 40 msec. before the first pulse then the electrical resistivity measurements could be made only 0.5 msec. after the pulse.

II.3.3. Kelvin Bridge Performance.

i) Sensitivity. With the preamplifier gain of 80 times and an oscilloscope voltage sensitivity of .2V/cm., 50% of the total displayable range corresponded to the total resistance change upon reversion. By projecting the photograph of the screen trace, measurements could be made to within 2%.

ii) Accuracy. The relative error in $\delta$ was about 2% and hence the resolution of the instrument corresponds to the expected error in the observation.

iii) Noise response. On pulse heating a Nichrome V wire to give a very small resistivity change, an initial transient lasting about 0.1 msec.
Figure II.5. Schematic diagram illustrating methods for reducing noise pickup. Notice the avoidance of large circuit loops, the use of twisted coaxial cables, the common ground, component shielding and leads at right angles to high current elements.

**to Kelvin Bridge**
was observed and this represents the shortest possible time after which accurate resistance measurements are obtainable. Hence the full advantages of pulse heating rise times of microseconds and thermo-couple response times have been incorporated with a sensitive measuring device. It is moreover interesting to note that the use of mechanical high voltage relays instead of spark gap triggers led to voltage transients that lasted for several milliseconds. In retrospect, it was appreciated that this was caused by the relatively long term coupling of the capacitor banks with the bridge circuit if a relay was used, even though an automatic on/off switch opened the relay after the shortest possible time.

iv) Repeatability. The trace was repeatably positioned to within 10% on the screen.

II.3.4. Procedures.

i) Arm equalisation. Periodically $R_1$ and $S_1$ were equalised to within 1% using a potentiometer. Hence $\gamma = 0.01$.

ii) Ratio Equalisation. Since the probes that were spot welded to the specimen have a high resistance and since it was not possible to accurately measure the probe lengths between the specimen and the rigid microclips that connected the probes to the bridge, before each experiment the Kelvin Double Bridge arm ratios were equalised by using a dummy arm to form a Wheatstone Bridge with each of the Kelvin Bridge arms. Ratio equalisation was simply achieved by adjusting the arm resistances $S_2$ and $R_2$ so that upon reversal of the dummy arm, no significant inbalance was observed. The effective limit of the equalisation was the variable resistance introduced with successive reversals but the use of powerful microclip contacts enabled an $\alpha$ of 0.05 and an $(\alpha-\beta)$ of 0.01 to be obtained.
For short reversion times (less than 50 msec.) Nichrome V was used as the probe material since it has a small thermal coefficient of resistivity so that the variation of the probe resistance due to thermal contact with the specimen is negligible. For long heat treatments it is necessary to use a probe material very similar to the specimen because heat losses due to the copper mounting blocks invariably caused a few degrees Centigrade temperature difference between the two probe/specimen interfaces. Since most resistance wire type alloys invariably have a high thermoelectric coefficient when in contact with simple metal alloys such as Aluminum – Copper, large thermoelectric voltages can develop as the heat treatment progresses. Hence in the majority of the pulse heating experiments of this investigation, Aluminum probes of .002 ins. in diameter were used. Other investigators (40) have employed dissimilar metallic probe materials for heat treatments of up to 100 msec. but they never investigated possible thermoelectric effects.

iii) Preset Bridge Inbalance. After the bridge ratio has been equalised the link was closed and a 0.2 Ampere current passed through the specimen. \( R_s \), the standard resistance, was adjusted to set the necessary inbalance which had been determined previously by trial-and-error. The link was simply a short piece of thick Copper braid that could be bolted down between the specimen block and the standard resistance.

Upon completion of these procedures the Kelvin Bridge was ready for operation but before the pulse heating sequence, the specimen mountings were loosened so that strains developed in the specimen due to thermal expansion and contraction did not cause plastic deformation of the specimen. However the mountings did have some inertia so a little
deformation could not be avoided, and this will be shown to have significantly affected the reaging kinetics after reversion.

II.4. Specimen Preparation.

An analysis of the alloy used in this investigation is given below; all concentrations are in weight percent.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>3.85</td>
</tr>
<tr>
<td>Fe</td>
<td>.02</td>
</tr>
<tr>
<td>Si</td>
<td>.02</td>
</tr>
<tr>
<td>Zn</td>
<td>.02</td>
</tr>
<tr>
<td>Mn</td>
<td>.01</td>
</tr>
<tr>
<td>Cr</td>
<td>.01</td>
</tr>
<tr>
<td>Other</td>
<td>.02</td>
</tr>
</tbody>
</table>

This alloy was kindly supplied by Dr. H. Aaron of the Scientific Research Laboratory of the Ford Motor Company, Dearborn, Michigan.

Specimens were prepared by swaging small pieces of an homogenised billet and then drawing .013 in. in diameter wires. Several intermediate anneals at 320°C were necessary. 11 cm. long wires were then homogenised in evacuated Pyrex capsules at 530°C for 12 hours before the capsules were shattered under ice-free water at 2°C. After 10 seconds the specimens were transferred to liquid Nitrogen prior to ageing at 70°C for 1000 minutes in a Nujol oil bath kept to within 0.5°C.

The ageing curve, given as the fractional change in specimen resistance as a function of ageing time, is shown in Figure II.6. No detectable differences in either the ageing behaviour of the subsequent reversion kinetics were observed if instead the wires were homogenised in a Silicon oil bath and plunged into ice-free water so the quench rates for the encapsulated specimens were probably reproducible. The resistivity of random samples from each capsule
Figure II.6. Isothermal ageing of an Aluminum \( \approx 4 \text{wt. pct.} \) alloy at 70°C. Fractional resistance change as a function of ageing time where \( R_0 \) is the resistance of the specimen after 11 minutes.
were measured at the end of the ageing treatment to ensure that a uniform as-aged structure had been developed. Finally, the ageing curve at 70°C agrees well with the results of Okamoto and Kimura (20) and Turnbull and Cormia (23) and a comparison with the results of the latter investigators is given in a later chapter.
III. THE DISSOLUTION OF SPHERICALLY
SYMMETRIC PRECIPITATES.

A general review of dissolution theory will be given in the next chapter and it is sufficient at this stage to remark that there have been no treatments describing the dissolution of precipitates in a finite matrix where the precipitate volume fraction is large and the precipitate shape cannot be described in terms of only one space co-ordinate. In view of the pronounced ellipicity of GP zones in Aluminum - Copper (assuming that the zones can be modelled as ellipsoids of revolution) it was of interest, in the absence of any reasonable analytic approach to the problem, to develop a finite difference method.

A discussion of the assumptions involved when modelling GP zones will also be deferred as will the application of the method to be developed in this chapter to give predictions regarding the kinetic behaviour of dissolving zones. Instead the mathematical principles and the numerical analysis involved will be discussed, followed by a brief description of the computational procedures and comparisons of generated results with other numerical and analytical predictions and with some experimental observations. These comparisons will serve as tests for the validity of the method.

III.1. Numerical Analysis.

The numerical methods that have been successfully applied to one-dimensional problems involving multi-phase, diffusion controlled, moving interface solutions to the diffusion equation are generally unsuited to multidimensional cases. For example, both the Murray-Landis
variable grid transformation and the interpolation methods described by Langford (43) would be inapplicable. The approach taken in this investigation is based on an idea developed by Lazaridis (44,45), in which the movements of the interface in the directions of the co-ordinate axes are calculated at each intersection of the interface with a superimposed grid. Lazaridis however, generated equations for the multidimensional solidification problem in Cartesian co-ordinates and limited his analysis to two-dimensional problems. In three dimensions, solids of revolution like an idealised GP zone in Aluminum - Copper, are more readily handled using polar co-ordinates and while the general three-dimensional problem is equally complex in both systems, a polar co-ordinate scheme with spherical symmetry has applications in many contexts.

III.1.1. Formulation of the Problem.

The system consists of two phases, a and b, bounded by surfaces \( S_a \) and \( S_b \), separated by an interface \( I \) at a position \( X(t) \) at a time \( t \). The problem is to find the position of the interface as a function of time subject to the appropriate boundary and initial conditions. The mathematical analysis is considerably simplified if the following assumptions are made:

a) interdiffusion coefficients independent of time and concentration in both phases.

b) molar volumes of both phases equal.

c) sharp, discrete interface.

d) time independent interfacial concentrations.

In principle all these assumptions can be relaxed, except perhaps assumption c), and any further restrictions will be invoked merely to simplify the numerical analysis.
The problem is to solve the diffusion equation in polar co-ordinates, Equation 3.1, in both phases subject to the conditions 3.2 to 3.5 at the fixed and moving boundaries, and to the initial conditions 3.6 and 3.7. We have:

\[
\frac{\partial c_i}{\partial t} = d_i \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_i}{\partial r} \right) + \frac{1}{r^2 \sin \phi} \frac{\partial}{\partial \phi} \left( \sin \phi \frac{\partial c_i}{\partial \phi} \right) \right] \tag{3.1}
\]

with

\[
c_a^0 \text{ at interface }, X_a \tag{3.2}
\]

\[
c_b^0 \text{ at interface }, X_b \tag{3.3}
\]

and

\[
\Delta c_i = 0 \tag{3.4}
\]

at the boundary corresponding to zero mass flow across a finite matrix element cell wall in a three-dimensional precipitate array.

Mass balance at the interface gives:

\[
\frac{1}{\partial t} \frac{\partial c_i^*}{\partial t} = \Delta c_a^* - k' \Delta c_b^* \tag{3.5}
\]

where

\[
c_i = f_i(r, \theta, \phi) \text{ at } t = 0 \tag{3.6}
\]

\[
X = g(r, \theta, \phi) \text{ at } t = 0 \tag{3.7}
\]

All variables are normalised using a reference length so we define:

\[
t' = \frac{D t}{r_o^2}, \quad k = \frac{D_a}{D_b}, \quad r' = \frac{r}{r_o}, \quad 1^* = \frac{c_a^0 - c_b^0}{r_o}
\]

and henceforth the primes will be dropped. Also, a constant \(d_i\) is equal to unity when \(i = a\) and is equal to \(k\) when \(i = b\), and the position of the interface at time \(t\) is \(\varepsilon(t), \psi(t), \varphi(t)\). Only precipitates of revolution are considered such that the \(z\)-axis of Figure III.1 is a symmetry axis. Furthermore, symmetry requires that there be no
Figure III.1. Polar Co-ordinate Scheme Used. The precipitate is symmetrical about the z-axis.

Figure III.2. Finite Array Element. Sphere of radius $r_s$ has same volume as the cube element.
mass flow across the x-z, y-z, x-y planes. Finally, each precipitate has been assumed to lie at the center of a spherical element, the volume of which is equal to the cubic cell of the finite array as indicated in Figure III.2, and the flux normal to this spherical surface is zero. Several authors have justified and used this construction (46, 47).

### III.1.2. Finite Difference Expressions.

Recognizing that there is no mass flow in the θ direction, the finite difference expression for the concentration at nodes removed from the interface is simply:

\[
c_{j}^{m+1,n} = c_{j}^{m,n} + \frac{d_{m}^{j} \Delta t}{\Delta r} \left[ \frac{c_{m+1,n}^{j+1} + c_{m-1,n}^{j-1} - 2c_{m,n}^{j+1}}{n\Delta\phi} \right] - \frac{1}{\Delta r} \left[ \frac{c_{m+1,n}^{j+1}}{\tan(m\Delta\phi)} + \frac{c_{m-1,n}^{j-1}}{\tan(m\Delta\phi)} \right]
\]

where the origin is at (m,n)=(0,0) and j refers to the j-th time interval, the interval being Δt.

At the interface the derivatives appearing in Equation 3.5 can be approximated by standard, second order finite difference expressions over unequally spaced intervals. For example, in phase b we have for the concentration gradient at the interface:

\[
\frac{\partial c_{b}}{\partial r} = \frac{2-\sigma r}{1-\sigma r} \frac{c_{m,n+1}}{r} - \frac{3-2\sigma r}{(1-\sigma r)(2-\sigma r)} c_{b}^{o} + \frac{1-\sigma r}{2-\sigma r} \frac{c_{m,n+2}}{r}
\]

where \(\sigma r\) is given by:

\[
\sigma r = \frac{\delta r}{\Delta r}
\]

and δr is the distance of the interface from a node in the radial direction as illustrated in Figure III.3 which shows a polar grid superimposed upon the finite array element of Figure III.2. Unfortunately, Equation 3.9 is singular at \(\sigma r = 0\) for the a phase and \(\sigma r = 1\) for the b phase. These singularities can be
Figure III.3. Polar Grid Superimposed on the Spherical Finite Array Element. The various parameters referred to in the text are indicated.
avoided by representing the concentrations at nodes near the inter-
face by a quadratic of the form:

\[ c_i = A(r-\varepsilon) + B(r-\varepsilon)^2 + C\varepsilon(\phi-\mu) + D\varepsilon^2(\phi-\mu)^2 + E\varepsilon(r-\varepsilon)(\phi-\mu) + c_i^0 \]  \hspace{1cm} (3.10)

This expression has the same order of magnitude truncation error as
the finite difference expression of the type corresponding to Equation
3.9. The equilibrium interface concentration is \( c_i^0 \). Thus four cases
can be distinguished depending on the magnitude of \( \sigma_i \) where \( i \) can be
a or b. These cases are given by:

\[ \sigma_i < \text{ or } = .5 \quad \text{and} \quad \sigma_i > .5 \]

and a suitable expression for the boundary motion must be developed
for each of these cases followed by the corresponding equations for the
concentrations at the interface nodes. In the next section the general
equation describing the motion of the interface in the directions of the
co-ordinate axes will be derived and the numerical relations for the
four types of nodes will follow from this equation if several auxillary
equations are also considered.

III.2. Mathematical Analysis.

III.2.1. Auxillary Equations.

In order to evaluate the constants appearing in the expansion 3.10
an auxillary set of differential equations is derived using the fact
that the interface is an isoconcentrate surface. Thus the time rate
of change of the interface concentrations vanish in both phases, or:

\[ \frac{\partial^2 c_i}{\partial \tau^2} = - \frac{\partial c_i}{\partial \tau} \frac{\partial \varepsilon}{\partial \tau} = - \frac{\partial c_i}{\partial \phi} \frac{\partial \mu}{\partial \tau} \]
Secondly, it is shown in Appendix D that two successive differentiations along lines tangential to the interface give:

\[
\frac{3c_i}{\partial r} + \frac{1}{\varepsilon} \frac{3c_i}{\partial \phi} \frac{3c_i}{\partial r} = 0 \quad (3.12)
\]

\[
\frac{3c_i}{\partial r} + \varepsilon \frac{3c_i}{\partial \phi} \frac{3c_i}{\partial \phi} = 0 \quad (3.13)
\]

\[
\frac{3^2}{\partial \phi} + 2\varepsilon \frac{3^2}{\partial \phi} \frac{3c_i}{\partial \phi} + \frac{2}{\partial \phi} \frac{3c_i}{\partial \phi} + \frac{2}{\partial \phi} \frac{3c_i}{\partial \phi} \left( \frac{3\varepsilon}{\partial \phi} \right)^2 = 0 \quad (3.14)
\]

\[
\frac{3^2}{\partial r} + \frac{2}{\partial r} \frac{3^2}{\partial r} \frac{3c_i}{\partial r} + \frac{1}{\varepsilon} \frac{3^2}{\partial r} \frac{3c_i}{\partial r} + \frac{1}{\varepsilon} \frac{3^2}{\partial r} \frac{3c_i}{\partial r} \left( \frac{3\varepsilon}{\partial r} \right)^2 = 0 \quad (3.15)
\]

### III.2.2. Interface Motion along Co-ordinate Axes.

The mass balance equation at the interface is given in a form equivalent to Equation 3.5 as:

\[
\frac{3c_a}{\partial n} - k^* \frac{3c_b}{\partial n} = 1 \frac{3c_i}{\partial n} \frac{3c_i}{\partial n} = 0
\]

It is shown in Appendix D that if the interface position is written as:

\[
r - \varepsilon(\phi, t) = \phi - \mu(r, t) = 0
\]

and recognizing that:

\[
\frac{3c_i}{\partial n} = \frac{3c_i}{\partial \phi} \frac{3c_i}{\partial \phi} = \frac{3c_i}{\partial r} \frac{3c_i}{\partial r} \left( \frac{3\varepsilon}{\partial \phi} \right)^2
\]

where \( \hat{r}, \hat{\phi}, \hat{n} \) are the radial, tangential and normal unit vectors, then
the motion of the interface in the direction of the co-ordinate axes are given by:

\[
1^* \frac{\partial \xi}{\partial t} = (1 + \frac{1}{\epsilon} \frac{\partial \xi}{\partial \phi})^2 \left( \frac{\partial^2 a}{\partial r^2} - k' \cdot \frac{\partial c}{\partial r} \right)
\]

\[
1^* \frac{\partial \eta}{\partial t} = \left( \frac{1}{\epsilon} + \left[ \frac{\partial \eta}{\partial \phi} \right]^2 \right) \left( \frac{\partial^2 a}{\partial \phi^2} - k' \cdot \frac{\partial c}{\partial \phi} \right) \tag{3.16}
\]

For nodes with \( \sigma_i > .5 \), expansions for the derivatives similar to Equation 3.9 are used while the expansion 3.10 is differentiated for nodes with \( \sigma_i < \) or = .5. For motion in the r-direction, the concentration gradients are:

\[
\frac{\partial c_b}{\partial r} = [A + 2B(r-\epsilon) + E\epsilon(\phi-\mu)]_{\epsilon,\mu} = A
\]

\[
\frac{\partial^2 c_b}{\partial \phi} = C
\]

Thus evaluation of the interface motion is possible if the expansion coefficients A and B are determined.

III.2.3. Concentration at Nodes near the Interface.

For interface nodes with both \( \sigma^r_i \) and \( \sigma^\phi_i > .5 \), the standard finite difference expressions describing the first and second derivatives over unequal intervals are used in Equation 3.1 while the nodes \( \sigma^r_i \) or \( \sigma^\phi_i < \) or = .5 require the evaluation of the coefficients in the expansion 3.10. For example, for a node with \( \Delta r \) less than \( \Delta r/2 \) we have:

\[
c^i_{m,n} = A \cdot \Delta r + B \cdot (\Delta r)^2 + c^0_i \tag{3.17}
\]

III.2.4. Evaluation of Expansion Coefficients.

Only the case for \( \sigma^r_a < .5 \) will be described as the expressions for the other cases are very similar. It has been shown that at the interface

\[
\frac{\partial c_b}{\partial r} = A \quad \text{and} \quad \frac{\partial^2 c_b}{\partial r^2} = 2B
\]
Furthermore: $\frac{\partial^2 c_a}{\partial \phi^2} = \varepsilon \cdot C, \quad \frac{\partial^2 c_b}{\partial \phi^2} = 2 \cdot \varepsilon \cdot D \cdot \frac{\partial^2 c}{\partial \phi^2} = \varepsilon \cdot E$ at $(\varepsilon, \mu)$

Substituting in the mass balance equation 3.16:

$$\frac{\partial \varepsilon}{\partial t} = \frac{1}{1 + \frac{1}{\varepsilon}} \frac{\partial}{\partial \phi} \left(2 \cdot \frac{\partial \varepsilon}{\partial \phi} \right) \cdot (A - k' \cdot g) \quad (3.18)$$

where $g$ is the normal finite difference expression for the concentration gradient at the interface in the $r$-direction adjacent to the node with co-ordinates $(m,n)$ (see Figure III.3). The gradient $g$ is given by:

$$g = \frac{3c_a - \partial c_b}{\Delta r \varepsilon, \mu} = \frac{1+2\sigma_r}{r(1+\varepsilon)} \cdot \frac{c_b^0 + \sigma_r c_{m+1,n}}{1 + \sigma_r} - \frac{1+\sigma_r \cdot c_m,n}{\sigma_r}$$

Now, Equation 3.11 gives:

$$\frac{\partial c_a}{\partial r} \frac{\partial \varepsilon}{\partial t} = \frac{3^2 c_r + 2 \cdot 3 c_r + 1}{r^2} \cdot \frac{3^2 c_r + 1}{r^2} \cdot \frac{3^2 c_r + 1}{r^2} \cdot \frac{3^2 c_r + 1}{r^2} \cdot \frac{3^2 c_r + 1}{r^2} \cdot \frac{3^2 c_r + 1}{r^2} \cdot \frac{3^2 c_r + 1}{r^2} \cdot \frac{3^2 c_r + 1}{r^2}$$

and therefore:

$$\frac{A}{1 + \frac{1}{\varepsilon}} \frac{\partial}{\partial \phi} \left(2 \cdot \frac{\partial \varepsilon}{\partial \phi} \right) \cdot (A - k' \cdot g) + 2 \cdot B + 2 \cdot A + 2 \cdot D + \frac{1}{\varepsilon \cdot \tan \mu} = 0 \quad (3.20)$$

Also the auxiliary equations 3.13 and 3.14 give:

$$C = -\varepsilon \cdot A \cdot \frac{\partial \varepsilon}{\partial \phi} \quad (3.21)$$

$$2 \cdot D + 2 \cdot E \cdot \frac{\partial \varepsilon}{\partial \phi} + A \cdot \frac{\partial^2 \varepsilon}{\partial \phi^2} + 2 \cdot B \cdot \frac{\partial \varepsilon}{\partial \phi} \cdot 2 = 0 \quad (3.22)$$

Finally, the expansion 3.10 gives:

$$c_{m-1,n} = -A \cdot (\Delta r + \delta r) + B \cdot (\Delta r + \delta r)^2 + c_a^0$$

from which:

$$B = \frac{A}{(1 + \sigma_r) \Delta r} + \frac{c_a^0 - c_{m-1,n}}{(1 + \sigma_r)^2 \cdot (\Delta r)^2} \quad (3.23)$$
Similarly, the expansion 3.10 also gives:

\[ c_{m-1,n} = -A \Delta r + B (\Delta r) - C \varepsilon \delta \phi + D \varepsilon \delta \phi + E \varepsilon \Delta r \delta \phi + c_a \]  

The simultaneous solution of Equations 3.18 to 3.24 gives a quadratic in \( A \):

\[ aA^2 + bA + d = 0 \]

in terms of the concentrations of the nodes which can be determined at any time using the standard finite difference expressions. The coefficients of the quadratic are given in Appendix D and the solution of the quadratic gives \( A \) which upon substitution in Equation 3.23, gives \( B \).

With \( A \) and \( B \) evaluated, the motion of the interface and the concentration at the interface node \((m,n)\) are determined from Equations 3.17 and 3.18.


In view of the considerably increased complexity of the method and the need to calculate the concentrations at many nodes, relative to the pseudo one-dimensional, spherical case, the \( a \) phase concentration was assumed to remain constant. This is a reasonable assumption for the GP zones studied in this investigation and for the \( \text{CuAl}_2 \) precipitate dissolution kinetics data of Baty et al (48) which was used to test the method. Secondly, the initial precipitate shape was assumed to be ellipsoidal with an aspect ratio, \( k \), less than unity. Thus the dissolution of needle-like precipitates was not investigated although the computer program could handle this case. Finally, the initial matrix concentration was assumed to be constant.

Given these additional assumptions, the concentrations at non-interface nodes and interface nodes with \( \sigma_1 > .5 \) and \( \sigma_1 < \sigma \) or \( \sigma = .5 \) and the interface movements along the directions of the co-ordinates were
calculated in this order after successive time increments. Periodically a fifth-order polynomial was fitted through the interface intercepts with the superimposed grid and this polynomial was numerically integrated to give the volume of the precipitate. Upon dividing this volume by the initial precipitate volume and taking the cube root, the dimensionless radius of the equivalent spherical particle results. Most comparisons with other theoretical predictions will use this parameter.

The zero mass flux boundary conditions were modelled by inserting a row of dummy nodes along the outside edges of the segment illustrated in Figure III.3 and setting the concentrations of these nodes equal to those of symmetrically opposed nodes within the segment after each time increment.

III.4. Stability and Accuracy.

III.4.1. Analytic Results.

In any finite difference solution to a partial differential equation it is necessary to examine the stability and accuracy of the solution. Lazaridis (44) shows that the coefficient of the $c_{m,n}$ term in Equation 3.8 must be positive at all times for stability. Hence:

\[ 1 - \frac{1}{(\Delta r)^2} \Delta t \cdot 2 \cdot \left[ 1 + \frac{1}{(n\Delta \phi)^2} \right] > 0 \]

giving:

\[ \Delta t < \frac{(\Delta r)^2}{2 \cdot [1 + (n\Delta \phi)^2]} \]  \hspace{1cm} (3.25)

since $d_1 = 1$ if only diffusion in the matrix occurs. It is seen that as $n$ tends to zero, $\Delta t$ also tends to zero so an instability at small sizes is anticipated. Hence, perhaps the most unfortunate restriction on the method results since dissolution at small sizes (or growth from zero size) is unstable. Instead a cut-off at some small $n$ ($n =$...
must occur such that the stability criterion for \( t \) is obeyed for \( n > n_{\text{min}} \). Although this limitation is not severe for spherical particles since a fine grid can be used, this becomes impractical for ellipsoidal precipitates because excessive computation time would be required.

In this study, the kinetics were mapped out roughly using a large time increment and subsequent computations were made under more accurate conditions, with the dissolution terminating after small volume fraction reductions. Typically an idealised zone with an initial aspect ratio of 0.25 was dissolved to a volume of 70% of its initial volume. Since it is the early time kinetic characteristics of dissolving zones that are of primary interest, this restriction did not hinder an analysis of the experimental results.

Given the condition defining the time increment we proceed to evaluate the parameters in the stability condition. First, the most crucial time is the initial stage of dissolution and an approximately equal mesh spacing along all co-ordinate directions at the initial position of the interface is preferred. A reasonable criterion therefore is to require that the average initial radial dimension multiplied by the increment angle is equal to the radial increment:

\[
\frac{c+a}{2} \Delta \phi = \Delta \phi . n_{\text{i}} . \Delta r . (1+k_{\text{i}}) = \Delta r
\]

Hence:

\[
\Delta \phi = \frac{2}{n_{\text{i}} (1+k_{\text{i}})}
\]

where \( k_{\text{i}} \) is the initial aspect ratio and \( n_{\text{i}} \) is the initial number of nodes for the major axis of the precipitate. Assuming an initially depleted matrix, the total mass balance gives:

\[
n_{\text{i}} = n_{s} \left( \frac{\bar{c}}{k_{\text{i}}} \right)^{1/3}
\]
where $c$ is the alloy composition and $n_s$ is the number of nodes along the radius of the spherical matrix element. Finally, if $f$ is the fractional change in volume of the precipitate then:

$$f = \frac{k_f n^{3}_{i} - k_f^{-2} n^{3}_{\text{min}}}{k_i n^{3}_{i}} = 1 - \frac{k_f^{-2} n^{3}_{\text{min}}}{c n^{3}_{s}} = 1 - \frac{k_f^{-2} n^{3}_{\text{min}}}{c n^{3}_{s}}.$$  

(3.28)

where $k_f$ is the final aspect ratio and $n_{\text{min}}$ is the number of nodes along the minor axis. Substituting in the stability condition 3.25, we have:

$$\Delta t > \frac{(\Delta r)^2}{2[1 + \frac{n_i[1+k_i]}{n_{\text{min}}}]^2} = \frac{(\Delta r)^2}{[1 + \frac{k_f^{-2}}{(k_i(1-f))^{1/3} \cdot \left(\frac{1+k_i}{2}\right)^2}]^2}$$  

(3.29)

The total time to effect a given fraction of dissolution is constant so the number of time increments $n$, is given by:

$$N \propto \frac{2}{(\Delta r)^2} [1 + \frac{k_f^{-2}}{(k_i(1+f))^{1/3} \cdot \left(\frac{1+k_i}{2}\right)^2}]$$  

(3.29)

Since the total computation time required $t_c$, is proportional to $N$ and to the total number of nodes, then:

$$t_c \propto \frac{n^s}{(\Delta r)^2 [1 + \frac{1}{k_i k_f(1-f)}^{1/3} \cdot \left(\frac{1+k_i}{2}\right)^2]}$$

Some useful conclusions can be drawn from this expression. First, the radial increment merely acts as a scaling constant and can therefore be set equal to unity. Secondly, if it is assumed that the dissolution is shape preserving (i.e. $k_i = k_f$) then:

$$t_c \propto 1 + (1 - f)^{-2/3} \cdot (1 + k)^2 \cdot (2k)^{-2}$$
The computation times given by this expression is plotted in Figure III.4 together with the time increment as given by Equation 3.29, and it is seen that the total computation time increases rapidly for $f$ greater than about 0.8 for all $k_1$ between 0.2 and 1.0. Computations did also show that $k$ initially increased and probably decreased at later times so an aspect ratio trajectory can be drawn as in Figure III.4. This illustrates the third point, namely that an instability may result at long times if an initial time increment is calculated based on shape preservation. Finally, it is important to recognize the danger of increasing the time interval as the dissolution proceeds because the stability criterion may be violated. In other methods this is the normal procedure as sluggish kinetics develop at long times.

III.4.2. Computed Results.

For the limiting case of a sphere, the time to achieve a given radius as a function of the total number of nodes is plotted in Figure III.5. The parameters used were those pertaining to CuAl$_2$ precipitates in an Aluminum - 4 wt.pct. Copper alloy at 520°C as detailed by Baty et al (48). Also plotted is the concentration error which is the composition of the alloy minus the cell wall concentration at the completion of the dissolution computer run. Both quantities are tending toward limiting values and the concentration error is seen to be less than .5% for only 15 nodes.

In Figure III.6 the experimentally determined dissolution kinetics of the CuAl$_2$ precipitates reported by Baty et al are compared to the numerical solutions given by Tanzilli and Heckel (49) and by the method of this investigation for spherical particles and for initially ellipsoidal precipitates with an aspect ratio of .5, corresponding to the value
Figure III.4. Computation time and dimensionless time increment needed to obtain a stable solution for the volume change on dissolution, as a function of the required fractional volume change. The computation constant is proportional to the total computation time and $k$ is the precipitate eccentricity, assumed to be constant during dissolution. The $k$ trajectory represents a varying eccentricity.
Figure III.5. Accuracy and Stability Analysis for the Limiting Case of a Spherical CuAl_2 precipitate in Al-4 wt. pct. Cu at 520°C. Completion time is the time to achieve a dimensionless radius of 0.5 and the concentration error is $c_{\text{cell wall}}$ minus alloy composition. Both change slowly and tend to limiting values as the number of nodes increases.
Figure III.6. A Comparison of Analytic and Finite Difference Solutions with the Experimental Observations of Baty et al (48) for CuAl₂ precipitates in an Al - 4 wt.pct. Cu alloy. Plotted are the perturbation and finite difference solutions of this investigation and the numerical results of Tanzilli and Heckel (49). The points refer to Baty et al's observations as determined by two different methods. The aspect ratio is k for initial ellipsoidal precipitates.
given by Baty et al. In the latter case, the dimensionless radius of
the equivalent spherical particle is plotted. Good agreement exists
between the two numerical methods for spherical precipitates and the
expected slower dissolution kinetics for ellipsoidal precipitates are
predicted. The experimental points are those given by Baty et al for
the largest initial mean particle size structures as these tended
to have precipitates with a pronounced ellipticity. Two methods were
used to generate the data and it is seen that an analysis based on the
time evolution of the particle size distribution agrees with the num-
merical results while that based on the mean particle size does not,
even though the particle ellipticity is taken into account.

It is perhaps worthwhile to remark that when the logarithm of
the volume of the dissolving precipitate is plotted as a function of
time as in Figure IV.3 of the next chapter, the two curves generated
by Tanzilli and Heckel for the CuAl$_2$ precipitates at 520°C and 540°C
show different long time characteristics, suggesting some computational
inaccuracies.

III.5. Conclusions.

A method for predicting the dissolution kinetics of spherically sym-
metric precipitates has been developed and computed results were
shown to be accurate and in partial agreement with existing data. In
view of the extreme computational simplicity for the limiting case of
a spherical precipitate, the Fortran IV program for this case is given
in Appendix E.
IV. A REVIEW OF DISSOLUTION THEORY.

Recent reviews of the mathematical methods for handling the dissolution by mass transport of finite second phases have been written from the metallurgical (50) and engineering (51) standpoints. Both sets of authors emphasise the intractability of the problem using known techniques, it being a non-linear, moving boundary (Stefan-like) problem, that unlike the growth of a second phase from zero initial size, has no similarity transformation (51). Such a transformation reduces the partial differential equation describing the system to a total differential equation by consolidating one or more of the independent variables into single variables. Also, consolidation of one or more of the auxiliary equations will usually be needed. The Boltzmann Transformation for the diffusion equation is a classic similarity transformation but it can only be used in a semi-infinite or infinite domain for otherwise, consolidation of the boundary conditions will not occur.

Recourse to approximate methods is necessary and these are conveniently described for isolated particles in an infinite matrix and for uniform arrays. All considerations will assume constant and equal molar volumes in both phases, constant interdiffusion coefficients, sharp interface boundaries, no initial concentration gradients and the absence of Gibbs-Thompson effects at the interfaces. These assumptions can usually be relaxed in the numerical methods but they invariably remain in the analytic solutions. In only two cases (Nolfi et al (47) and Ham (46)) have non-equilibrium effects at the interface in a precipitate array been considered while Aaron (52) considered this possibility for an isolated particle using the numerical integration of
an analytic expression describing the interface position.

IV.1. Isolated Particles in an Infinite Matrix.

The various approximate solutions have adopted one of the following:

- a) time independent diffusion field (53, 54, 55)
- b) stationary interface (56)
- c) linearised concentration gradients (57, 58)
- d) reversed growth
- e) perturbation methods (51, 59, 60)
- f) numerical methods based on finite difference solutions to the diffusion equation (49, 61)

Only planar, cylindrical and spherical precipitates have been considered and Aaron et al. (62) examined a) to d) and showed that the stationary interface approximation is to be preferred since it is simpler to use, accurate at early times and satisfies the boundary conditions. Results based on the approximation for the various geometries are given in Table IV.1 for both diffusion control and interface reaction control. It should be noted that after long times both types of reaction control assume the same form of kinetic law for spherical precipitates but an identical law for planar ones. Secondly, the boundary velocity is apparently infinite at zero time for the dissolution of spherical precipitates under diffusion control.

Duda and Ventras however, have recently shown that the stationary interface approximation solution is simply the first term of a perturbation solution (59, 60), and a perturbation solution for the dissolution of a bubble by convection and diffusion is in good agreement with a finite difference solution (61). In view of this success, the relevant equations for the diffusional dissolution of precipitates will
Table IV.1

Summary of Results given by the Stationary Interface Approximation for Dissolution. These are taken from Carslaw and Jaeger (55), Whelan (56), Nolfi et al (47). The time \( t^* \), in seconds, refers to the time to attain a given kinetic law. The variables are specified on the next page.

<table>
<thead>
<tr>
<th>Planar</th>
<th>Cylindrical</th>
<th>Spherical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interface reaction control.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Y_0 = -\Omega K \Delta c_o e^{z^2} \text{erfc} z )</td>
<td>( \dot{t} = -\Omega K \Delta c_o \left( 1 + K \frac{r_o}{r} \right) \frac{D}{\sigma r} \text{erfc} \left( \frac{z}{\sigma r} \right) e^{z^2} )</td>
<td></td>
</tr>
<tr>
<td>( z = K (Dt)^{1/2} / D )</td>
<td>( z = (Dt)^{1/2} / \sigma r_o )</td>
<td></td>
</tr>
<tr>
<td>for short ( t ) ( (t &lt; t^*) )</td>
<td>( \dot{t} = -\Omega K \Delta c_o )</td>
<td>( \dot{t} = -\Omega \sigma K \Delta c_o )</td>
</tr>
<tr>
<td>( t^* = \frac{10^{-2}}{K^2} )</td>
<td>( t^* = \frac{D}{(K+D/r_o)^2} )</td>
<td></td>
</tr>
<tr>
<td>for long ( t )</td>
<td>( \dot{t} = -\Omega \sigma K r_o \Delta c_o )</td>
<td>( \dot{t} = -\Omega \sigma K r_o \Delta c_o )</td>
</tr>
<tr>
<td>( Y_0 = -\Omega \sigma K \Delta c_o \left( \frac{1}{\pi Dt} \right)^{1/2} )</td>
<td></td>
<td>( \dot{t} = -\Omega \sigma K r_o \Delta c_o \left( \frac{1}{D(\pi Dt)^{1/2}} \right)^{1/2} )</td>
</tr>
<tr>
<td>Diffusion control.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Y_0 = -\Omega \Delta \Delta c_o \left( \frac{1}{\pi Dt} \right)^{1/2} )</td>
<td>( \frac{\partial c}{\partial r} \bigg</td>
<td>_{r=r_o} = -\Omega \Delta \Delta c_o \cdot \left( \frac{1}{r_o} \right) \left( \pi Dt \right)^{-1/2} )</td>
</tr>
<tr>
<td>( 4 \Delta c_o F(Dt/r_o) \left( \frac{1}{r_o} \right)^2 )</td>
<td></td>
<td>( \dot{R} = \frac{R}{2 \left( \pi Dt \right)^{-1/2}} )</td>
</tr>
<tr>
<td>for short ( t )</td>
<td></td>
<td>( \dot{R} = -\Omega \Delta c_o \left( \frac{D}{\pi t} \right)^{1/5} )</td>
</tr>
<tr>
<td>( \dot{t} = -\Omega \Delta \Delta c_o \cdot \left( \frac{1}{2r_o} \right) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( R = \frac{r_o - \Omega \Delta \Delta c_o t}{2r_o \left( \pi Dt \right)^{-1/2}} )</td>
<td></td>
</tr>
<tr>
<td>for long ( t )</td>
<td></td>
<td>( \dot{R} = -\Omega \Delta c_o \left( \frac{D}{\pi t} \right)^{1/5} )</td>
</tr>
</tbody>
</table>
Variable specifications for Table IV.1.

$Y_o, r_o$ the initial dimensions of the precipitates.

$R$ the stationary interface radius approximation, radius at time $t$.

$\Delta c_o = c_{b0} - c_{b}^o$ where $c_{b0}$ is the equilibrium concentration in the matrix at the interface, and $c_{b}^o$ is the initial matrix concentration.

$\sigma = (Kr_o/D +1)^{-1}$ where:

$K$ is the first order interfacial reaction constant,

$D$ is the diffusion coefficient in the matrix.

$\Omega$ is the molar volume of the precipitate phase $a$, per unit mass of solute.

$F$ is a complex function of $Dt/r_o$. (see Reference 55)
be developed and compared with the numerical results of Tanzilli and Heckel (49) and of the method described in the previous chapter.


The assumption and variable definitions of the previous chapter will be maintained. The diffusion equation in polar co-ordinates for radial symmetry is:

\[
\frac{\partial c'}{\partial t'} = \frac{1}{r'}^2 \frac{\partial^2 c'}{\partial r'^2} + 2 \frac{\partial c'}{r'} \frac{\partial c'}{\partial r'}
\]

where \( c' = \frac{c - c_{bo}}{c_{bo}} \), \( t' = \frac{D t}{r'^2 o} \), \( r'^{'} = \frac{r}{r_o} \), \( R' = \frac{R}{r_o} \). The initial matrix concentration is \( c_{bo} \). The appropriate boundary conditions are:

\( c'(r'^{'} , 0) = 0 \), \( c'(\infty , t') = 0 \), \( c'(R'^{'} , t') = 1 \) and

\[
\frac{d r'^{'} }{d t'} = k' \frac{\partial c'}{\partial r'} \mid_{R'^{'}=1}
\]

where \( k' = \frac{c_{bo}^o - c_{bo}^o}{c_{bo}^o - c_{bo}} \) with \( R'(0) = 1 \).

Henceforth all primes will be dropped. Following Duda and Ventras (52) we make the variable transformations:

\( \xi = \frac{r}{R} \), \( \rho = c \cdot \xi \)

and thus:

\[
\frac{\partial \rho}{\partial t} + 2k! \int_{\xi=1}^{0} \frac{\partial \rho}{\partial \xi} \frac{d t'}{\partial \xi} + \frac{\partial t}{\partial \xi} = \frac{\partial \rho}{\partial \xi} - 2k! t - k! (\rho - \xi \frac{\partial \rho}{\partial \xi}) \left( \frac{\partial \rho}{\partial \xi} \right) - 1
\]

\( \xi=1 \)

\[
= \frac{\partial^2 \rho}{\partial \xi^2}
\]

(4.1)

with: \( \rho(\xi,0) = 0 \), \( \rho(\infty , t) = 0 \), \( \rho(1,t) = 1 \)

and:

\[
\frac{R^2}{p} = 1 + 2k! \int_{\xi=1}^{0} \frac{\partial \rho}{\partial \xi} \frac{d t'}{\partial \xi} - 2k! t
\]

(4.2)

Assuming a solution in terms of ascending powers of the perturbation
parameter \( k \):

\[
\rho = \rho_o + k \rho_1 + k'^2 \rho_2 + \ldots \tag{4.3}
\]

and substituting into Equation 4.1 we have:

\[
\frac{\partial \rho_o}{\partial t} = \frac{\partial^2 \rho_o}{\partial \xi^2}
\]

with

\[
\rho_o(\xi,0) = \rho_o(\infty,t) = 0 \quad \text{and} \quad \rho_o(1,t) = 1.
\]

Also:

\[
\frac{\partial \rho_1}{\partial t} + 2 \frac{\partial \rho_o}{\partial t} \int_0^t \frac{\partial \rho_o}{\partial \xi} d\xi' - 2t \frac{\partial \rho_o}{\partial t} + (\xi \frac{\partial \rho_o}{\partial \xi} - \rho_o)(1 - \frac{\partial \rho_o}{\partial \xi}) = \frac{\partial^2 \rho_1}{\partial \xi^2}
\]

with

\[
\rho_1(\xi,0) = \rho_1(\infty,t) = \rho_1(1,t) = 0 , \quad \text{and a similar expression for } \rho_2 \text{ is obtained by substituting for } \rho_1. \quad \text{The zero order solution is:}
\]

\[
\rho_o = \text{erfc} \left( \frac{\xi - 1}{2\sqrt{t}} \right)
\]

Substitution of this expression into the equations for \( \rho_1 \) and \( \rho_2 \) give two further partial differential equations that can be solved by standard methods using operational transformations. Incorporation of the solutions into the perturbation expansion 4.3 gives an expression for \( \rho \) which on differentiation and substitution into Equation 4.2 gives the boundary position as:

\[
R^2_p = 1 - k'(t + \sqrt{t/\pi}) + k'^2 \left( I_2(t) - I_1(t) \right) \tag{4.4}
\]

where \( I_1(t) \) is a complex double integral that has been evaluated by Duda and Ventras and is given to within 1% as:

\[
I_1(t) = 0.68\sqrt{t}
\]
Also: \[ I_2(t) = \frac{t^{1.5}}{3\pi^{.5}} + t.(1/2\pi+1/\pi^{1.5}+1/8) + t^5(2/\pi-0.5) \]

Note that on differentiation Equation 4.4 and setting \( R \) equal to unity we have:
\[
\frac{dR_p}{dt} = \frac{-k' + k'}{2\sqrt{\pi t}}
\]
being the zero time stationary interface solution for the boundary velocity in terms of the dimensionless parameters.

In Figure IV.1, \( R^2_p \) as given by the perturbation method, the stationary interface approximation, Tanzilli and Heckel's numerical finite difference solution and the finite difference method developed in the previous chapter, are plotted as a function of the dimensionless diffusion time. The physical parameters used were those given by Baty et al (48) for Aluminum – 4wt.pct. Copper with CuAl\(_2\) precipitates dissolving at 520°C. Because the curves for the stationary interface approximation and for the perturbation solution overlap, the parameter \( P \), is given. \( P \) is:
\[
P = \frac{R^2_{perturbation} - R^2_{stationary}}{R^2_{stationary}}
\]
It is seen that both analytic solutions overestimate the amount of dissolution and that the numerical and analytical solutions converge at early times. Moreover, the perturbation solution is more accurate at an early time since the parameter \( P \) is positive for \( Dt/r_o^2 \) less than about 0.2. This increased accuracy will occur over longer time ranges as the interfacial movement becomes more pronounced in situations with larger \( k' \) values. It is therefore suggested that the perturbation solution should be used instead of the stationary interface approximation solution and the troublesome requirement that the roots of an implicit equation be found in the latter case can be avoided.
Figure IV.1. A Comparison of the Precipitate Dissolution Kinetics as Predicted by Numerical Methods, and Analytic Solutions Assuming a Stationary Interface and a Perturbation Expansion. Physical parameters used are due to Baty et al (48) for CuAl₂ precipitates.

IV.3.1. Analytic Methods.

For very small volume fractions (volume fraction, \( v \), less than .001) Ham (46), using the mathematical device of expanding the matrix solute density in terms of the eigenfunctions of the appropriate boundary value problem, developed expressions describing the dissolution and growth of precipitates in a finite array. Recently Nolfi et al (47) used the same technique for large volume fractions (\( v \) greater than .01) and they considered all cases between diffusion control and interface reaction control whereas Ham only analysed the two limiting cases. However Ham was able to permit interface movement while Nolfi et al assumed a stationary interface, although they did outline a labourious method for determining the interface position as a function of time.

Both sets of authors stated the problem as follows: spherical particles of uniform concentration are uniformly distributed in a matrix that is initially of concentration \( c_{b_0} \). The diffusion equation is solved subject to the boundary condition of zero mass flow across a spherical element of radius \( r_s \), situated symmetrically about a precipitate of radius \( r_o \) and of a volume equivalent to the cube matrix element as illustrated in Figure III.2. The boundary condition at the inter-phase interface (where the two phases are \( a \) and \( b \)) is:

\[
D \frac{\partial c}{\partial r} \bigg|_{r=r_o} = K \cdot c(r_o, t)
\]

for both Nolfi et al's treatment of the general case and Ham's treatment of the interface controlled case. For diffusion control, Ham takes:

\[
c(r_o, t) = c_{b_0}
\]

The notation of the preceding chapter has been maintained. Table IV.2 summarizes the results for both high and low volume fractions and
Table IV.2

Parameters Describing the Rate of Change of the Average Matrix Concentration, \( \dot{c} \), for Precipitates in Uniform Arrays. The low volume fraction case (\( v < .001 \)) is due to Ham (46) and the high volume fraction case (\( v > .1 \)) is due to Nolfi et al (47). Law given valid for times \( t > t^* \) (secs.)

\[
with \quad \dot{c} \propto \exp(-t) \quad for \quad t > t^*
\]

<table>
<thead>
<tr>
<th>Diffusion control</th>
<th>Interface Reaction Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v &lt; .001 )</td>
<td></td>
</tr>
<tr>
<td>Stationary interface.</td>
<td>( \kappa = 3vD ) ( r_s^2 )</td>
</tr>
<tr>
<td></td>
<td>( \kappa = 3v(D/K_r + 1)^{1/3} ) ( r_s^2 )</td>
</tr>
<tr>
<td>( t^* ) = ( \frac{1}{D} \left( \frac{r_s}{4.5} \right)^2 )</td>
<td></td>
</tr>
<tr>
<td>Slowly moving interface.</td>
<td>( \kappa = 2.\frac{D}{r_s^2} (k')^{1/3} )</td>
</tr>
<tr>
<td></td>
<td>( \kappa = \frac{K_r}{r_s} (k')^{2/3} )</td>
</tr>
<tr>
<td>( t^* ) = ( 0.5r_s^2 ) ( D(c_b^o - c_{bo})^{1/3} )</td>
<td>( t^* ) = ( 1.2r_s ) ( (c_b^o - c_{bo})^{2/3} )</td>
</tr>
<tr>
<td>( v &gt; .1 )</td>
<td></td>
</tr>
<tr>
<td>Stationary interface.</td>
<td>( \kappa = a_o^2 \frac{D}{r_s^2} )</td>
</tr>
<tr>
<td>( t^* ) = ( 10.\frac{r_s^2}{D}a_1^2 )</td>
<td></td>
</tr>
</tbody>
</table>

where \( a_n (1-v) = \tan^{-1} \left( \frac{a_n [1-\sigma v]}{1+K \alpha_n v^2} \right) + n\pi \)

\( \sigma = \left( K_r / D + 1 \right)^{-1} \)
expressions for the rate of change of the average matrix concentration, \( \dot{c} \), over specified time ranges are given. In all cases, after an initial transient of duration \( t^* \), linear \( \log(\dot{c}) \) behaviour is predicted.

IV.3.2. Finite Difference Methods.

The finite difference method for treating the dissolution of spherically symmetric precipitates has been discussed along with comparisons between this new method and that of Tanzilli and Heckel (49) for the limiting case of a sphere. It was shown that the method of this investigation underpredicted the position of the interface to a very small extent relative to the Tanzilli and Heckel solution and that ellipsoidal precipitates dissolved more slowly than spherical precipitates of the same volumes. In view of these successes, the dissolution of GP zones in an Aluminum - 4wt.pct. Copper alloy was modelled by assuming the zones to be ellipsoids with aspect ratios of 0.25 uniformly distributed in a solute depleted matrix. The approximations inherent in this model are recognized since zones may only be discs that are copper-rich and one to two atoms thick (8) and that it may be meaningless to attribute an equilibrium interfacial concentration as given by the coherent solvus as determined by the classical reversion technique of Beton and Rollason (6).

IV.4. The Dissolution Kinetics of Idealised GP Zones.

The most useful parameter in describing the kinetics is the volume of the precipitate and since the results of this investigation and of Tanzilli and Heckel for spherical precipitates showed that a plot of \( \log(\text{volume}) \) versus the dimensionless time, \( \frac{Dt}{r_o^2} \), was almost linear (Figure IV.2), a similar plot for the idealised GP zone is given in Figure IV.3. It is seen that the zone volume decreases rapidly for
Figure IV.2. Dissolution of Spherical CuAl₂ Precipitates in Al - 4 wt.pct.Cu.: a Comparison of the finite difference solutions of Tanzilli and Heckel (49) and of this investigation.

- a): 520°C
- b): 540°C
- 1: This study
- 2: Tanzilli
Figure IV.3 Dissolution of Ellipsoidal GP Zones in an Al - 4 wt.pct. Cu alloy at 200°C and 250°C, Assuming an Aspect Ratio of .25. The volume of the zone is 'vol' and the interface equilibrium concentration is \( c_b^0 \) in the matrix while the zones are pure Copper. Volume fraction is .025, based on data due to Okamoto and Kimura (20).
times less than about 0.05 and thereafter dissolves at a considerably slower rate. This effect lasts for much longer than the initial 'start-up' transients inherent in any finite difference technique and is due to the rapid dissolution of the disc in the plane of the disc leading to a temporary saturation of the volume between, and in the plane of, discs. Also plotted in Figures IV.2 and IV.3 are the logarithms of the rates of change of the volumes for spherical and zone-like precipitates and a linear curve to about a volume of .25 is given by the former while no linearity is observed for the latter. This implies that Nolfi et al's analytic theory, which predicts \( \log(c) \), proportional to \( \log(\text{volume}) \), to be linear with time for spherical precipitates is in reasonable agreement with the numerical results but that it is seriously in error for ellipsoidal precipitates with small aspect ratios and volume fractions greater than about .2.

It should be noted that the amount of computation needed to effect a 25% change in volume was large (about 2 minutes computation time) so the overall characteristics of the dissolution process were mapped out using a large time increment, and the more accurate results that have been reported were obtained employing more accurate computation parameters. The volume fractions used were based on the values given by Okamoto and Kimura (20) and they represent an upper limit to the precipitate volume fraction. Alternatively, for an Aluminum - 3.85 wt. pct. Copper alloy, if the zones are assumed to be pure Copper and the matrix pure Aluminum and taking the ratio of Copper to Aluminum atomic radii to be 0.89 (63), then the volume fraction is 0.01 being intermediate between the low and high volume fraction analytic cases outlined above, with Ham's low fraction solution preferred.
IV.5. Conclusions.

If it assumed that the resistivity of the specimen is proportional to the precipitate volume fraction, as will be discussed in the next chapter, the experimentally determined resistance changes occurring during reversion will be analysed in terms of $\log(R)$, $\log(R)$, $R$ and $R^{2/3}$ versus time, where $R$ is the specimen resistance. These parameters are described by one or more of the theories discussed in this chapter.
In order to correlate the predictions of dissolution theories with experimental observations made during reversion heat treatments, it is necessary to understand the relationship between the observed property and the parameters specified by the dissolution theories. Attention will be focussed on selected properties, namely specimen hardness or yield strength, and electrical resistivity because the former have been used to determine a reversion temperature and the latter relates to the experimental technique employed in this investigation to follow the reversion kinetics. Only Aluminum alloys with approximately 4 wt. pct. Copper will be considered and because of the effects of homogenisation temperature (19), quenching medium and quench medium temperature (14), only results relating to homogenisation temperatures in the range 510-540°C with quenches into water at 0°C will be be considered. Subsequent ageing treatments and property measurement temperatures will specified.

V.1. Property Changes on Ageing.

Hardy (64) observed a slow increase in hardness to a plateau followed by a further increase for all temperatures between 25°C and 190°C. Silcock et al(65) showed that the GP zone size behaved identically.

The electrical resistivity changes are more complex and it is convenient to consider separately changes as measured at low (liquid Nitrogen) and high (ageing temperature greater than 0°C) temperatures, since the total specimen resistivity is made up of an intrinsic, temperature independent contribution, $\rho_o$, due to electron scattering processes at low temperatures, and a thermal contribution due to scattering by
thermal vibrations at higher temperatures, $\rho_t$. Hence:
\[ \rho = \rho_o + \rho_t \]
Measurements made at liquid nitrogen temperatures effectively give the intrinsic component.

It is now widely recognized that most Aluminum--based alloys which form coherent solute clusters give an intrinsic resistivity peak as the coherent zone size increases on ageing (Figure V.1, Curve A) but that this peak disappears at high measuring and ageing temperatures (Figure V.1, Curve D) because the thermal contribution dominates and the kinetics become very rapid. At intermediate measuring and ageing temperatures (Figure V.1, Curve B) the kinetics are slower and the thermal resistivity contribution smaller, so large, easily observable increases occur and this feature has been used extensively by Turnbull and his co-workers for studying the ageing kinetics (14,18,23).

V.2. Property Changes During Reversion.

Figure V.2 shows the change in yield point and hardness (7,6) upon reverting Aluminum--4 wt.pct. Copper alloys aged for about 1 day at room temperature. Above approximately 200°C these properties decrease to a constant minimum value in apparently about 2 to 7 minutes. However, in both investigations early time data of less than 2 minutes was not reported and even if it had been, there is the possibility that on quenching specimens partially reverted above 200°C for short times, rapid regrowth of undissolved zones or the nucleation of new ones in a highly segregated solid solution would occur, thereby distorting the reversion kinetics as determined at room temperature. This possibility will be discussed in more detail in a later chapter.

Figure V.3 depicts resistivity changes observed during the reversion
Figure V.1. Resistivity Changes Observed during the Ageing of Aluminum -- 4 wt.pct. Copper alloys. Heat treatments are given in Table V.1. Initial observed resistance is $R_0$. 

![Graph showing resistivity changes over ageing time](image-url)
### Table V.1

Preageing Heat Treatments for the Alloys (Al=4 wt.pct.Cu) of Figure V.1.

<table>
<thead>
<tr>
<th>Curve</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy comp.,wt.pct.Cu.</td>
<td>4.0</td>
<td>4.4</td>
<td>4.0</td>
<td>4.0</td>
<td>3.85</td>
</tr>
<tr>
<td>Homogenisation T.,°C.</td>
<td>530</td>
<td>540</td>
<td>540</td>
<td>540</td>
<td>530</td>
</tr>
<tr>
<td>Quench, water at 0°C for:</td>
<td>10sec.</td>
<td>0secs.</td>
<td>?</td>
<td>?</td>
<td>10secs.</td>
</tr>
<tr>
<td>Ageing T.,°C.</td>
<td>40</td>
<td>0</td>
<td>70</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>Measuring T.,°C.</td>
<td>-196</td>
<td>0</td>
<td>70</td>
<td>75</td>
<td>70</td>
</tr>
<tr>
<td>Reference.</td>
<td>20</td>
<td>18</td>
<td>23</td>
<td>23</td>
<td>this study.</td>
</tr>
</tbody>
</table>

### Table V.2

Pre-reversion Heat Treatments for the Alloys (Al=4 wt.pct.Cu) of Figure V.3.

<table>
<thead>
<tr>
<th>Reversion T.,°C.</th>
<th>100</th>
<th>140</th>
<th>180</th>
<th>190</th>
<th>205</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy comp.,wt.pct.Cu.</td>
<td>5.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Measuring T.,°C.</td>
<td>100</td>
<td>-196</td>
<td>-196</td>
<td>-196</td>
<td>-196</td>
</tr>
<tr>
<td>Homogenisation T.,°C.</td>
<td>510</td>
<td>530</td>
<td>530</td>
<td>530</td>
<td>520</td>
</tr>
<tr>
<td>Quench T.,°C.</td>
<td>?</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Quench time,secs.</td>
<td>?</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Ageing T.,°C.</td>
<td>25</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>a)100,b)25</td>
</tr>
<tr>
<td>Ageing time.</td>
<td>24hr.</td>
<td>10^2min.</td>
<td>10^2min.</td>
<td>10^2min.</td>
<td>a)24hr.,b)118hr.</td>
</tr>
<tr>
<td>Reference.</td>
<td>67</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>68</td>
</tr>
</tbody>
</table>
Figure V.2. Mechanical Properties as Observed at Room Temperature after Reversion at Various Temperatures. Yield point data due to Petov (7); hardness data due to Saulnier (66). All alloys are Aluminum with approximately 4 wt.pct. Copper aged to the slow reaction stage.
Figure V.3. Resistivity Changes Observed during the Reversion of Aluminum - 4 wt.pct. Copper alloys at Various Indicated Reversion Temperatures. Heat treatments given in Table V.2; all alloys aged to slow ageing reaction stage. Solid curve measured at reversion temperature; other curves at -196°C. Note zone size dependence of change shown by curves a) and b) due to Herman and Fine (68).
of Aluminum -- 4 wt. pct Copper alloys alloys also aged to the slow reaction stage of GP zone formation. The exact details of the heat treatments are given in Table V.2. Measurements made in liquid Nitrogen and at the reversion temperatures are included and while the former show an irregular decrease at 205°C or a continual increase, depending on the ageing treatment, and a maximum for reversion at 190°C, the latter show a continual decrease as was observed in this investigation. There are also some obvious discrepancies: first, the 190°C and the 180°C curves that are reported by Shimizu and Kimura (25) show appreciably different total resistance changes upon reversion. Secondly, the time scales differ markedly between the various investigations. Both of these difficulties may be caused by transformation during the quench form the reversion temperature.

V.3. Interpretation of Resistivity Changes due to GP Zones.

V.3.1. Intrinsic Resistivity Contribution.

a) Early stages of ageing, (characterised by \( \rho_a \) increasing to a maximum).

Several theories have been proposed to explain the intrinsic resistivity behaviour of small GP zones (69-78). A comparison of two recent theories by Griffin and Jones (70) and Hillel (71) is shown in Figure V.4 and there is reasonable agreement between the two theories for the intrinsic resistivity increase due to disc-like zones in Aluminum -- Copper. The zone size is specified in terms of the zone radius divided by the matrix lattice spacing, and the number of atoms in the zone.

The origin of the resistivity maximum however, remains in debate as some theories (70) predict a continual increase with zone size of the intrinsic resistivity contribution of a zone but invoke the nature of
Figure V.4. A Comparison of two recent theories due to Griffin and Jones (70) and Hillel (71), for the intrinsic resistivity contribution of a zone in Aluminum -- copper.
the transformation, in this case competitive coarsening of zones, as the cause of the resistivity decrease at long times while others predict the attainment of a critical state, for example a maximum scattering when the linear dimensions of the zones become comparable to the conduction electron mean free path (69,71). Furthermore, Leroy (74) recently substantiated the proposal that two types of solute atom groupings develop. Other authors (61,75-77) have pointed out the shortcomings of attributing the resistivity maximum to dislocations or stress fields (78, 79)

It was hoped that low temperature electrical resistivity measurements of preaged alloys reverted for short times above the metastable GP zone solvus would serve to distinguish between these possibilities but the erratic results that were obtained denied this. The origins of these results will be discussed along with the appropriate but extensive experimental modifications that would be required to ensure reproducible observations of the low temperature resistivity after reversion.

b) Later stages of ageing, (characterised by $\rho_o$ decreasing continually).

Apart from Hillel's theory as applied to disc-like zones, most theories predict that Mattheisson's Law is obeyed by alloys aged to give large zones. For example, Rossiter and Wells (69) give:

$$\rho = \rho_z + \rho_b + \rho_c$$

where $\rho_z$, $\rho_b$, $\rho_c$ are the intrinsic resistivity components due to the zones, zone/matrix interfaces and the matrix respectively while Hillel (71) for spherical zones gives:

$$\rho = \rho_{ph} + \rho_{1} + N_z \rho_z$$

where $\rho_{ph}$, $\rho_{1}$, $\rho_z$ are the phonon scattering, solute atom and zone intrinsic
resistivities, $c$ is the matrix concentration and $N_z$ the number of zones. Essentially these expressions and others like them, attempt to proportion the total resistivity between various components and it is unfortunate that in most cases the observed resistivity changes at the later stages of ageing are consistent with most of the proportioning schemes adopted. There does however remain a significant anomaly that has yet to be explained and this is the observation made by Herman and Fine (68) that is shown in Figure V.3, wherein the intrinsic resistivity of aged alloys can both increase and decrease during reversion depending on the preageing treatment. Following Okamoto and Kimura (20) we have:

$$\rho = \rho_o \left( N_z, R_z, c \right)$$

where $R_z$ is the zone radius. On differentiation of this expression:

$$\frac{dp}{dt} = \frac{\partial \rho_z}{\partial c} \frac{dc}{dt} + \frac{\partial \rho_z}{\partial R_z} \frac{dR_z}{dt} + \frac{\partial \rho_z}{\partial N_z} \frac{dN_z}{dt}$$

Initially, $\frac{dN_z}{dt} t=0 = 0$

As before, Rossiter and Wells give:

$$\rho = \rho_z + \rho_b + \rho_c$$

and thus:

$$\frac{dp}{dt} = \frac{\partial \rho_z}{\partial c} \frac{dc}{dt} + \frac{\partial \rho_b}{\partial R_z} \frac{dR_z}{dt}$$

where $\frac{\partial \rho_z}{\partial c} = 0$ since the zones remain of uniform concentration.

and $\frac{\partial \rho_z}{\partial R_z} = 0$ since the change of resistivity is small,

and $\frac{\partial \rho_b}{\partial c} = \frac{\partial \rho_c}{\partial R_z} = 0$. Now for disc-like zones at zero time:
\[
\frac{dc}{dt}_{t=0} = \frac{dR_z^2}{dt}_{t=0} = 2r_0 \frac{dR_z}{dt}_{t=0}
\]

where the initial precipitate radius is \( r_0 \). Thus:

\[
\frac{d\rho}{dt}_{t=0} = (-ar_0 \rho_c + a \rho_b) \frac{dR_z}{dt}_{t=0}
\]

where \( a \) is a constant. Hence the initial rate of resistivity change can be positive or negative according to whether:

\[
\frac{\partial \rho}{\partial \rho_c} > \text{ or } < \frac{\partial \rho}{\partial r_0} \frac{\rho_c}{\rho_b}
\]

For Aluminum -- 4 wt.pct. Copper alloys aged at 25°C for 118 hours, \( r_0 \) is about 45Å while 24 hours gives an \( r_0 \) of about 100Å at 100°C and hence it is possible for the initial resistivity to increase or decrease depending on the zone size achieved during ageing. The zone sizes are those determined by Hirano and Iwasaki (80).

V.3.2.Thermal Resistivity Contributions.

At high measuring temperatures the thermal resistivity contribution dominates and although there have been no theoretical treatments describing the thermal resistivity contribution due to GP zones, it is known that the usual effect of increasing the matrix solute concentration is to increase the thermal resistivity contribution due to the matrix. For example, changing the matrix concentration from zero to 2 at. pct. Copper in Aluminum, increases the resistivity by 70% at 0°C (14). Separating these two contributions, we have:

\[
\rho = N_z \rho_z (R_z) + c \rho_1
\]

using the notation of the previous section.

At early times during ageing the rapid nucleation and growth of
zones is accompanied by a sharp decrease in the matrix solute concentration while at longer times, \( R_z \) is increasing very slowly, \( c \) is decreasing slowly and \( N_z \) is changing appreciably due to competitive coarsening. Hence the zone contribution passes through a maximum while the matrix contribution decreases continually. Schematically, these trends are illustrated in Figure V.5 and a maximum at short times may be observed.

During reversion, \( c \) increases while \( N_z \) and \( R_z \) decrease and since a continual thermal resistivity decrease is observed, one must suppose that the contribution due to an increase in the matrix concentration is more than offset by the decreasing contribution due to the zones, as illustrated in Figure V.6. However the very arbitrary nature of these suppositions must be recognized and in the absence of any accurate theoretical predictions for the thermal resistivity contribution due to GP zones, it will be assumed that the zone volume is proportional to \( \rho_z \).

Since:

\[
\frac{dc}{dt} = \frac{dV_z}{dt}
\]

assuming:

\[
\rho = \rho(V_z, N_z, c)
\]

then:

\[
\frac{dp}{dt} = \frac{\partial \rho}{\partial V_z} \frac{dV_z}{dt} + \frac{\partial \rho}{\partial N_z} \frac{dN_z}{dt} + \frac{\partial \rho}{\partial c} \frac{dc}{dt}
\]

Now from Equation 5.1 we have:

\[
\frac{\partial \rho}{\partial V_z} = N_z \frac{\partial \rho}{\partial N_z}, \quad \frac{\partial \rho}{\partial N_z} = \rho_z, \quad \frac{\partial \rho}{\partial c} = \rho_1
\]

and thus:

\[
\frac{dp}{dt} = \rho_z \frac{dN_z}{dt} + (\rho_1 + \alpha N_z \frac{\partial \rho}{\partial N_z}) \frac{dc}{dt}
\]
Figure V.5. Schematic Resistivity Variations During Ageing. \( N_z \) is the zone density, \( R_z \) is the zone radius, \( c \) is the matrix concentration, \( \rho_z \) the resistivity contribution of a zone and \( \rho_1 \), is the contribution due to a solute atom.

Figure V.6. Schematic Resistivity Variations During Reversion. Symbols as defined above.
It will further be assumed that the distribution of zone sizes is narrow so that upon dissolving the zones above the GP zone solvus, the number of zones remains constant. This is a reasonable approximation because long ageing treatments and careful quenching procedures were used. Hence we have:

\[ \frac{dp}{dt} \propto \frac{dc}{dt} \]

and at early times where the zone size is large and slowly changing:

\[ \frac{dp}{dt} \propto \frac{dV}{dt} \propto \frac{dR}{dt} \]

This assumed proportionality between the observed high temperature resistivity will be used in conjunction with the predictions of dissolution theories to interpret the experimental resistivity decay curves obtained during reversion.
VI. EXPERIMENTAL RESULTS.

The experimental results for the following series of experiments will be given:

a) resistivity measurements made during reversion.
b) double pulse heat treatments during reversion.
c) resistivity measurements made during the reageing of reverted specimens.
d) resistivity measurements made at -196°C on partially reverted specimens.

In subsequent chapters these observations will be analysed, interpreted and discussed.

VI.1. Resistivity Measurements Made during Reversion.

Above 200°C two very distinct reversion stages were observed at early times as shown in Figure VI.1 which is an oscilloscope photograph recording the Kelvin Double Bridge output and the thermocouple voltage output. The reversion temperature is 206°C and the rapid initial rate of decay, henceforth to be called the fast reversion reaction stage, lasts for about 350 milliseconds and is followed by a considerably slower rate of resistance decay, corresponding to a slow reversion reaction stage, which lasts for several seconds. It is helpful to discuss these two stages separately.

VI.1.1. Fast Reversion Reaction.

Figures VI.2 to VI.4 are examples of typical oscilloscope photographs of the Kelvin Double Bridge output obtained during the fast reaction. Figure VI.2 is a multiple sweep trace showing the fast and slow reversion reactions at 208°C and Figures VI.3 and VI.4 show the bridge and thermocouple outputs obtained at 218°C and 250°C.
Fig. VI.1 a) Thermocouple and Kelvin Double Bridge outputs for reversion of Al – 4 wt. pct. Cu at 206°C

Upper trace: thermocouple, .4 mV/div. vertical.
Lower trace: bridge, .125 V/div. vertical.
Horizontal scale: 20 msec/div.

Fig. VI.1 b) Multiple sweep oscillograph of Kelvin Double Bridge voltage output of Fig. VI.1 a)

Vertical scale: .04 V/div.
Horizontal scale: 4 msec/div.
Fig. VI.2. Kelvin Double Bridge voltage output for the reversion of an Al - 4 wt. pct. Cu alloy at 208°C; multiple sweep oscillograph showing initial fast and subsequent slow reactions.

Vertical scale: 40 mv/div.
Horizontal scale: 4 msec/div.

Fig. VI.3. Thermocouple and Kelvin Double Bridge voltage outputs for the reversion of an Al - 4 wt. pct. Cu alloy at 218°C; fast initial reaction only shown.

Upper trace, bridge: 40 mV/div. vertical
Lower trace, thermocouple: .125 mV/div. vertical
Horizontal: 10 msec/div.
Fig. VI.4. Thermocouple and Kelvin Double Bridge voltage outputs for the reversion of an Al - 4 wt. pct. Cu alloy at 250°C; initial fast reaction only shown.

Upper trace, bridge: 40 mV/div. vertical
Lower trace, thermocouple: .1 mV/div. vertical
Horizontal scale: 4 msec/div.

Fig. VI.5. Kelvin Double Bridge voltage output for the reversion of an Al - 4 wt. pct. Cu alloy at 173°C; multiple sweep oscillograph showing no initial fast reaction.

Vertical scale: 40 mV/div.
Horizontal scale: 4 msec/div.
Fig. VI.6 a) Kelvin Double Bridge voltage output for the reversion of an Al - 4 wt. pct. Cu alloy at 196°C. Initial fast reaction does not occur.

Vertical scale: 40 mV/div.
Horizontal scale: .1 sec/div.

Fig. VI.6 b) Thermocouple voltage output for the reversion of an Al - 4 wt. pct. Cu alloy at 196°C; same experiment as Fig. VI.6 a).

Vertical scale: 1 mV/div.
Horizontal scale: .1 sec/div.
Fig. VI.7. Thermocouple and Kelvin Double Bridge voltage outputs for the reversion of an Al - 4 wt. pct. alloy at 204°C, showing initial fast and subsequent slow reactions.

Upper trace, thermocouple: .4 mV/div. vertical
Lower trace, bridge: 40 mV/div. vertical
Horizontal scale: .1 sec/div.

Fig. VI.8. Thermocouple and Kelvin Double Bridge voltage outputs for the reversion of an Al - 4 wt. pct. Cu alloy at 223°C.

Upper trace, bridge: .1 V/div. vertical
Lower trace, thermocouple: .4 mV/div. vertical
Horizontal scale: .1 sec/div.
Fig. VI.9. Thermocouple and Kelvin Double Bridge voltage outputs for the reversion of an Al - 4 wt. pct. alloy at 215°C; double pulse heating experiment during initial fast reaction.

Upper trace, thermocouple: .4 mV/div. vertical
Lower trace, bridge: .1 V/div. vertical
Horizontal scale: 4 msec/div.

Fig. VI.10. Kelvin Double Bridge voltage output for the reversion of an Al - 4 wt. pct. Cu alloy at 215°C; double pulse heating experiment during initial fast reaction.

Vertical scale: 40 mV/div.
Horizontal scale: 10 msec/div.
Fig. VI.11 a) Kelvin Double Bridge voltage output for the reversion of an Al - 4 wt. pct. Cu alloy at 196°C; double pulse heating experiment with first pulse below 200°C and second pulse above 200°C giving a high apparent activation energy.

Vertical scale: .1 V/div.
Horizontal scale: 4 msec/div.

Fig. VI.11 b) Thermocouple voltage out for the reversion of an Al - 4 wt. pct. Cu alloy at 196°C; same experiment as Fig. VI.11 a).

Vertical scale: .4 mV/div.
Horizontal scale: 4 msec/div.
An extensive fast reaction did not occur at temperatures below 200°C as illustrated in Figure VI.5 and VI.6 for reversion at 196°C and 173°C. However, a more rapid rate of initial resistivity decay could be detected but this stage only lasted for 10 to 20 milliseconds and it caused a very small amount of decay. A typical example is shown in Figure VI.5 where the initial stages of the multiple sweep have a steeper gradient.

A series of resistivity curves for temperatures between 204°C and 250°C were obtained and following the enlargement of the oscilloscope photographs onto a screen and tabulation of the data by recording the intercepts of the traces with a superimposed mesh, a fifth order polynomial was fitted in the least squares sense, using a computer. Subsequently, the curves could be differentiated or plotted on different scales and the program graphed the outcome of these manipulations. In the next chapter this computer generated data will be analysed.

VI.1.2. Slow Reversion Reaction.

Figures VI.1, VI.2, VI.7 and VI.8 are examples of typical oscillographs taken at reversion temperatures of 206°C, 208°C, 204°C and 223°C. using a .5sec/cm time scale. It was observed that only at intermediate temperatures was a resistance decay tending to a constant value obtained while at lower and higher temperatures a more linear decay to longer times was given. Hence it was impossible to make accurate observations of the total resistivity change upon reversion because the temperature of the specimen could not be maintained after about 5 seconds, and the temperature range over which the decay to a constant intermediate time value was very limited (about 20°C). The temperature dependence
of the slow reversion reaction stage therefore, could not be examined in so great a detail as that for the fast reaction.

VI.2. Double Pulse Heat Treatments during Reversion.

The resistivity changes during reversion heat treatments in which the specimen was pulsed to a temperature $T_1$ and then pulsed after various times to a temperature $T_2$ were observed. Typical oscillographs are given in Figures VI.9 and VI.10. In the former both the bridge and thermocouple outputs are recorded while in the latter the temperature was recorded on a second oscilloscope.

VI.2.1. Instantaneous Activation Energy for Reversion.

The "change of slope" method previously described gives the instantaneous activation energy for the process. If the rates of resistivity change before and after the second pulse are $m_1$ and $m_2$ then:

$$\log_e \frac{m_1}{m_2} = - \frac{Q}{k} \frac{T_2 - T_1}{T_1 T_2}$$

where the instantaneous activation energy is $Q$. Two cases were experimentally distinguishable, depending on whether $T_1$ is greater or less than 200°C.

$T_1$ greater than 200°C.

A series of measurements were made for $T_1 = 215°C$ and Table VI.1 gives the results. $m_1$ and $m_2$ were determined from least squares fits of fifth order polynomials through the tabulated resistivity curve data. It is seen that there is an immediate change in the instantaneous activation energy for reversion from 1 ev. during the fast reaction to 2 ev. during the slow reaction. Also there is no dependence on $Q$ with the temperature difference between the first and second pulse, to within the limit of the experimental technique.
### Table VI.1

Instantaneous Activation Energies as Determined by the 'Change of Slope' Method: \( T_1 \) greater than 200°C. \((T_1 = 215°C)\)

<table>
<thead>
<tr>
<th>Time at ( T_1 ) (msecs)</th>
<th>( m_1 ) (arbitrary units)</th>
<th>( m_2 ) (arbitrary units)</th>
<th>( T_2-T_1 ) (°C.)</th>
<th>( Q_i ) (ev)</th>
<th>Reaction Type at ( T_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>41.80</td>
<td>75.0</td>
<td>11.00</td>
<td>1.10</td>
<td>fast</td>
</tr>
<tr>
<td>117</td>
<td>5.00</td>
<td>17.4</td>
<td>24.00</td>
<td>1.04</td>
<td>fast</td>
</tr>
<tr>
<td>178</td>
<td>49.30</td>
<td>123.5</td>
<td>20.50</td>
<td>0.94</td>
<td>fast</td>
</tr>
<tr>
<td>205</td>
<td>9.00</td>
<td>63.0</td>
<td>20.50</td>
<td>2.01</td>
<td>slow</td>
</tr>
<tr>
<td>370</td>
<td>11.60</td>
<td>105.0</td>
<td>22.00</td>
<td>2.06</td>
<td>slow</td>
</tr>
</tbody>
</table>

### Table VI.2

Instantaneous Activation Energies as Determined by the 'Change of Slope' Method: \( T_1 \) less than 200°C, \( T_2 \) greater than 200°C. \((T_1 = 196°C)\)

<table>
<thead>
<tr>
<th>Time at ( T_1 ) (msecs)</th>
<th>( m_1 ) (arbitrary units)</th>
<th>( m_2 ) (arbitrary units)</th>
<th>( T_2-T_1 ) (°C.)</th>
<th>( Q_i ) (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>94</td>
<td>7.00</td>
<td>71.1</td>
<td>22.00</td>
<td>2.05</td>
</tr>
<tr>
<td>123</td>
<td>9.01</td>
<td>84.0</td>
<td>22.00</td>
<td>2.01</td>
</tr>
<tr>
<td>252</td>
<td>11.10</td>
<td>119.0</td>
<td>22.00</td>
<td>2.03</td>
</tr>
</tbody>
</table>
Table VI.3

Instantaneous Activation Energy as Determined by the 'Change of Slope' Method: $T_1$ less than 200°C, $T_2$ less than 200°C.

<table>
<thead>
<tr>
<th>Time at $T_1$ (msecs)</th>
<th>$T_1$ (°C)</th>
<th>$T_2$ (°C)</th>
<th>$m_1$ (arbitrary units)</th>
<th>$m_2$ (arbitrary units)</th>
<th>$Q_1$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>176</td>
<td>197</td>
<td>7.50</td>
<td>43.40</td>
<td>1.50</td>
</tr>
<tr>
<td>255</td>
<td>172</td>
<td>194</td>
<td>10.40</td>
<td>51.20</td>
<td>1.60</td>
</tr>
</tbody>
</table>
$T_1$ less than 200°C., $T_2$ greater than 200°C.

The same procedures for $T_1$ less than 200°C were carried out and the results are given in Figure VI.11, showing a typical oscillograph for $T_1=196°C$, and Table VI.2. It is seen that an extensive fast reaction does not occur during the first pulse and that upon pulsing above 200°C for the second heat treatment, the fast reaction was initiated thereby giving a large instantaneous activation energy. Moreover $Q_1$ was constant over a wide range of a wide $T_1$ reversion time range. Unfortunately, experiments conducted within the first 10 to 20 milliseconds to determine whether the very slightly faster initial rate of decay corresponded to a definite reversion stage with a unique activation energy were inconclusive because the resistivity changes were too small to be accurately observed over such short times.

$T_1$ less than 200°C., $T_2$ less than 200°C.

Table VI.3 gives the results for this case and the activation energy is seen to be constant and equal to about 1 ev. Unfortunately reversion times greater than about 1 second could not be investigated because the temperature of the specimen, as maintained by the joule heating effect, varied excessively at these long times.

VI.2.2. Estimation of the Percentage Change in Resistivity Produced by the Fast Reversion Reaction.

The series of double pulse experiments made at $T_1=215°C$ enable an estimate of the percentage change in resistivity due to the fast reaction, $\delta_f$, to be made since the temperature rise and the voltage increase due to the second pulse is recorded. Assuming a structure independent thermal coefficient of resistivity, $\omega$, then $\Delta V_t$, the voltage change due to the instantaneous temperature increase $\Delta T$ is:
\[ \Delta V_t = i \cdot \rho_1 \cdot \omega \cdot \Delta T \]

where \( \rho_1 \) is the specimen resistance immediately before the second pulse. Now the fast reaction gives a resistance change of \( \Delta \rho_f \), and a voltage change of \( \Delta V_f \) so:

\[ \Delta V_f = i \cdot \Delta \rho_f \]

\[ \Delta V_t = i \cdot \omega \cdot \Delta T \cdot (\rho_o + \Delta \rho_f) \]

where \( \rho_o \) is the initial resistance. On dividing these expressions, \( i \), the direct current which was kept constant, is eliminated and on expanding in terms of a binomial series we have:

\[ \frac{\omega \cdot \Delta T \cdot \Delta V_f}{\Delta V_t} = \frac{\Delta \rho_f}{\rho_o} \left[ 1 - \frac{\Delta \rho_f}{\rho_o} + \ldots \right] \]

Keeping first order terms only the final result is:

\[ \delta_f = \frac{\omega \cdot \Delta T \cdot \Delta V_f}{\Delta V_t} = \omega \cdot \lambda \]

In Figure VI.12 the experimental values for the function \( \lambda \) are plotted for various reversion times at 215°C and it is seen that a maximum is reached at about 200 milliseconds which corresponds closely to the completion time of the fast reaction at this temperatures as determined by the isothermal experiments (see Figure VII.1). An exhaustive list of the temperature coefficient of resistivity of Aluminum - Copper alloys is given in Table VI.4 and values are plotted in Figure VI.13. Assuming a mean value of \( \omega = 0.0021 \) then the percentage change of specimen resistance due to the fast reaction is:

\[ \delta_f \times 100 = \omega \cdot \lambda \cdot 100 = 0.0021 \cdot 12 \cdot 100 = 2.5\% \]

An error of 15\% would be appropriate as the errors in measuring \( \Delta T \), \( \Delta V_f \) and \( \Delta V_t \) are all on the order of 3\% and the assumption of a constant temper-
Figure VI.12. Experimental Values for the Function $\lambda$ versus the Reversion Time at $T_1 = 215^\circ C$. $\lambda$ is proportional to the fast reaction resistivity.

$$\lambda = \frac{\Delta T \cdot \Delta V_i}{\Delta V_i}, \quad ^\circ C.$$ 

Figure VI.13. Thermal Coefficient of Resistivity Data of Table VI.4 Plot.
Table VI.4

The Thermal Coefficient of Resistivity for Aluminum-Copper Alloys in the Range, 100 - 300°C.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. Coef., $\alpha, ^\circ\text{C}^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (99.992%)</td>
<td>0.0042</td>
<td>81</td>
</tr>
<tr>
<td>Al (99%)</td>
<td>0.0040</td>
<td>81</td>
</tr>
<tr>
<td>Al (99.9%)</td>
<td>0.0039</td>
<td>82</td>
</tr>
<tr>
<td>Al 4wt.pct.Cu</td>
<td>0.0023</td>
<td>81</td>
</tr>
<tr>
<td>Al 4wt.pct.Cu</td>
<td>0.0020</td>
<td>23</td>
</tr>
<tr>
<td>Al 4wt.pct.Cu</td>
<td>0.0019</td>
<td>14</td>
</tr>
<tr>
<td>Al 5.1wt.pct.Cu</td>
<td>0.0016</td>
<td>83</td>
</tr>
</tbody>
</table>
ature coefficient of resistivity would introduce a further error of 5% as indicated by Figure VI.13 for the reported values of \( \omega \). Current variations of 1% would also be possible although the specimen temperature did remain to within 2°C.

In principle the Kelvin Double Bridge could have been calibrated but laborious calibration procedures would have been required prior to every test to ensure that amplifier drift and probe resistance variations had been accounted for. However since an accurate estimate of \( \delta_f \) and of the resistivity contributions of the other stages is of little interest in the absence of even reasonable interpretations of resistivity changes during reversion, the value of \( 2.5 \pm 0.4 \% \) is considered to be sufficiently accurate in terms of its usefulness, which is as a parameter to determine what structural change is occurring during the fast reaction. This will be discussed in the next chapter.

VI.3. The Reageing of Partially Reverted Specimens.

The resistance changes observed upon reageing the specimens at 28°C in a temperature bath controlled to within 0.1°C, after various heat treatments are given in Figure VI.14. The initial resistance \( \rho_0 \), was determined by extrapolation of the data to zero time, the time of the first measurement being about 2 minutes after the quench to room temperature. In all cases no incubation time was observed. Secondly, the initial rate of resistivity change was the same for specimens reverted for .28 seconds at 250°C and for 2 minutes at 205°C. Thirdly, the initial rate passes through a maximum for an increasing reversion time at constant temperature as shown by the curves obtained after reverting at 250°C for .085, .28 and 3.9 seconds.

An extensive investigation of reageing after reversion was not
Figure VI.14. Resistivity Changes Observed during the Reageing of an Aluminum -- 3.85 wt.pct. Copper alloy at 28°C after Various Reversion Treatments. Initial resistance is $\rho_0$: reversion after $10^2$ min. at 70°C.
conducted because a comparison of the observed reageing kinetics with data reported by Herman and Fine (68) for the reageing reaction following plastic deformation showed strong similarities. These investigators demonstrated that an incubation time on the order of tens of minutes was observed if great care was taken not to plastically deform the specimen and that small amounts of plastic deformation (1 - 2%) during the reageing process gave an immediate and very rapid rate of resistance increase. The exact origin of the plastic deformation is of interest because reageing studies are valuable so the various possibilities, their likely causes, magnitudes and remedies, will be discussed in a later chapter. It is sufficient at this stage to remark that the expected plastic deformations using the specimen mounting procedures and quenching methods of this investigation should not give a plastic strain of more than .5% and whether or not this is sufficient to cause the effects demonstrated by Herman and Fine is not known, although the results given here suggest that it is.

VI.4. Resistivity Measurements Made in Liquid Nitrogen After Reversion at 215°C.

Specimens were reverted at 215°C for various times before being quenched with cold ethanol. The specimen's resistance in liquid Nitrogen before and after the heat treatment was measured and the percentage change in the specimen resistivity given by \( \Delta \rho / \rho_0 \) where \( \rho_0 \) is the resistance before reversion, as a function of reversion time is plotted in Figure VI.15. In all cases an increase was observed in agreement with the results of Shimizu and Kimura (25) but the data was widely scattered and lay outside the probable error limits.

Using the present apparatus, in situ measurements in liquid Nitrogen
Figure VI.15. The Resistivity of an Aluminum -- 3.85 wt.pct. Copper Alloy at -196°C after Reversion at 215°C, as a Function of the Reversion Time. $\rho_0$ is the specimen resistance before reversion; probable errors are indicated.
were not possible and instead the specimen was mounted and pulsed after the initial resistivity determination and subsequently removed form the cold ethanol boat. Care was taken to ensure that the lead resistances remained the same but inevitably a small contact resistance variation was introduced because it was necessary to isolate the second Kelvin Double Bridge that was used, otherwise the high voltages developed during pulse heating would damage the bridge. Furthermore, quenching to -20°C would introduce more plastic strain than that encountered on quenching to room temperature as in the previous section. There it was shown that percentage changes in the specimen resistances would be about 0.15% for one minute's reageing at room temperature. Since the specimens were held at room temperature for about half a minute while they were being removed from the mountings, this, together with the extra plastic deformation, would explain some of the observed resistance scatter.

This scatter persisted at other reversion temperatures and although very rapid resistivity increases were observed, attempts to collect reproducible and consistent data were abandoned. Clearly, considerable modifications to the pulse heater specimen mounting assembly were needed.

VI.5. Conclusions.

The results presented in this chapter will form the basis of a possible interpretation for the mechanism of reversion of an Aluminum — 3.85 wt.pct. Copper aged to the slow reaction stage. However, this interpretation will be preceded by a detailed analysis of the resistance decay curves obtained during reversion.
VII. ANALYSIS OF EXPERIMENTAL RESULTS

The isothermal resistance decay curves, both above and below 200°C will be discussed. Subsequently, the results of the other experiments will be incorporated to give a fuller description of the reversion kinetics of GP zones in an Aluminum - 3.85 wt.pct. Copper alloy.

The resistance decay curves, as has been described, were tabulated and a least squares, fifth order polynomial was fitted through the data. In order to check that this polynomial accurately represents the original curves at all temperatures, the oscilloscope photographs were projected onto a screen and the curves were traced out and these are reproduced in Figure VII.1 for typical high and low temperature cases. Also plotted are several points given by the least squares fitted polynomials and it is seen that these polynomials accurately represent the resistance decay curves.

The fast and slow reversion reactions will be considered separately and the time to completion of the fast reaction, \( t_{cf} \), was determined by extending the least squares fitted curve to that time that gave a zero rate of resistance decay. In order to facilitate comparisons between the computer generated outputs for different experiments, the amount of resistance decay accomplished by the fast reaction was assumed to be unity at time zero and zero at time \( t_{cf} \). This quantity will be called the fast reaction fraction, \( x_f \), so:

\[
\begin{align*}
  x_f &= 1 \text{ at } t = 0 \\
  x_f &= 0 \text{ at } t = t_{cf}
\end{align*}
\]

Figure VII.2 shows that the true fast reaction fraction, \( X_f \), which is the ratio of the amount of resistance decay occurring during the fast
Figure VII 1. A Comparison of the Projected Oscilloscope Traces for the Fast Reversion Reaction and The Least Squares, Fifth Order Fitted Polynomial. Points given by polynomial.
Figure VII.2. The Temperature Dependence of the True Fast Reversion Reaction Fraction, $X_f$, and of the Fast Reaction Completion Time, $t_{cf}$. Activation energies are given by a least squares fitted line.
reversion reaction to the total resistance decay during reversion, is linear with 1/T where T is the absolute temperature of reversion and that $X_f$ is given by:

$$\log_e X_f = \log_e X_f^0 + \frac{0.34}{k g T}$$

where $k_g$ is the gas constant (in ev.T$^{-1}$.mole$^{-1}$). Hence the true fast reaction fraction has an apparent activation energy of 0.34 ± 0.05 ev.

The assumption that a time to completion of the fast reaction can be estimated is equivalent to postulating that the fast and slow reactions occur successively and not concurrently. However, it will be shown that the slow reaction following the fast reaction at temperatures above 200°C has different kinetic characteristics to the slow reaction occurring below 200°C so this assumption is considered to be reasonable. A source of error is introduced in determining the time to completion of the fast reaction because invariably the rate did not achieve a zero value although it was tending to zero very rapidly, a feature that the computer program made use of in estimating the completion time. However, the computed and experimentally estimated completion times were always to within 5% of each other.

The predictions of the various dissolution theories that have been reviewed suggested that the following parameters should be investigated as a function of time:

a) rate of resistance decay, particularly at early times.

b) logarithm of the rate of resistance decay at times greater than some critical time $t^*$.

c) resistance to the 2/3 power, particularly at long times.

d) logarithm of the resistance.

The computer program calculated each of these quantities and graphed the results on normalized scales in which:
where \( y \) is a particular parameter. The actual value of \( y \) can be obtained by multiplying the normalised parameter by the scale factor, \( y_{\text{max}} - y_{\text{min}} \), and adding \( y_{\text{min}} \). These two quantities are given in Tables referred to by the relevant Figures. All linear \( \log y_{\text{norm}} \) versus \( 1/T \) plots will have a line drawn through the points that was calculated by minimizing the least squares' deviation of the points from the line, and the slope of the line will give an activation energy.

**VII.1. Fast Reversion Reaction.**

**VII.1.1. Initial Rate of Resistance Decay and Fast Reaction Completion Time.**

In Figure VII.2 the time to completion of the fast reversion reaction is plotted as a function of \( 1/T \) and the least squares line gives an activation energy of \( 0.80 \pm 0.04 \text{ ev} \).

The rate of resistance decay was not constant at early times and the initial rate was finite. This behaviour persisted even though measurements were made only \( 1 \) msec. after the pulse to temperature.

Diffusion controlled dissolution theory predicts an infinite rate of decay regardless of precipitate shape, so the finite rate indicates an interface reaction controlled step. In Figure VII.3 the initial rate of decay of the fast reaction fraction, \( \dot{x}_f(t=0) \), is plotted as a function of \( 1/T \) and an activation energy of \( 0.82 \pm 0.04 \text{ ev} \). results. The stationary interface approximation for precipitates dissolving in an initially depleted matrix gives:

\[
\frac{dR}{dt} = -\Omega K c_b^0
\]  

(7.1)

Okamato and Kimura (20) give the heat of solution of a GP zone in an
Figure VII.3. Temperature Dependence of the Initial Rate of Decay of The Fast Reaction Fraction, $x_f$. The resistivity change of the specimen is given by $X_f X_f$ where $X_f$ is the true fast reaction fraction.
Aluminum -- 4 wt.pct. Copper alloy to be about 0.02 ev. per gram atom of Copper and since this is much smaller than the activation energy for Copper atom diffusion (0.5 ev. or larger), Equation 7.1 is equivalent to assuming that the flux of atoms leaving the zones at time zero is proportional to the rate of change of the zone volume. Hence:

\[ \frac{dR_z}{dt} = j = \frac{2\pi r_0 h c_0^z \nu}{a^4} \]

where the zones are assumed to be discs of concentration \( c_0^z \), and of thickness \( h \), in a matrix with a lattice parameter \( a \). The radius of the zones \( R_z \) is initially \( r_0 \) and \( \nu \) is the Copper atom jump frequency. The activation energy determined from the initial rate should therefore reflect the activation energy for Copper atom migration as was concluded above. It has been assumed that the zones dissolve at their peripheries.

However, first it is necessary to account for the temperature dependence of the true fast reaction fraction since the state attained at the end of the fast reaction is not temperature independent. The rate of resistance change is given by:

\[ \frac{dp}{dt} = \frac{d(x_f X_f)}{dt} = x_f^o \frac{dx_f}{dt} \]

and thus:

\[ \log_e \frac{dp}{dt} = \log_e \frac{dx_f}{dt} + \frac{0.34}{kT} + \log_e x_f^o \ (7.2) \]

where the temperature dependence of \( x_f^o \) as given by Equation (7.0) has been substituted. The total resistance change has been assumed to be constant and independent of the measuring temperature. The former assumption is very reasonable provided a completely random solid solution is formed at the completion of reversion and the most serious possible complication, the formation of other more stable precipitates has been
shown to be very unlikely in times of less than one minute (84). The second assumption implies that the thermal coefficient of resistivity of the as-aged structure is the same as that for the as-reverted state and it is shown in Appendix F that given reasonable values for the coefficient as a function of zone size, then the fast reaction fraction is accurate to 5%. However, rather larger sources of error were probably introduced by the extrapolation of the slow reaction curves to the time for a zero rate of resistance change in order to determine the resistance at completion, and by the difficulty in estimating the end of the fast reaction. Thus the initial rate of decay gives an activation energy of \(0.82 - 0.34 \pm 0.06\) ev = \(0.48 \pm 0.06\) ev, using Equation 7.2.

VII.1.2. Rate of Resistance Decay at Longer Times.

The logarithm of the fast reaction fraction decay rate, \(x_f\), is plotted in Figures VII.4, 5 and 6 for twelve temperatures between 206°C and 250°C. It is seen that the linear range extended from zero time increases from 0.3 to 0.7 on the normalised time scale as the temperature of reversion increases. Moreover the pronounced inflexion occurring at low temperatures has disappeared at high temperatures and that there is a systematic change-over between these two extremes.

In Figure VII.7, slopes of the log \(x_f\) plots are given as a function of \(1/T\) and an activation energy of \(0.63 \pm 0.04\) ev. results when both the time zero slopes and the average value of the almost linear stage slopes are considered. The temperature dependence of the true fast reaction fraction does not affect this activation energy since on differentiating Equation 7.2 we have:

\[
\frac{d \log_e}{dt} \frac{dx_f}{dt} = \frac{d \log_e}{dt} \frac{dx_f}{dt}
\]
Figure VII.4. Logarithm of the Rate of Change of the Fast Reaction Fraction at Various Indicated Reversion Temperatures.

Temperatures in °C.
Figure VII.5. Logarithm of the Rate of Change of the Fast Reaction Fraction at Various Indicated Reversion Temperatures. Both co-ordinates are normalised in terms of the parameters given in Table VII.1. \( x_f \) is the fast reaction fraction, \( t_{cf} \) is the fast reaction completion time.
Figure VII.6. Logarithm of the Rate of Change of the Fast Reaction Fraction at Various Indicated Reversion Temperatures. Both co-ordinates are normalised in terms of the parameters given in Table VII.1. $x_f$ is the fast reaction fraction, $t_{cf}$ is the fast reaction completion time.
Table VII.1
Normalisation Parameters for log $\dot{x}_f$ versus time $t$, Curves for the Fast Reversion Reaction. $\dot{x}_f$ is the rate of change with time of the fast reaction fraction and $t_{cf}$ is the completion time of the fast reaction.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Reversion Temp. °C</th>
<th>Vertical, $\dot{x}_f$ Min</th>
<th>Max-Min</th>
<th>Completion time, msecs</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII.4</td>
<td>206</td>
<td>-.6945</td>
<td>2.745</td>
<td>373</td>
</tr>
<tr>
<td></td>
<td>208</td>
<td>-.8121</td>
<td>2.854</td>
<td>343</td>
</tr>
<tr>
<td></td>
<td>215</td>
<td>-.4989</td>
<td>3.224</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>218</td>
<td>-.5054</td>
<td>2.964</td>
<td>227</td>
</tr>
<tr>
<td>VII.5</td>
<td>219</td>
<td>-.5681</td>
<td>3.038</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>229</td>
<td>-.7241</td>
<td>3.491</td>
<td>224</td>
</tr>
<tr>
<td></td>
<td>229</td>
<td>-.4216</td>
<td>3.344</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>239</td>
<td>-.01938</td>
<td>3.155</td>
<td>136</td>
</tr>
<tr>
<td>VII.6</td>
<td>243</td>
<td>-1.786</td>
<td>.7590</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>247</td>
<td>-1.506</td>
<td>.7590</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>-2.578</td>
<td>1.657</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>-3.345</td>
<td>2.990</td>
<td>85</td>
</tr>
</tbody>
</table>
Figure VII.7. Temperature Dependence of the Gradients of the Linear Stages of the Log \( k_f \) versus time Plots at Different Reversion Temperatures. Both initial and minimum gradients are plotted; the average value gives an activation energy of \( 0.63 \pm 0.04 \) ev.
It is necessary to estimate the times for the onset of linearity for \( \log e \) \( x_f \) versus time and Table VII.2 gives these times as predicted by the various dissolution theories, based on the following parameters:

a) volume fraction of precipitate, \( v \):

Minimum value = 0.001, corresponding to a disc-like zone 10 A° thick and 30 A° in radius such that the radius of the equivalent spherical precipitate is \([30 \cdot 10]^{1/3}\) A°. The zones are 200 A° apart.

Intermediate value = 0.01, corresponding to zones of pure Copper in a depleted matrix for an Aluminum - 4 wt.pct. Copper alloy. The ratio of the Copper to Aluminum atomic radii is 0.89 (63).

Maximum value = 0.025. Taken from the data of Okamoto and Kimura (20) and described previously (Chapter IV., Section 4).

b) precipitate concentration is unity.

c) matrix concentration is initially 0.005 at.pct. Copper. (85)

d) diffusion coefficient is \( 4.0 \times 10^{-7} \), based on an activation energy of 0.63 ev. at 200°C.

The estimated times for the onset of linearity, \( t^* \), as given in Table VII.2, suggest that the diffusion controlled dissolution of zones with an activation energy of 0.63 ev for solute diffusion, would give linear \( \log \dot{x}_f \) kinetics after only 1 millisecond as was observed.

VII.1.3. Other Parameters that Possibly Describe the Reversion Kinetics.

Neither the computer generated \( \log x_f \) versus time nor those parameters that may describe the radius of the equivalent spherical particle, such as \( x_f^{2/3} \), gave linear stages. This suggests that the resistance decay is not a simple exponentially decaying process as others have assumed when analysing discrete reversion data (17) and also that the zones cannot be considered as isolated precipitates with no diffusion
Table VII.2

Estimates of $t^*$, the Time in Seconds for the Onset of Linear $\log \dot{x}_f$ versus Time Behaviour for Dissolving GP Zones in an Al - 3.85wt.pct. Cu Alloy at 200°C. $x_f$ is the fast reversion reaction fraction.

<table>
<thead>
<tr>
<th>Solution type</th>
<th>Volume fraction</th>
<th>Diffusion control</th>
<th>Interface reaction control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stationary interface</td>
<td>$v &lt; .001$</td>
<td>$2. \times 10^{-8}$</td>
<td>-</td>
</tr>
<tr>
<td>Moving interface</td>
<td>&quot;</td>
<td>$5. \times 10^{-5}$</td>
<td>120</td>
</tr>
<tr>
<td>Stationary interface</td>
<td>$v &gt; .1$</td>
<td>$3. \times 10^{-4}$</td>
<td>.033</td>
</tr>
<tr>
<td>Finite difference</td>
<td>$v = .025$</td>
<td>$5. \times 10^{-8}$</td>
<td>-</td>
</tr>
</tbody>
</table>

Table VII.3

Normalisation Parameters for $\log \dot{x}$ versus time $t$, Curves for the Fast and Slow Reactions of Figure VII.8. $\dot{x}$ is the rate of change with time of the fast or slow reversion fraction and $t_c$ is the completion time of the fast reaction or the duration of the slow reaction that is plotted.

<table>
<thead>
<tr>
<th>Reversion Temp. °C</th>
<th>Reaction</th>
<th>Vertical, $\dot{x}$</th>
<th>$t_c$ (secs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>206</td>
<td>fast</td>
<td>-1.959</td>
<td>3.413</td>
</tr>
<tr>
<td>241</td>
<td>fast</td>
<td>-.6157</td>
<td>2.508</td>
</tr>
<tr>
<td>206</td>
<td>slow</td>
<td>-1.786</td>
<td>.7590</td>
</tr>
<tr>
<td>241</td>
<td>slow</td>
<td>-1.506</td>
<td>.6452</td>
</tr>
<tr>
<td>173</td>
<td>slow</td>
<td>-2.578</td>
<td>1.657</td>
</tr>
<tr>
<td>196</td>
<td>slow</td>
<td>-3.345</td>
<td>2.990</td>
</tr>
</tbody>
</table>
field overlap as this would lead to parabolic kinetics at long times, regardless of the precipitate shape.

VII.2. Slow Reversion Reaction.

VII.2.1. Activation Energy of the Slow Reversion Reaction.

As it was not possible to accurately measure the resistance change to completion, thereby obtaining normalized curves, an estimate of the activation energy during the initial stages of the slow reaction (i.e. for reversion times of less than 2 seconds) is given as follows:

If the slope of the log $\rho$ versus time plots during the fast and slow reactions are $\kappa_f$ and $\kappa_s$ respectively and assuming that:

$$\kappa \propto D \propto \exp \frac{Q}{kT}$$

Thus:

$$\log_e \frac{\kappa_f}{\kappa_s} = - \frac{Q_f - Q_s}{kT}$$

assuming that the fast and slow reactions occur sequentially and do not overlap. A plot of $\log \frac{\kappa_f}{\kappa_s}$ versus $1/T$ should give a straight line but unfortunately, because it was necessary to measure both the fast and slow reactions from the same oscilloscope trace in order to remove many sources of error such as Kelvin Bidge calibration variations, temperature measurement errors, time scale changes and applied voltage variations, the very different time scales of the two reactions made an adequate observation of each stage very difficult. However two good traces were obtained and their log $\kappa$ curves during the fast and slow reactions are given in Figure VII.8. The normal fast reaction characteristics are shown as well as the pronounced linearity over the central section of the slow reaction. For the slow reaction, as for the fast reaction, the slow reaction fraction is defined as follows:
Figure VII.8. Logarithm of the Rate of Decay of the Reaction Fraction for both the Fast and Slow Reactions at Indicated Temperatures. Both co-ordinates are normalised in terms of the parameters given in Table VII.3. Both the slow and fast reactions at two temperatures above 200°C are given together with two reaction curves below 200°C. \( t_c \) is the completion time of the fast reaction or the duration of the slow stage.
\[ \begin{align*}
x_s &= 1 \text{ at } t = t_{cf} \\
x_s &= 0 \text{ at } t = t_{sf}
\end{align*} \]

where the time to completion of the slow reaction is \( t_{sf} \). From Equation 7.3 we have:

\[
\log_e \frac{\kappa_f}{\kappa_s} \frac{T_1}{T_2} = \frac{Q_f - Q_s}{k_g} \frac{T_2 - T_1}{T_2 T_1}
\]

Values for \( \kappa_f \) and \( \kappa_s \) at the two temperatures are:

\[
\begin{array}{ccc}
\text{Reversion T.,°C.} & \kappa_f & \kappa_s \\
206 & -3.849 & -0.4112 \\
241 & -8.992 & -0.4582 \\
\end{array}
\]

giving \( Q_f - Q_s = 0.44 \text{ ev.} \) and thus the activation energy for the slow reversion reaction is \( 1.07 \pm 0.06 \text{ ev.} \). This is considered to be a reasonably accurate estimate because the temperature difference between the two experiments was large and almost equal to the full range used in the isothermal, fast reversion reaction above 200°C, studies.

VII.3. The Origins of Resistivity Changes during Reversion.

During the fast reversion reaction the specimen resistivity measured at the reversion temperature falls by about 2% in 200 msecs. (for reversion at 215°C.), but increases by about 1% if measured at -196°C. and on reageing at 28°C a rapid resistivity increase to a maximum change of about 1% occurs (measured at 28°C.). Several processes can contribute to these changes:

a) vacancy decay to sinks.

Vacancies in Aluminium have an intrinsic resistivity \( \rho_{iv} \), of between
3.0 \(\mu\Omega \text{cm./at.pct.}\) (86) and 1.1 \(\mu\Omega \text{cm./at.pct.}\) (87) and at temperatures between -196°C and 100°C the deviation from Mattheisson's Law due to vacancies is constant and their resistivity contribution is \(1.12\sigma_{iv1}\) (88). Simmons and Balluffi(86) have extended the application of the constant deviations to temperatures near the melting point. Hence the resistivity decrease observed during reversion when measurements are made at the reversion temperature could be partly due to vacancy decay but there must also be another process occurring because a low measuring temperature increase is observed.

Large \((\sim 1\mu)\) dislocation loops that are \(\approx 1\mu\) apart have been observed in the as aged alloy (89) and since the diffusion distance of vacancies at 200°C in 0.5 seconds (the duration of the fast reaction at this temperature) is about 15\(\mu\), some vacancy decay is possible. Other, as yet unobserved loops or vacancy aggregates may also act as sinks. However Flynn (90) shows that the intrinsic resistivity contribution of an aggregate containing \(n\) vacancies is:

\[
\sigma_{ivn} = n\sigma_{iv1}
\]

for \(n\) between 2 and \(10^4\). The aggregates proposed by Turnbull et al (14) lie well within this range so the specimen's intrinsic resistivity should not change during the early stages of aggregate growth or coarsening. Information regarding the high temperature resistivity of aggregates is scarce.

The intrinsic resistivity of a line defect in Aluminum is \(2 - 3 \times 10^{-13} \mu\Omega \text{cm./cm.}^3\) (91) while that for a stacking fault is \(3 \times 10^{-7} \mu\Omega \text{cm./cm.}^2\) (92), so both loop coarsening and loop growth would give a specimen resistivity decrease at low measuring temperatures.
b) Decomposition of vacancy - solute atom aggregates.

The only vacancy solute aggregates likely to exist in the mature, as-aged alloy are vacancy-solute atom pairs and zones with associated vacancies. The intrinsic resistivity of a pair is appreciably less than the sum of the individual resistivities of a vacancy and a solute atom. For example, if the contribution of the solute atom is unaltered then the intrinsic resistivity of a bound vacancy is typically $0.36 \times \sigma_{iv_1}$ and $0.75 \times \sigma_{iv_1}$ for Zinc and Silicon impurities in Aluminum (93). For Aluminum - 3.85 wt.pct. Copper, assuming that the intrinsic resistivity of a bound vacancy is $0.5 \times 3 \ \mu\Omega\cdot\text{cm.}/\text{at.pct. vacancies}$, and the specimen resistivity is $4 \ \mu\Omega\cdot\text{cm.}$ (14) then a change in the bound vacancy concentration of 0.027 at.pct. would give a 1% resistivity change. The maximum total vacancy concentration is 0.007 (i.e. the equilibrium vacancy concentration at the homogenisation temperature) and assuming a vacancy-solute binding energy of 0.15 ev. (94), only a fraction of the 1% resistivity increase can be attributed to the readjustment of the vacancy-solute atom equilibrium.

For large solute atom-vacancy aggregates there is very little information available. However, if Flynn's remarks concerning vacancy aggregates are reasonable, then the loss of vacancies associated with zones may not cause a resistivity change and the predominant effect would be a change in the resistivity contribution due to zone dissolution.

VII.4. Comparisons of the Slow Reversion Reactions above and below 200°C

Two typical log $x$ versus time curves for the slow reaction below 200°C are given in Figure VII.8 together with the curves for both the fast and slow reactions above 200°C. The characteristics of the curves
for the slow reaction above and below 200°C are seen to be very different and in particular the initial transient, non-linear stage is absent below 200°C but it is present for the slow reactions following the fast reactions.

VII.5. Summary of Experimental Results.

Two distinct early-time kinetic stages have been shown to occur above 200°C. The first of these, the fast reversion reaction, has a large (2.5% at 200°C) resistance change associated with it and this quantity decreases as the reversion temperature is increased. The initial rate of resistance decay gave an apparent activation energy of 0.82 ± 0.04 ev. but when this was corrected for by the temperature dependence of the fast reaction fraction, it gave an activation energy of 0.48 ± 0.06 ev. The logarithm of the rate of resistance change plots gave an activation energy of 0.63 ± 0.04 ev and the predicted times for the onset of the linear behaviour suggested that this activation energy is that for solute diffusion. The completion time of the fast reaction gave an apparent activation energy of 0.80 ± 0.04 ev. The slow reaction involved an activation energy of 1.07 ± 0.06 ev. and showed different kinetic characteristics above and below 200°C.

The double pulse heating gave a variety of apparent activation energies, depending on the temperatures and reversion times involved. If the pulse was applied during the fast reaction an activation energy of 1.0 ev resulted but this increased to 2.0 ev. if the pulse occurred during the slow reaction above 200°C. On the other hand, if the first pulse temperature was below 200°C, activation energies of about 1.5 and 2.0 ev. were obtained if the second temperature was below or above 200°C respectively.

Finally, the rate of reageing studies showed that the initial rate
of resistivity increase passed through a maximum as the reversion time increased, and the resistivity of the reverted specimens at $-196^\circ\text{C}$ prior to reageing also showed a maximum with about a one percent change in resistivity that occurred after a very short time (150 milliseconds).
VIII. INTERPRETATION OF RESULTS

The various mechanisms for the enhanced solute diffusivity during the slow ageing reaction of Aluminum - Copper alloys have recently been reviewed by Herman (30). Briefly, they are:

a) the 'vacancy cluster' mechanism (14) in which an excess vacancy concentration is in equilibrium with vacancy clusters.

b) the 'GP zone' mechanism (95, 96) in which vacancies are trapped by the zones and slowly released during the slow reaction.

c) the slow reaction 'vacancy pump' mechanism (30) in which solute atom-vacancy complexes diffuse to the zone where the solute atom is retained but the vacancy is released. However, there are vacancies associated with the zone so an additional activation is required for the vacancy return, namely the binding energy between the vacancy and the zone associated vacancies.

d) the 'long range stress field' mechanism (97) in which vacancy decay is inhibited by the elastic stress field developed around the zones.

e) the 'amoeba-like zone' mechanism (98) in which mobile solute atom - vacancy clusters move through the matrix.

f) the 'surface oxide film' mechanism (98) in which vacancies are prevented from escaping or pumped back into the matrix by an oxide film.

Several authors (20, 22) have shown that only the first two mechanisms need be considered while the third has only been suggested very recently. Okamoto and Kimura (20) and Murty and Vasu (22) both concluded that the 'vacancy cluster' mechanism is to be preferred since the 'GP zone' mechanism does not predict excess vacancy lifetimes of sufficient
duration. No detailed analysis of the slow reaction 'vacancy pump'
model has been made and in view of the poor agreement between the mod-
el's predictions and experimental data for the fast reaction during
ageing (31), it is anticipated that this situation may persist when
the model is applied to the slow reaction. At this stage it is sufficient
to remark that the 'pump' concept would explain the slow reaction act-
viation energy of about 1.0 ev. and the duration of the reaction.

The 'vacancy cluster' and 'GP zone' mechanisms have also been ex-
amined in the light of recent observations of the reversion kinetics
in an Aluminum - 4 wt.pct. Copper alloy by Shimzu and Kimura (25) who
showed that the temperature dependence of the rate of change at zero time
of the resistivity increase (measured in liquid Nitrogen) gave an activa-
tion energy of 1.0 ev. while the cross-cut method in which the
temperature dependence of the time required to attain a 0.6% resis-
tivit increase was observed, gave an activation energy of 1.3 ev. This
activation energy remained the same for larger cross-cut percentages.
The shortest reversion times were .5 seconds at all temperatures, the
highest temperature being 190°C, so neither very short reversion times
nor the kinetics above the most probable GP solvus temperature of
190°C + 10°C (see Figure VIII.1) were considered. However, their results
did suggest that the 'GP zone' mechanism is inappropriate since it
predicts a constant activation energy of 1.0 ev. after the equilibrium
concentration of vacancies has been established at the reversion temp-
erature. Identical conclusions were reached for an Aluminum - 1.3 at.
pct. Silver alloy by Murty and Vasu (26).

VIII.1. The Inapplicability of the 'Vacancy Cluster' and 'GP Zone'
Mechanisms.
Figure VIII.1. The Coherent Metastable Solvus Curve as Determined By Various Investigators, for Aluminum - Copper Alloys.
The results of this investigation show in fact, that both the 'vacancy cluster' and the 'GP zone' mechanisms do not apply since on pulsing to any temperature, an initial stage should occur during which the excess vacancy concentration does not depend on the reversion temperature but only on the ageing temperature. Hence this stage will have an activation energy of about 0.5 ev. corresponding to copper atom diffusion in an excess vacancy concentration. However, an extensive fast reaction was only observed above 200°C with perhaps a trace of one below this temperature and there is no obvious modification that could be made to either mechanisms to produce this dramatic discontinuity at 200°C.

Secondly, the fast reversion reaction above 200°C was shown to involve the diffusion controlled dissolution of zones with an activation energy of 0.64 ev. for solute diffusion and this process lasts for 120 msecs. at 206°C and 80 msecs. at 250°C. The 'vacancy cluster' mechanism predicts that the time required for a vacancy to be emitted from a cluster, \( t_{em}^{vc} \), is given approximately by;

\[
t_{em}^{vc} = \frac{1}{\nu} \cdot \exp\left(\frac{E_f + E_m - \Delta E}{kT}\right)
\]

while that for the 'GP zone' mechanism, \( t_{em}^{gp} \), is:

\[
t_{em}^{gp} = \frac{1}{\nu} \cdot \exp\left(\frac{E_f + E_m - E_{bz}}{kT}\right)
\]

where \( E_f \) is the formation energy of a vacancy, \( E_m \) is its migration energy, \( \Delta E \) is the increase in energy of a vacancy in equilibrium with a small dislocation loop and \( E_{bz} \) is the binding energy of a vacancy to a zone. \( \nu \) is the vacancy vibration frequency and is assumed to be the Debye
frequency. Other investigators apparently set \( v = 10^{14} \) which is ten times greater than the more normal value \((100)\). For \( v = 10^{13} \) we have:

\[
\begin{array}{cc}
206^\circ C & 250^\circ C \\
t_{vc}^{em} \text{ msecs.} & 40 & 4 \\
t_{gp}^{em} \text{ msecs.} & .3 & .05 \\
\end{array}
\]

where \( E_f = 0.76 \pm 0.02 \text{ ev.} \) \((86)\), \( E_m = 0.5 \pm 0.04 \text{ ev.} \) \((20)\), \( E = 0.3 \text{ ev.} \) \((20)\) and \( E_{bz} = 0.5 \text{ ev.} \), this being the difference between the activation energies for the fast and slow ageing reaction. Experimental values for the fast ageing reaction activation energy are:

- \( 0.47 \pm 0.05 \text{ ev.} \) Kimura et al \((19)\)
- \( 0.47 \pm 0.03 \text{ ev.} \) Okamoto and Kimura \((20)\)
- \( 0.51 \pm 0.03 \text{ ev.} \) DeSorbo et al \((18)\)
- \( 0.51 \pm 0.05 \text{ ev.} \) Turnbull et al \((14)\)
- \( 0.53 \pm 0.02 \text{ ev.} \) Leroy \((21)\)

while for the slow ageing reaction we have:

- \( 1.0 \pm 0.05 \text{ ev.} \) Okamoto and Kimura \((20)\)
- \( 1.0 \pm 0.04 \text{ ev.} \) Turnbull and Cormia \((23)\)

The 'GP zone' vacancy emission time is seen to be one hundred times less than the fast reversion reaction linear log \( x_f \) stage time, \( t_{1s} \), (for the diffusion controlled dissolution of zones). However \( t_{vc}^{em} \), the 'vacancy cluster' vacancy emission time is only a factor of ten times smaller so this mechanism cannot be ruled out, since appreciable loop coarsening could occur within \( t_{1s} \) and the slow reversion reaction could correspond to the second stage predicted by the 'vacancy cluster' mechanism. On the other hand, if Shimzu and Kimura's value of \( 10^{14} \) is used for the vibration frequency the 'vacancy cluster' mechanism can be discounted.
The results of the double pulse heating experiments also reveal a third discrepancy between the experimental observations and the predictions of the 'vacancy cluster' and the 'GP zone' mechanisms. It was shown that an apparent activation energy of 2 ev. resulted if the first pulse temperature was less than 200°C and that of the second pulse was greater than 200°C while an energy of about 1.5 ev. was given if the second pulse temperature was also less than 200°C. It was suggested that the high apparent activation energy occurred because the fast reaction was initiated above 200°C even after short heat treatments below 200°C. Any mechanism that invokes an excess matrix vacancy concentration in equilibrium with a discontinuity, whether it be a vacancy aggregate, a GP zone or a large dislocation loop with microscopic regions of high local curvature (89), must predict an initial stage during which the vacancy concentration is independent of the reversion temperature and therefore, a 'slope change' activation energy that is independent of the first and second pulse temperatures provided the second pulse is applied before the vacancy equilibration time at the second temperature, as was the case referred to in the double pulse experiments mentioned above.

VIII.2. Interpretation of Reversion Kinetics based on the Slow Reaction 'Vacancy Pump' Model.

VIII.2.1. Formulation of the Model.

The assumptions made by Girifalco and Herman (29) in the original formulation of the 'vacancy pump' model are:

a) most solute atoms exist as vacancy-solute complexes.

b) small binding energy between a vacancy and a solute atom in a zone.
c) small interaction energy between a zone and a vacancy and a zone and a complex.

d) complex diffusion appreciably faster than solute atom diffusion.

Herman (30) recently suggested that the third assumption may only apply at short ageing times and that vacancies may become clustered in the vicinity of more mature zones. Hence the operation of the pump would require an additional activation energy namely \( E_a \), the interaction energy between a vacancy and the vacancies associated with the zones. The clustering of vacancies near zones has been proposed by Herman (101) for the high rates of reversion in Aluminum - Copper alloys; by Berry (33) for the internal friction characteristics of complex, pseudo-binary, aged Aluminum-base alloys; by Cohen et al (32) for the electromicroscopic evidence after reversion of dislocation loops at the prior locations of zones in aged Gold - Nickel and Aluminum - Zinc alloys.

It is now proposed that the first assumption may also not apply when the reversion of a well aged Aluminum - Copper alloy is being considered since a large number of vacancies may be released by the zones and only a fraction of these vacancies will form solute atom-vacancy complexes. Moreover, the migration energy of these complexes will not include the additional activation energy \( E_a \).

Subsequently, a local equilibrium will be attained between the vacancies associated with the zone and the matrix vacancies near the zone. Thenceforth, dissolution of the zones by the diffusion of complexes will require the additional activation energy and effectively there has been a change-over from diffusion controlled to interface reaction controlled dissolution, with activation energies of \( (E'_m - E_{bv}) \) and \( (E'_m - E_{bv} + E_a) \) respectively. (The complex migration energy is \( E'_m \) and the solute atom
-vacancy binding energy).

At longer reversion times the zones will have dissolved to such an extent that they no longer have vacancies associated with them so there will be no vacancies available for release nor associated vacancies restraining the escape of complexes into the matrix. The activation energy for reversion in this final stage should be the activation energy for solute diffusion in an equilibrium concentration of vacancies, namely 

\[(E_f + E_m' - E_{bv})\] where \(E_f\) is the vacancy formation energy (102).

VIII.2.2 Comparison of Predicted and Experimentally Determined Activation Energies.

The diffusion of Copper in Aluminum requires an activation energy 

\[E_f + E_m' - E_{bv} = 1.30 \pm 0.03 \text{ ev. (103)}\]

where the vacancy formation energy \(E_f\) is \(0.76 \pm 0.02 \text{ ev. (86)}\). Values for the binding energy \(E_{bv}\) have recently been reviewed by King and Burke (94) who suggest that values above 0.15 ev. should be discarded in agreement with recent measurements made by Miraille et al (104) who give a value of \(0.16 \pm 0.04 \text{ ev.}\). According to the slow reaction 'vacancy pump' model, the additional activation energy \(E_a\), is the difference between the fast and slow ageing reaction activation energies which have been tabulated above. An energy of 0.5 ev. would therefore be reasonable. Herman (30) suggests that \(E_a\) should be similar in magnitude to the divacancy binding energy which Damask and Dienes (105) give to be between 0.1 and 0.6 ev.

According to the model proposed for reversion, the initial rate of resistivity change should reflect the activation energy for a solute atom to jump into an adjacent vacancy. Fortuitously or otherwise, this is the case since an energy of \(0.48 \pm 0.06 \text{ ev.}\) is obtained, in agreement with the predicted value of 0.5 ev. However, it has been shown that the
initial stages of the fast reversion reaction involve the diffusion controlled dissolution of zones with a solute migration energy of 0.63 ± 0.04 ev. and that the initial transient, non-linear log rate of resistivity decay stage is not observed, in agreement with the theoretically predicted times that are considerably shorter than the resolution limit of the pulse heater (0.5 msec.). Hence the initial rate of change probably gives an apparent activation energy.

The discrepancy between the values for solute diffusion during the fast ageing and reversion reactions (0.5 and 0.6 ev. respectively) may possibly be due to a complex-zone interaction energy that is required during reversion, when the complexes are diffusing away from the zone, but not during ageing, when complexes move to the zones. Alternatively, this complex-zone interaction energy increases the matrix concentration by an amount δc₁. Now a general parameter that describes the interplay of the interface, precipitate and initial matrix concentrations (cᵢ, cₓ, and cₘ respectively) during dissolution or growth under diffusion control is K, the ratio of concentrations defined by:

\[ K = \frac{cᵢ - cₘ}{cₓ - cᵢ} \]

The change in K, δK, for a change in cᵢ of δcᵢ is simply:

\[ δK = \frac{(cₓ - cᵢ) \cdot δcᵢ}{(cₓ - cᵢ) \cdot (cᵢ - cₘ)} \]

During growth cᵢ/cₘ is small while during dissolution cₘ/cᵢ is small. Hence on expanding the expression for δK in terms of cᵢ/cₘ and cₘ/cᵢ we have:

\[ δK_{\text{growth}} \propto \frac{δcᵢ}{cₘ}^2 \quad \text{and} \quad δK_{\text{diss}} \propto \frac{δcᵢ}{cᵢ}^2 \]
The initial concentrations for growth and dissolution are .02 (the alloy composition) and .005 (85) so the effect of a small change in $c_i$ is very pronounced for dissolution but this is not the case for growth.

The second stage of reversion when a local equilibrium between the matrix vacancies and the remaining zone associated vacancies is achieved, should have an activation energy for reversion equal to that for the slow ageing reaction. This has been confirmed by the results of this investigation and those of Shimizu and Kimura (25). Finally, Shimzu and Kimura have also observed the third predicted stage with an activation energy of 1.3 ev.

**VIII.2.3. Completion Time of the Fast Reaction Fraction.**

The time to completion of the fast reaction gave an activation energy of $0.80 \pm 0.04$ ev. Assuming that vacancies and complexes diffuse at approximately equal rates, then if the cessation of the fast reaction corresponded to the decay of excess vacancies to a certain concentration, an activation energy of between 0.5 and 0.6 ev. should be given by the completion time. Moreover, the cessation of the fast reversion reaction does not correspond to the attainment of a certain zone size because the fraction of the total resistance change caused by the fast reaction decreases strongly with temperature (Figure VIII.2).

The proposed model predicts that neither possibility should occur since a temperature dependent fraction of the released vacancies will form complexes and both complexes and single vacancies diffuse equally rapidly into the matrix. Cessation of the fast reaction occurs when a local equilibrium is established between the remaining zone-associated vacancies and the matrix vacancies near the zone. This equilibrium will be a function of the zone size and therefore of the number of solute atoms that have diffused away as complexes and thus the complet-
ion time should be proportional to the complex mobility and the fraction of released vacancies that exist as complexes which will be given approximately by the solute atom-vacancy binding energy $E_{bv}$. Hence the completion time should give the sum of the complex mobility and the binding energy $(R'_m + E_{bv})$ which is $0.63 + 0.15 = 0.78$ ev. and agrees with the experimentally determined value.

VIII.2.4. The Absence of the Fast Reversion Reaction Below 200°C.

As has been previously remarked, there is some evidence of an initial fast reaction below 200°C but it only lasts for 10 to 20 msecs. as opposed to 400 msecs. at 206°C. Moreover, the fraction of the total resistance decay caused by this stage is only about .01. Estimates of the initial rate of resistivity decay below 200°C indicate that the extrapolation of the initial rate from temperatures above 200°C to temperatures below 200°C was possible, as is shown in Figure VIII.2 where several experimental points are seen to lie on the lower limit of the initial rate of resistivity decrease.

According to the model proposed for reversion, the absence of an extensive fast reaction implies the release of a few vacancies and this would be the case if only an adjustment between the matrix and zone associated vacancies occurred. If however, significant numbers of the associated vacancies were released then a pronounced fast reaction would result and the critical temperature at 200°C may be due to the destabilization of zones above this temperature. This catastrophic destabilization over a small temperature range further implies the existence of a large number of uniform, stabilized zones in a well aged Aluminum - 3.85 wt. pct. Copper alloy. Figure VIII.3 gives most of the published zone size data for various ageing treatments and the treatment used in this
Figure VIII.2. Extrapolation of the Initial Rate of Resistivity Change to Temperatures Below 200°C. Dashed curve is the initial rate for the fast reaction fraction; solid lines are given if the temperature dependence of the fast reaction fraction is included.
Figure VIII.3. Variation of GP Zone Size with Ageing Time for Al=4wt.pct.Cu.

Source Ref.
- Silcock et al 65
- Kawano " 105
- Nicholson et al 106
- Parsons " 107

Ageing temperatures are indicated in °C.

Ageing time, mins.

Zone radius, Å

- 130
- 110
- 90
- 70
- 50
- 30
- 10

- 10^1
- 10^2
- 10^3
- 10^4
investigation (1000 mins. at 70°C) is about five times shorter than the
time required to attain the hardness plateau during which Silcock et al
(65) have shown the zone size to be unchanging. Thus it cannot be stated
that there is a large number of zones of a constant and unchanging size
in the as-aged alloy, that may result from the stabilization of zones
by associated vacancies. However, this stage has almost been reached.

VIII.3. Reageing after Reversion Treatments above 200°C.

In view of the complexities of the proposed mechanisms for reversion
& the likelihood that plastic strains are present on quenching, it is
impossible at this stage to use the reageing characteristics of part-
ially reverted alloys to distinguish between the alternative proposals.
In particular, the maximum initial rate of reageing at intermediate
reversion times cannot definitely ascribed to a certain kinetic process.
It is however, reasonable to suggest that the plastic deformations are
reproducible because long time reversion treatments at 205°C and 250°C
gave the same initial rate of resistivity increase and hence the maximum
rate is caused by a second effect superimposed upon the effects of
plastic deformation. If this is the case then the reageing behaviour
after intermediate reversion treatments implies an enhanced solute
diffusivity which is predicted by the 'vacancy pump' mechanism since the
second stage, corresponding to an intermediate reversion treatment,
involves interface reaction controlled dissolution with a local equil-
ibrium between matrix and zone associated vacancies near the zones and an
excess vacancy concentration in the bulk of the matrix. Upon reageing,
a rapid initial reaction would therefore be anticipated.

VIII.4. The Origin of Specimen Strains during Pulse Heating and
Quenching.
It is worthwhile to consider the origins of specimen strains because they undoubtedly affect the property measurements made at low temperatures following reversion treatments. Upon pulse heating, strains are caused by the following:

a) the 'pinch effect' of a high electric current $i$, passing through the specimen (110). The pressure $p$, at the center of a solid cylinder of radius $R_c$, resistivity $\rho_c$ and bulk modulus $\mu$ is:

$$p = \frac{\mu i^2}{4\pi^2 R_c^2}$$

and typically gives 1000 p.s.i. at the cylinder axis. This should not give extensive plastic deformation.

b) the differential heating of the specimen produced by the 'skin effect' in which a higher current passes through the surface layers (111). By ensuring that the specimen thickness is significantly less than the skin depth, uniform heating results.

c) the forces produced by the interaction of the specimen current with the magnetic fields of the earth and the leads to the specimen (36). These forces can be made to cancel each other by positioning the specimen correctly.

d) the constraint of the specimen mountings. If rigid mounts were used the thermal expansion of about 1% for Aluminum alloys pulsed 200°C would produce significant plastic deformation.

Upon quenching, strains are developed by the following:

a) the hydrodynamic forces of the quenching fluid. Jackson (112) shows that these forces typically produce strains of 0.1%.

b) the differential cooling of the specimen. Jackson has shown that this effect rarely produces strains exceeding $10^{-3}$%. 

c) the specimen mounting constraint. This prevents the stress-free contraction of the specimen.

The mounting constraint appears to be the most severe problem and the use of 200 gm., but non-rigid mounting blocks did not remove the effect. A possible solution may involve a vertical wire specimen suspended from a rigid clamp with the other end immersed in a liquid or powder conductor, the former preferably having a low melting point. This would permit the specimen to expand and contract freely of a large temperature range. Moreover, if pre-cooled Helium gas quenching and subsequent rapid immersion in liquid Nitrogen was used, a stress-free quench to low temperatures may be achieved.
IX. SUMMARY AND CONCLUSIONS

The reversion kinetics of pre-precipitates in a classic age-hardening alloy system were investigated by using pulse heating techniques and a very sensitive specimen resistivity measuring apparatus. The time and temperature dependencies of the activation energy for reversion were investigated by comparing the isothermal resistivity changes occurring during reversion with the predictions of dissolution theories, and by the change of slope method in which an effectively instantaneous temperature rise to the second reversion temperature was achieved by using the pulse heater.

An extensive early time diffusion controlled dissolution of zones with an activation energy of 0.63 ev. for solute diffusion, only took place at reversion temperatures above 200°C. This 'fast' reaction was followed by a 'slow reaction' with an activation energy of 1.0 ev. The maximum time investigated being about 4 seconds. The change of slope method proved to be a very reliable and convenient technique for distinguishing the various kinetic stages.

The results obtained were shown to disagree with the predictions of the currently accepted 'vacancy cluster' model for reversion in which an excess concentration of vacancies is in equilibrium with a small, as yet unobserved, dislocation loop or void. This model predicts three stages with activation energies for solute diffusion of 0.5, 1.0 and 1.3 ev. in Aluminum - 4 wt.pct. Copper. The first stage corresponds to an initial excess vacancy concentration that is independent of the reversion temperature. This is followed by a period of time when the vacancies equilibrate with the vacancy clusters at the high, rev-
erion temperature. However, the clusters coarsen rapidly so the excess equilibrium vacancy concentration they can maintain decreases until the thermal equilibrium concentration exists. The 1.0 ev. stage therefore corresponds to the stage when the vacancy clusters have not coarsened appreciably while the 1.3 ev. stage results when solute diffusion occurs in the thermal equilibrium vacancy concentration achieved at long reversion times.

An alternative mechanism based on the slow ageing reaction 'vacancy pump' model was proposed, in which vacancies and solute atom-vacancy complexes are released from the zones and until a local equilibrium is established between the remaining zone associated vacancies and the matrix vacancies, rapid complex diffusion with an activation energy of 0.63 ev. can occur. Once local equilibrium is achieved, subsequent dissolution by complex migration requires an additional activation energy to overcome the interaction between the vacancy in the complex and the remaining zone associated vacancies. Hence an energy equal to the activation energy for the slow ageing reaction results. Finally, at small zone sizes, most of the zone associated vacancies will have been released so there are no vacancies available for complex formation and the 1.3 ev., thermal equilibrium vacancy concentration stage is predicted.

The onset of the extensive fast reaction above 200°C was attributed to a catastrophic destabilisation of the GP zones above this temperature. It was shown that a few vacancies were probably released below 200°C corresponding to a readjustment of the equilibrium between the zone associated vacancies and matrix vacancies near the zones. Above 200°C however, readjustment and the release of the associated vacancies would
ensure that many vacancies were available for complex formation and both complexes and single vacancies would diffuse into the matrix.

It was therefore concluded that the zones in an Aluminum - 3.85 wt. pct. Copper alloy are probably stabilised by vacancies and the results of this investigation may represent the first direct evidence for this effect.

Attempts to characterize further the kinetic features of reversion through low temperature resistivity measurements and subsequent reaging treatments on partially reverted specimens, were distorted by the effects of plastic deformation during the pulse heating and quenching cycle. This is probably also the case when conventional heat treatment techniques are used so the low temperature resistivity measurements reported by other investigators should be scrutinised carefully.

Methods for overcoming the problem were outlined.

Finally, a simple and accurate perturbation solution for the time dependence of the interface position for spherical precipitates dissolving in a finite matrix was derived and this solution should be used instead of the more complex stationary interface solution which has been preferred to date. In the course of the investigation however, it became apparent that extensive diffusion field interaction for the dissolving GP zones was likely so the perturbation method was not developed any further. Attempts to formulate a reasonable perturbation solution for precipitates dissolving in a finite matrix were unsuccessful so a finite difference method was developed that enabled the dissolution (and growth from non-zero dimensions) of spherically symmetric precipitates to be handled. Unfortunately the volume fraction of pre-precipitates is very low and their eccentricity very pronounced
so that predicting their dissolution kinetics required considerable computation. However, it could be concluded that the linear logarithm of the rate of change of the average matrix concentration with time behaviour that is predicted by existing analytical theories for dissolution in a finite matrix, may not occur when a precipitate of high volume fraction and pronounced eccentricity is dissolving by diffusion control.

For the limiting case of a spherical precipitate the numerical method developed gave stable and accurate results and since the computational procedure is relatively simple when compared to existing finite difference implementations for predicting dissolution kinetics, it is suggested that this new technique should be preferred.
X. SUGGESTIONS FOR FUTURE WORK

i) The extensive application of Pulse Heating techniques to the study of reversion of alloys subjected to a variety of heat treatments prior to reversion, should illuminate further, ageing and reversion mechanisms. Double pulse heating methods are also particularly sensitive.

ii) The proposed association of vacancies with zones is analogous to the recent computer results showing the association of vacancies with coherent Cobalt precipitates in Copper (34). The coherency loss of these precipitates has also been shown to occur with an activation energy that is appreciably smaller than the activation energy for solute diffusion (114), suggesting that an excess vacancy concentration is present at the interface. The early time dissolution kinetics of these precipitates would be directly related to this excess vacancy concentration and it is therefore suggested that relationship between the dissolution kinetics and the coherency loss of coherent precipitates should be investigated using pulse heating methods.

iii) The defect structure of pre-precipitates may also determine the morphology of subsequent, more stable precipitates and for example, the opposing views (84,113) regarding the relationship of GP zones to \( \Theta' \) precipitates in Aluminum - Copper alloys may be reconciled.

iv) The perturbation and finite difference solutions developed for the dissolution of precipitates should be extended. In particular, non-uniform precipitate arrays could be treated by considering the finite difference method in spheroidal co-ordinates.
APPENDIX A

Description of the Pulse Heater; Circuit and Components.

A diagram describing the pulse heater is given in Figure A.1 where the circuit for the capacitor banks, specimen and DC heat assemblies are correct while the subsidiary circuitry is schematic. It is convenient to discuss separately the six sub-assemblies that make up the pulse heater.

A.1. Power Supplies.

The power supplies for both capacitor banks are identical in all respects and consist of variable step-down transformers that permit very fine voltage adjustments, in series with two power packs that rectify and step-up the applied AC input. Two switches must be operated to charge up the capacitors: one cuts out short circuiting resistors across the capacitor terminals and must be held down at all times during the pulse heat treatment. The other switch causes a 115 VAC signal to be applied to the transformers.

After the charging current has decayed to a certain value, a current limiting resistor is switched out of the circuit and the capacitors are considered to be fully charged when the current falls to some low value. It would however be preferable to monitor the high voltage across the capacitors and perhaps incorporate a feedback circuit so that a preset high voltage could be maintained since it was found that significant short time line voltage variations occurred so repeatable pulsing to certain temperature was difficult to achieve. In general, using the relatively simple procedure of observing the applied AC voltage just before each pulse, the temperature rise could be predicted to within 5°C.
Figure A.1: Capacitor Discharge Pulse Heater Assembly Diagram.

- Assembly number.
- Relay Coil.
- Timer.
- Latching Circuit.
- Ignition Coil.
- Relay Contacts.
- Switch.

The diagram includes various components and connections such as a firing switch, valve, bypass, and 6V and 12V specifications.
A.2. Capacitor Bank and Discharge Assembly.

Coaxial cables from the power supplies led to the capacitor banks which were housed in a steel cabinet under the specimen mounting chamber. Two spark-gap triggers in parallel discharged the capacitors. The spark-gaps were round tipped Tungsten rods in adjustable mountings and a spark was initiated with an automotive high voltage ignition coil. Heavy copper braid led from the banks to the specimen mounts and one of these mounts was earthed and in fact, served as the common earth for the entire apparatus to avoid ground loops. The braid leads were twisted a few times to minimise noise pick-up and to change the inductance of the discharge circuit and thereby alter the time constant of the capacitor voltage decay. However, this constant refers to the envelope of the rapidly cycling and decaying voltage ("ringing") and since the spark-gap ceases to pass the current when the voltage has fallen to a given value, only a few cycles will occur so adjustment of the envelope time constant is not important.

A.3. Specimen and DC Heating Current Assembly.

During the capacitor charging cycle, the DC heating current was initiated by latching a relay and the current was regulated with a bank of heavy duty resistors. No attempt was made to have a feedback loop so that specimen temperature changes would cause compensating current changes, because these systems are only stable after a few tens of seconds. Also it was felt that considerable noise pick-up would occur.

A shorting resistor permitted low currents to be effected and a current reversing relay was incorporated. These were required for the Kelvin Double Bridge and Three-wire thermocouple balancing procedures. A 12V Lead-acid accumulator supplied typical DC currents of between 10
to 20 Amperes. Initial fears that a line voltage operated, constant current generator would produce excessive noise may be unfounded. The resistor bank and accumulator were housed in another steel cabinet under the specimen and twisted 20 Gauge coaxial cables led to the specimen. The firing switched closed a by-pass relay so that the current, previously initiated, was routed through the specimen.


Attached to the by-pass relay was an adjustable microswitch which caused a relay to open. The relay's contacts acted as a pair of points for the first capacitor bank spark-gap trigger and careful adjustment ensured that the by-pass relay contacts had ceased bouncing before the spark was initiated. This was about 30 milliseconds after the by-pass relay had closed and in this time the specimen only heated up by about 10 Degrees Centigrade.

The firing switch also started an electronic timer which closed a relay whose contacts acted as points for the second spark.

A.5. Quench Control.

A quench valve that released compressed air at 30p.s.i. was activated by a second timer that was started by the firing switch. The air served to pressurize a flexible bottle that contained the quenching fluid in a multiple quench nozzle arrangement or simply to expel water, back filled to the valve, out of a 1/4 inch diameter tube in a single nozzle arrangement.


The DC heating current switch that caused pre-initiation of the current latched a relay so that the quench timer could terminate the DC current by unlatching the same relay.
APPENDIX B

Common Mode Rejection (CMR) Derivations.

The CMR of a voltage measuring device is equal to the ratio of \( V_{cm} \), the potential that exists equally on both inputs and between these inputs and ground, to the equivalent differential input that it produces, \( V_{eq} \). Hence:

\[
CMR = \frac{V_{cm}}{V_{eq}}
\]

B.1. Two-wire Thermocouple.

Following Mayhead (115), an amplifier in series with a two-wire thermocouple is equivalent to a Wheatstone Bridge. If the amplifier is assumed to be balanced then we have the circuit given in Figure B.1. For a Wheatstone Bridge:

\[
V_{eq} = V_{cm} \left( \frac{R_1}{R_1 + R_3} + \frac{R_2}{R_2 + R_4} \right)
\]

where \( R_1 \) and \( R_2 \) are the lead resistances from the amplifier to the thermocouple junction and \( R_3 \) and \( R_4 \) are the amplifier input resistances. For the balanced differential isolated amplifiers typical used in most oscilloscopes; \( R_3, R_4 \gg R_1, R_2 \) and \( R_3 = R_4 = R_a \) so:

\[
CMR (2\text{-wire}) = \frac{R_a}{R_1 - R_2}
\]

B.2. Three-wire Thermocouple.

A schematic diagram in Figure B.2 shows a three wire thermocouple in series with an amplifier and it illustrates the double earthing problem since both the specimen and the amplifier will be earthed. The circuit for a balanced differential amplifier is given in Figure B.3 and following a Wye-Delta transformation the considerably simplified cir-
Figure B.1. A Two-wire Thermocouple in Series with an Amplifier.

Figure B.2. A Three-wire Thermocouple in Series with an Amplifier, Showing the Double Earthing Problem.
Figure B.3. Circuit for a Three-wire Thermocouple in Series with an Amplifier.

Figure B.4. Partial Circuit Diagram following a Wye-Delta Transformation.
cuit of Figure B.4 results and \( V_{eq} \) is now given by:

\[
V_{eq} = V_{cm} \cdot \left( \frac{R_1 + R_p}{R_1 + R_p + R_3} - \frac{R_2 + R_q}{R_2 + R_q + R_4} \right)
\]

where: \( R_p = R_6 \cdot (R_7 + R_5)/R_s \) and \( R_q = R_8 \cdot (R_7 + R_5)/R_s \)

with \( R_s = R_5 + R_6 + R_7 + R_8 \)

As for the two-wire case, a balanced isolated differential amplifier is used so the CMR becomes:

\[
CMR = \frac{R_a}{(R_1 + R_p) - (R_2 + R_q)} = \frac{R_a}{R_1 - R_2 + (R_5 + R_7)(R_6 - R_8)/R_s}
\]

For \( R_5, R_6 \gg R_7, R_8 \):

\[
CMR = \frac{R_a}{R_1 - R_2 + \frac{R_5(R_6 - R_8)}{R_5 + R_6}} \quad (B.1)
\]

However, the bridge is balanced to compensate for the DC current's superimposed voltage due to the finite spacing of the probes that are spot-welded to the specimen. Hence \( R_5/R_6 = R_7/R_8 = h \) and thus:

\[
CMR = \frac{R_a}{R_1 - R_2 + \frac{h(R_6 - R_8)}{h + 1}} \quad (B.2)
\]

It is only necessary to adjust the bridge so that the two terms in the denominator are of the same order of magnitude so:

\[
\frac{h(R_6 - R_8)}{h + 1} = R_1 - R_2 \quad (B.3)
\]

If the Peltier Effect at the probe/specimen interface is to be small the bridge current must be low and thus:
or, since the bridge is balanced:

\[(h + 1)(R_7 - R_8) \gg 0\]  \hspace{1cm} (B.4)

and the noise criterion B.2 becomes:

\[
\frac{(h + 1)^2(R_1 - R_2)}{h} \gg 0
\]

Now, the thermocouple probes are positioned \(w\) ohms apart with an error of \(\frac{\Delta w}{w}\) and hence \(h\) varies between \((1 + 2.\Delta w/w)\) and \((1 - 2.\Delta w/w)\).

The worst possible case would be for the former value so:

\[
2.(1 + \frac{\Delta w}{w}).(R_1 - R_2) \gg 0
\]

or:

\[
2.(1 - \frac{\Delta w}{w}).(R_1 - R_2) \gg 0
\]

We conclude that the Peltier Effect restriction implies that a large lead resistance imbalance can be tolerated since from Equation B.5, \((R_1 - R_2)\) can be 550 Ohms for a 10% positioning error and yet the CMR will only be halved.

Alternatively, substituting for \(h\) in Equation B.3, gives for the worst case:

\[
\frac{R_a}{R_1 - R_2 + (1 - \frac{\Delta w}{w}).(R_6 - R_8)}
\]

\[
= \frac{R_a}{R_1 - R_2 + (1 - \frac{\Delta w}{w}).(R_6 - R_8)/2}
\]

where second order terms have been ignored. The Peltier Effect criterion gives:

\[
2.(1 - \frac{\Delta w}{w}).(R_6 - R_8) \gg 0
\]
and on comparing Equations B.6 and B.7 it is seen that the modified Peltier Effect Criterion, B.7, will hold only if the CMR is reduced severely.


The Kelvin Double Bridge circuit with the output fed into an isolated balanced differential amplifier is shown in Figure B.5. Once again, since the specimen and the amplifier are both earthed, ground loops can occur.

Two Delta-Wye transformations can be applied and the circuit shown in Figure B.6 results where:

\[ p_a = \frac{R_2 R_x}{R_t}, \quad p_b = \frac{R_x R_2}{R_t}, \quad p_c = \frac{R_2 (1+\beta)}{R_t} \]

\[ q_a = \frac{R_1 R_0}{R_t}, \quad q_b = \frac{R_0 R_1 (1+\alpha)}{R_t}, \quad q_c = \frac{R_2 (1+\alpha)}{R_t} \]

where: \( R''_t = R_o + R_1 (2+\alpha) \)

\[ R'_t = R_x + R_2 (2+\beta) \]

Yet another Delta-Wye transformation can be applied to give the circuit shown in Figure B.7 where:

\[ x = \frac{(q_a + R_s) (p_b + q_b) / R''_t}{R'''_t}, \quad y = \frac{p_a (p_b + q_b) / R'}{R'''_t} \]

\[ z = \frac{p_a (q_a + R_s) / R''}{R'''_t} \]

where: \( R'''_t = R_s + p_a + p_b + q_a + q_b \)

A simple application of Kirchoff's Law gives:

\[ V_{eq} = \frac{-V_{cm a} (R_3 + q_c + x - R_3 [1+\epsilon] - p_c - y) / [(2R_a + x + y + p_c + q_c + R_3 [2+\epsilon])z]}{R_2 + q_a + x} \cdot (R_3 + q_a + R_1 + x) \cdot (R_3 [1+\epsilon] + p_c + R_a + y) \]

Since:

\[ R_a >> R_3 >> R_2 = R_1 >> R_o > R_s > R_x \]

the only term of significance is an \( R_a^2 \) term in the numerator, and on expansion we have:
Figure B.5. A Kelvin Double Bridge in Series with an Amplifier, Showing the Double Earthing Problem.

Figure B.6. A Kelvin Double Bridge in Series with an Amplifier; Circuit following two Delta-Wye Transformations.
Figure B.7. Circuit of Figure B.6. following a Delta-Wye Transformation.
CMR = \frac{R_a}{(q_c-p_c-R_3+q_a-p_a+R_s)[p_b+q_b]/[R_s+p_a+p_b+q_a+q_b]}

Now: \quad q_a = \frac{R_1 R_o}{(R_o + 2R_1)[1 + R_1/(R_o + 2R_1)]}

and so by the Binomial Theorem:

\[ q_a = \frac{R_1 R_o}{R_o + 2R_1} \cdot (1 - \frac{R_1}{R_o + 2R_1}) = \frac{R_o}{2} \cdot \left(1 - \frac{\alpha}{2}\right) \]

with similar expressions for the other terms. Thus:

\[ CMR = \frac{2R_a}{R_1(1-\alpha/2) - R_2(1-\beta/2) - 2\epsilon R_3 + \frac{q_a-p_a+R_s}{2R_s} + \frac{1}{p_a+q_a}} \]

The last term in the denominator is very small so we have:

\[ CMR = \frac{R_a}{R_1(1-\alpha/2) - R_2(1-\beta/2) - 2\epsilon R_3} \]

It is convenient to write \( R_2 = R_1(1+\gamma) \) and thus

\[ CMR \text{ (Kelvin Double Bridge)} = \frac{R_a}{\frac{R_1}{2} \left(\frac{[\alpha-\beta]}{2} + \gamma\right) + R_3 \epsilon} \]

This expression is equivalent to that for the two- and three-wire thermocouples except for the additional term in the denominator.

Summarising, the CMR's for two configurations that to date have not been derived, show that the lead resistance imbalance is always of crucial importance (unless Peltier Effect minimization in a 3-wire thermocouple is desired) and that Kelvin Bridge parameters must be chosen with some care.
Kelvin Double Bridge Output Characteristics.

In deciding upon suitable Kelvin Double Bridge parameters both the accuracy and the sensitivity of the bridge must be examined. In this Appendix the appropriate expressions describing these quantities will be derived.

The bridge configuration of Figure 11.2 will be assumed where \( V_1 \) and \( V_2 \) are the applied and output voltages, \( R \) is the link resistance, \( R_s \) the standard resistance. The specimen resistance is \( R_x = R_s (1+\delta) \) while the ratio arm resistances are \( R_1, R_2 = R_1 (1+\alpha), S_1 = R_1 (1+\gamma) \), and \( S_2 = R_1 (1+\beta)(1+\gamma) \). In general the bridge will give a zero output voltage at some finite value of \( \delta \), called \( \delta_0 \), and subsequent changes in the output voltage will be ascribed to a change in \( \delta \), called \( \delta_x \). Hence:

\[
\delta = \delta_0 + \delta_x
\]

and the problem is to determine the error in \( \delta_x \) if it is assumed that the output voltage is proportional to \( \delta_x \). Figure 11.3 depicts the problem and the quantity of interest is the fractional error in \( \delta_x \), \( \Delta \delta_x/\delta_x \).

The bridge sensitivity is given by the magnitude of the constant of proportionality relating \( \delta_x \) and the output.

C.1. Output Voltage.

Since the measuring instrument, in this case an oscilloscope, draws no current, the Figure 11.2 circuit can be simplified to that of Figure C.1. The total resistance in series with the applied voltage then becomes:

\[
\frac{1}{R_t} = \frac{1}{R_1 + R_2} = \frac{1}{R_s + R_x + (S_1 + S_2)R_x} \frac{R_x}{R_x + S_1 + S_2}
\]
and the external current becomes:
\[ i = \frac{V_1}{R_t} \]

Now: \[ i_1 = \frac{V_1}{(R_1 + R_2)} \] so we have:
\[ i - i_1 = \frac{V_1(S_1 + S_2 + R_\lambda)}{(R_s + R_x)(S_1 + S_2 + R_\lambda) + (S_1 + S_2)R_\lambda} \]

while Kirchoff's Law gives:
\[ i_2 = \frac{V_1 R_\lambda}{(R_s + R_x)(S_1 + S_2 + R_\lambda) + (S_1 + S_2)R_\lambda} \]

Finally:
\[ V_2 = R_1 i_1 - (i - i_1)R_s - i_2 S_2 \]

so that upon substituting for the currents and using the definitions of the resistances in terms of \( R_1 \) and \( R_s \), we have:
\[ V_2 = \frac{R_\lambda R_1 (\alpha - \beta) + R_\lambda R_1[1+\gamma][2+\beta]R_\lambda R_s (\delta - \alpha)}{R_s (2+\delta)(R_\lambda R_1[1+\gamma][2+\beta] + R_\lambda R_1[1+\gamma][2+\beta])} \]  \( \text{(C.1)} \)

C.2. Fractional Error in \( \delta_x \)

The various terms in Equation C.1 will be written as:
\[ R_\lambda' = \frac{R_\lambda}{R_1 (1+\gamma)(2+\beta)} \]
\[ R_\lambda\alpha = \frac{(\alpha - \beta)R_\lambda}{(2+\beta)(1+\gamma)} \]
\[ R_\lambda'' = (R_\lambda' + 1)R_s \]
\[ V_1' = \frac{V_1}{2 + \alpha} \]

Recognizing that \( \delta = \delta_o + \delta_x \) then:
\[ V_2 = V_1' \cdot \frac{R_\lambda\alpha + R_\lambda'' (\delta_o - \alpha + \delta_x)}{(R_\lambda + R_\lambda''[2+\delta_o])(1 + \frac{R_\lambda''\delta_x}{R_\lambda + R_\lambda''[2+\delta_o]})} \]

The denominator can be expanded in terms of a Binomial Series to give:
\[ V_2 = \frac{V'_1(R'_\ell + R''_\ell)[\delta - \alpha]}{R} + \frac{V''_1}{R} \times \frac{1}{R} - \frac{V''_1}{R} \times (R'_\ell + R''_\ell)[\delta - \alpha] \frac{\delta}{2R} \]

\[ - \frac{V'_1(\ell'')^2}{2R^2} \left( \frac{\delta}{x} \right)^2 + \frac{V'_1(\ell')^2}{4R^3} (R'_\ell + R''_\ell)[\delta - \alpha] \left( \frac{\delta}{x} \right)^2 + \ldots \]

(C.2)

If \( V_2 \) is assumed to be proportional to \( \delta_x \) then a value \( \delta'_x \) will be observed for the same value \( V_2 \). Hence:

\[ \frac{V'_1}{R} \left( 1 - \frac{R'_\ell + R''_\ell[\delta - \alpha]}{R} \right) \frac{\delta'}{x} = \]

\[ \frac{V'_1(\ell'')^2}{2R^2} \left( \delta_x \right)^2 + \frac{V'_1(\ell')^2}{4R^3} (R'_\ell + R''_\ell)[\delta - \alpha] \left( \delta_x \right)^2 \]

where: \( R = R'_\ell + R''_\ell + R'_\ell \)

Now:

\[ \frac{\Delta \delta}{\delta_x} = \frac{\delta'_x - \delta_x}{\delta_x} \]

so:

\[ \frac{\Delta \delta}{\delta_x} = \frac{- \frac{R'_\ell \delta_x}{2(\ell''[2 + \delta_o] + R'_\ell)}}{2} \]

When \( V_2 = 0, \delta = \delta_o \) and Equation C.2 gives:

\[ \delta_o = - \frac{R'_\ell R'_\perp (\beta - \alpha)}{R_s (R'_\ell + R'_\perp [1 + \gamma].[2 + \beta])} \]

Hence:

\[ \frac{\Delta \delta}{\delta_x} = - \frac{\delta_x}{2[(2+\alpha) + \frac{R'_\ell R'_\perp (2+\gamma+\alpha)}{R_s [R'_\ell + R'_\perp (1+\gamma)(2+\beta)]}]} \]

For a zero link resistance, this reduces to \( -\delta_x/(2[2 + \alpha]) \) which is the
fractional error in $\delta_x$ for a Wheatstone Bridge.

The effect of the link resistance is given as follows:

as $R_x$ tends to $\infty$, fractional error tends to

$$-\delta_x \frac{R}{2(2+\alpha+R_1[2+2\gamma+\alpha])} \frac{R_s}{R_s}$$

as $R$ tends to 0, fractional error tends to

$$-\delta_x \frac{1}{2(2+\alpha)}$$

so the ratio of the errors for zero and infinite link resistances is:

$$1 + \frac{R_1(2 + \gamma)}{2R_s}$$
Derivation of Equations Presented in Sections III.2.1. and 2.2.and 2.4.

D.1. Interface Motion in the Directions of the Superimposed Grid lines.

Considering the two-dimensional situation in which concentration gradients do no occur in the \( \theta \) direction of a \((r,\theta,\phi)\) polar co-ordinate scheme, the position of the interface can be written as:

\[
f(r,\phi,t) = r - \varepsilon(\phi,t) = \phi - \mu(r,t) \tag{D.1}
\]

Now:

\[n = \frac{\nabla f}{|\nabla f|}\]

where \( \nabla f = \frac{\partial f}{\partial r} \hat{r} + \frac{\partial f}{\partial \phi} \hat{\phi} \) and \( \hat{n} \) is a unit vector normal to the interface and \( \hat{r} \) and \( \hat{\phi} \) are unit vectors in the radial and tangential directions.

Motion in the \( r \)-direction only will be analysed as the procedure is the same for the \( \phi \)-direction. From Equation D.1 we have:

\[
\frac{\partial f}{\partial r} = |\nabla f| \hat{r} \cdot n = - \mu \quad \text{and} \quad \frac{\partial f}{\partial \phi} = |\nabla f| \hat{\phi} \cdot n = 1 \tag{D.2,3}
\]

The mass balance at the interface gives:

\[
\frac{\partial c_a}{\partial n} - \frac{\partial c_b}{\partial n} = (c_a^0 - c_b^0) \cdot \frac{dn}{dt} \tag{D.4}
\]

where \( a \) and \( b \) refer to the precipitate and matrix phases respectively and \( c_a^0 \) and \( c_b^0 \) are the time independent interface concentrations. Now:

\[
\frac{dn}{dt} = \frac{\partial c}{\partial t} \cdot \hat{r} = \epsilon \cdot \frac{\partial c}{\partial t} \cdot \hat{\phi} \tag{D.5}
\]

and we can write:

\[
\frac{\partial c_i}{\partial n} = n \cdot \hat{r} \cdot \frac{\partial c_i}{\partial r} + n \cdot \hat{\phi} \cdot \frac{\partial c_i}{\partial \phi} \tag{D.6}
\]
We also have the auxiliary equation:

\[
\frac{\partial c_i}{\partial \phi} + \varepsilon \frac{\partial c_i}{\partial r} \frac{\partial r}{\partial \phi} = 0 \tag{D.7}
\]

This equation will be derived in the next section.

The simultaneous use of Equations D.2 to D.7 yields:

\[
(c_a^0 - c_b^0) \frac{\partial \varepsilon}{\partial t} = (1 + \frac{1}{\varepsilon} [\frac{\partial \varepsilon}{\partial \phi}]^2). (D_a \frac{\partial c_a}{\partial r} - D_b \frac{\partial c_b}{\partial r})
\]

and this is the equation given in the text.


We define two lines which determine the tangent plane to the surface \( r = (\theta, \phi, \tau) \) at some constant time \( \tau \). Two such tangent lines are:

\[
r - r_o = \varepsilon.(\phi - \phi_o) \frac{\partial \varepsilon}{\partial \phi} \theta_o, \phi_o \tag{D.8}
\]

\[
r - r_o = \varepsilon.(\theta - \theta_o) \frac{\partial \varepsilon}{\partial \theta} \theta_o, \phi_o
\]

As before, we only consider changes in the \( r, \phi \) plane. Now, the interface is an isoconcentrate surface so:

\[
\hat{e} \cdot \nabla c_i = \hat{e}. \left[ \frac{\partial c_i}{\partial r} + \frac{\phi \cdot \partial c_i}{\partial \phi} + \frac{\theta}{\varepsilon \sin \phi} \frac{\partial c_i}{\partial \theta} \right] = 0
\]

where \( \hat{e} \) is the unit vector along the tangent line given by Equation D.8. This vector is easily found and the simplification of Equation D.9 leads to the auxiliary equations given in the text.

The second set of auxiliary equations is generated by considering the fact that the product \( \hat{e} \cdot \nabla c_i^2 \) is also zero at the interface.
D.3. Coefficients of the Quadratic Given in Section III.2.4.

Following the notation given in the text we have for the quadratic:

\[ aA^2 + bA + d = 0 \]

\[ a = (1 + \frac{\partial \varepsilon}{\partial \phi} \cdot \frac{1}{(n - 2 + \sigma_r) \Delta r}) \Delta \phi \cdot q \]

\[ b = -1 \cdot (2q \cdot \frac{\partial \varepsilon}{\partial \phi} + \Delta \phi \cdot \sigma_r \cdot \frac{\partial ^2 \varepsilon}{\partial \phi^2} \cdot (n - 2 + \sigma_r)^{-1}) - \frac{a \cdot g}{k' \cdot (1 + \sigma_r) \Delta r} \]

\[ -\frac{2.1 \cdot s}{(1 + \sigma_r) \Delta r} - q \cdot \Delta \phi \cdot 1 \cdot \frac{(2 \partial \varepsilon \cdot \cotan[(m-l)\Delta \phi])}{(n - 2 + \sigma_r) \Delta r} \]

\[ d = 2.1 \cdot \frac{\partial \varepsilon}{\partial \phi} \cdot \left( c_b^0 - c_m^0 \right) + \frac{(c_{m+1,n}^0 - c_b^0) \cdot s}{(1 + \sigma_r)^2(\Delta r)^2} \]

Where:

\[ q = \Delta \phi \cdot \frac{\partial \varepsilon}{\partial \phi} - \Delta r \cdot \sigma_r \]

\[ s = \frac{\partial \varepsilon}{\partial \phi} \cdot \left( \frac{[\Delta r \cdot \sigma_r]^2}{[\Delta \phi]^2} + [\Delta \phi]^2 \right) - \Delta r \cdot \Delta \phi \cdot \sigma_r \cdot \left( \frac{\partial \varepsilon}{\partial \phi} \cdot 2 - 1 \right) \]
APPENDIX E

PROGRAM TO COMPUTE THE DIMENSIONLESS RADIUS OF A SPHERICAL PRECIPITATE DISSOLVING BY DIFFUSION CONTROL IN A FINITE MATRIX.

NO DIFFUSION IN THE PRECIPITATE WILL BE ASSUMED.

OTHER VARIABLES: A IS PRECIPITATE RADIUS, R IS NORMALISED PRECIPITATE RADIUS, RS IS THE RATIO OF DISTANCE OF INTERFACE FROM THE NEAREST NODE TO THE NODE SPACING (ASSUMED TO BE UNITY), A11 IS A CONCENTRATION EXPANSION COEFFICIENT.

DIMENSION C(50),CN(50)

INPUT: NUMBER OF NODES NN, ALLOY CONC. CBAR, EQUILIBRIUM INTERFACE CONC. CCE, UNIFORM PRECIPITATE CONC. CIA, INITIAL MATRIX CONC. CIB, TIME INTERVAL DT.

READ (5,100)NN,CBAR ,CIB, CIA, CIB, DT

100 FORMAT (1I10,5F10.0)

NN1=NN-1
A=NN1*CBAR**(1./3.)
WRR=1.
NC=A/DR+1
RS=NC-A/CR
R=A/AD

INITIALIZE MATRIX CONCENTRATIONS.

10  C(I)=CIB

20  NC=A/DR+1
    RS=NC-A/CR
    R=A/AD

TERMINATE DISSOLUTION WHEN R IS LESS THAN .001.

IF (R.LT..001)GC TO 7C

T=NO*DT/(AD*AD)

IF (R.GT.WRR)GO TO 25

WRR=WRR-.005

CUTPLT IS PRECIPITATE RADIUS R, EVERY .005.
CONC. AT NEXT TIME INCREMENT AT NON-INTERFACE NODES.
DO 30 I=NC1,NN1
CN(I)=C(I)+DT*(C(I+1)*(-1./I)+C(I-1)*(-1./I)-2.*C(I))
CN(1)=C(1)+DT*(C(2)*1./I+1)-C(0)
CN(0)=C(0)+DT*(C(1)*(-1./I)+C(0)*(-1./I)-2.*C(0))
CN(NN)=CN(NN-2)
IF (RS.LE.5) GO TO 40
C CONC. AT INTERFACE NODE WHEN RS GREATER THAN .5.
CN(NC)=C(NC)+DT*(2.*(C(NC+1)*RS*RS+C(NC)*(1.-RS*RS)-CWB)/
1(RS*(1.+RS)*NC)+2.*(CWB-C(NC)*(1.+RS)-RS*C(NC+1))/(RS*(1.+RS)))
C CONC. GRADIENT AT INTERFACE WHEN RS GREATER THAN .5.
A11=((1.+RS)*CN(NC)/RS-(1.+2.*RS)*CWB/(RS*(1.+RS))-RS*CN(NC+1)/
1(RS*(1.+RS)))
GO TO 50
C CONC. AT INTERFACE NODE AND CONC. GRADIENT AT INTERFACE WHEN RS LESS
C THAN OR EQUAL TO .5.
40 B=2.*CL*(1./(NC-RS)-1./(1.+RS))
CT=2.*CL*(CN(NC+1)-CCE)/(1.+RS)**2
A11=((B-SQRT(B*B+4.*CT))/2.*
CN(NC)=(A11)+(((CN(NC+1)-CWB)/(1.+RS)-A11)/(1.+RS))*RS*CWB
C CALCULATE BOUNDARY MOVEMENT.
50 A=A-A11*DT/CL
C SUBSTITUTE NEXT TIME INTERVAL CONCENTRATION MATRIX.
DO 60 I=NC,NN1
60 C(I)=CN(I)
NC=NC+1
C RETURN FOR ANOTHER TIME INTERVAL.
GO TO 20
C AT COMPLETION CALCULATE CONCENTRATION ERROR = CELL WALL-ALLOY CONCS.
70 CERR=CBAR-C(NN-1)
PRINT 130,CERR
130 FORMAT (1HO,CERR
STOP
END
The Effect of a Structure Dependent Thermal Coefficient of Resistivity on Fast Reaction Fraction.

It is necessary to show that the difference between the thermal coefficients of resistivity of the alloy during the fast and slow reversion reactions introduce only a small error when the fast reaction fraction $X_f$, is assumed to represent a particular alloy structure.

At a temperature $T_1$, as is shown in Figure D.1, the fast reaction resistance drop is $\Delta \rho_f$ while the slow reaction drop is $\Delta \rho_s$. At $T_2$ the time zero resistance increases to $\rho(1 + \omega_f \Delta T)$ where $\omega_f$ is the thermal coefficient of resistivity of the as-aged alloy, and at infinite time the resistance has increased to $(\rho - \Delta \rho_f - \Delta \rho_s)(1 + \omega_s T)$ where $\omega_s$ refers to the fully reverted alloy. The resistance at $T_1$ at the time $t_{cf}$ is $(\rho - \Delta \rho_f)$ while at $T_2$ it can be approximated by the average of the temperature change resistances, or:

$$\rho_{t_{cf}} = (\rho - \Delta \rho_f)(1 + \frac{\omega_f + \omega_s \Delta T}{2})\text{ where } \Delta T = T_1 - T_2$$

The fast reaction fraction is defined as:

$$X_f = \frac{T_1}{\rho_{t_{to}}} - \frac{T_1}{\rho_{t_{cf}}} / \frac{T_1}{\rho_{t_{to}}} - \frac{T_2}{\rho_{t_{to}}}$$

so the fractional change in the fast reaction fraction $\Delta X_f/X_f$, on reverting at the higher temperature $T_2$ is:
Figure F.1. Schematic Diagram Showing Specimen Resistivity Changes During the Fast and Slow Reversion Reactions at Two Temperatures.
\[ \frac{\Delta X_f}{X_f} = \frac{\rho (1 + \omega_f \Delta T) - (\rho - \Delta \rho_f) (1 + \omega_f \Delta T / 2)}{\rho (1 + \omega_f \Delta T) - (\rho - \Delta \rho_f \Delta \rho_s) (1 + \omega_s \Delta T / 2)} - \frac{\Delta \rho_f}{\Delta \rho_f + \Delta \rho_s} \]

Defining \( \Gamma_f = \Delta \rho_f / \rho_f \) and \( \Gamma_s = \Delta \rho_s / \rho_s \), and on expanding the denominator in terms of a binomial series and ignoring second order terms, we have:

\[ \frac{\Delta X_f}{X_f} = \frac{\Delta T (\omega_f - \omega_s)}{2 \Gamma_f} \left( 1 - \frac{\Gamma_f}{\Gamma_f + \Gamma_s} - \frac{\omega_f - \omega_s}{\Gamma_f + \Gamma_s} \right) \]

Typically, at 225°C, \( \Gamma_f = 0.025 \), \( \Gamma_s = 0.002 \), \( \omega_f = 0.002 \), \( \omega_f - \omega_s = 0.0005 \) so for a 25°C temperature rise:

\[ \frac{\Delta X_f}{X_f} = 0.04. \]

Hence a fractional error of about 4% is anticipated if the measured fast reaction fraction is taken be a property of the alloy structure and is independent of the reversion temperature.
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For example, see Refs. 6, 7 and 65.


110 For example, see Refs. 36 and 112.
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