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Lin, Chun-Sien

THE BREAKDOWN OF SILVER DIFFUSION BARRIER IN THE MODEL COPPER-SILVER-NICKEL DIFFUSION TRIPLE

The Ohio State University

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The Breakdown of Ag Diffusion Barrier in the Model Cu-Ag-Ni Diffusion Triple

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the degree Doctor of Philosophy in the Graduate School of The Ohio State University

By Chun-Sien Lin, M.S.

* * * * *

The Ohio State University

1985

Reading Committee: John P. Hirth Robert A. Rapp Paul G. Shewmon

Approved By

John P. Hirth, Adviser Department of Metallurgical Engineering

Robert A. Rapp, Adviser Department of Metallurgical Engineering
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Chun-sien Lin
1985
VITA

Jan 8, 1952 .......... Born - Taiwan, Rep. of China

1974 .................. B.S., Metallurgy, Chen-Kung National University, Taiwan, R.O.C.

1976 .................. M.S., Metallurgy, Chen-Kung National University, Taiwan, R.O.C.

1981 .................. M.S., Metallurgy, The Ohio State University, Columbus, Ohio

1979-1985 .......... Graduate Research Associate, The Ohio State University, Columbus, Ohio
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Chapter I
INTRODUCTION

The degradation arising from interdiffusion, particularly in high temperature coating systems and the metallization processes for integrated circuits, has drawn the attention of the metallurgists for years. The diffusion barrier, or diffusion blocking layer, is usually a necessity for those devices which require either prevention or control of the interdiffusion between dissimilar phases in intimate contact. The thickness of these diffusion barriers may range from several angstroms to several microns, and the application temperatures cover a wide range up to a thousand degrees Celsius. Therefore, one mechanism which can successfully interpret the behavior of one type of diffusion barrier may not apply to others. However a fundamental investigation can certainly supply valuable information for understanding the behavior of the diffusion barrier.

This work attempted to study morphological change and interdiffusion behavior of the diffusion barrier by employing a model system with a Ag layer as the diffusion barrier
between Cu and Ni end members which otherwise exhibit an isomorphous binary, as shown in Figure 1. The Cu-Ag binary, presented in Figure 2, has solubility limits for Cu in Ag of about 13.5 at% and about 96 at% Ag in the Cu-rich phase at 760 °C. As Figure 3 shows, the Ag-Ni system is a binary in which Ni has a very low solubility in Ag, while Ag has about 1 at% solubility in Ni at 760 °C. Without the Ag barrier layer, Cu and Ni would interdiffusion within a short period of time when in intimate contact at 760 °C.

![Figure 1: The phase diagram for Cu-Ni binary system [1]](image)

Some relevant work, including a computer module for the calculation of the interdiffusion coefficients, is also introduced in this study. The next chapter presents a literature survey for the relevant fields of this work.
**Figure 2:** The phase diagram for Cu-Ag binary system [1]

**Ag-Ni Silver-Nickel**

**Figure 3:** The phase diagram for Ag-Ni binary system [2]
Chapter II
LITERATURE REVIEW

2.1 BOLTZMANN-MATANO (B-M) METHOD

The B-M method, which was introduced by Matano in 1933, is commonly used in interdiffusion studies. It does not intend to solve Fick's second law,

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D(C) \frac{\partial C}{\partial x} \right) \]

Instead, the concentration-dependent diffusivities are obtained indirectly. The Equation 1 is derived by the substitution of the Boltzmann variable \( \lambda = x \sqrt{t} \) and the imposition of the following boundary conditions: both derivatives of \( C \) vs \( X \) vanish at \( X = X^- \) and \( X = X^+ \), that is,

\[ \frac{dC}{dX} = 0 \text{ at } X = X^- \text{ and } X = X^+. \]

\[ D(C^*) = \frac{1}{2t} \left( \frac{\partial X}{\partial C} \right)_C \int_{C^-}^{C^*} (X - X_m) dC \]  \hspace{1cm} (1)

where \( C \) is the concentration (moles/cm\(^3\)), \( D \) is the diffusivity, \( X \) is the penetration distance (cm), \( t \) is the diffu-
sion time (sec), $C^{-}$ is the concentration at $X = X^{-}$, $C^{*}$ is the concentration at which $D$ is calculated, and $X_{m}$ is the Matano interface. The detailed derivation of Equation 1 can be found in many texts [3],[4].

2.2 MATANO INTERFACE

In Equation 1, $X_{m}$ is defined by

$$\int_{C^{-}}^{C^{+}} (X - X_{m}) \, dC = 0 \quad (2)$$

which can be derived from Equation 1, and the boundary conditions stated above [3]. This equation is based on the conservation of mass for the case of constant molar volume and uniform cross-sectional area of the diffusion path. In Figure 4, $X_{m}$ represents the interface past which equal amounts of atoms of two species have diffused.

Equation 2 can be further written as two integrals:

$$\int_{C^{-}}^{C^{*}} (X - X_{m}) \, dC + \int_{C^{*}}^{C^{+}} (X - X_{m}) \, dC = 0 \quad (3)$$

A change of integration variables yields,

$$\int_{0}^{C^{*}-C^{-}} (X - X_{m}) \, dC' + \int_{C^{*}-C^{+}}^{0} (X - X_{m}) \, dC = 0 \quad (4)$$
Figure 4: Cross hatched areas separated by $X_m$ are equal
where \( C' = C - C^- \), \( C'' = C - C^+ \). Performing an integration by parts, and assuming

\[
(X - X_m) = u \quad \text{du} = dx \\
C' \quad \text{dv} = dC' \quad v = C'
\]

we find the first integral

\[
I_1 = (X - X_m) C' \int_0^{C^*-C^-} - \int_0^{X^*-X^-} (C - C^-) \, dx
\]  

(5)

For further simplification, this equation is evaluated at \( C^* = C_m \), that is at \( X^* = X_m \). Then Equation 5 becomes,

\[
I_1 = - \int_{X_m}^{X^*} (C - C^-) \, dx
\]

or,

\[
I_1 = - \int_{X^-}^{X_m} (C - C^-) \, dx
\]

Similarly, the second integral of Equation 3 can be partially integrated with the assumptions

\[
(X - X_m) = u \quad \text{du} = dx \\
C'' \quad \text{dv} = dC'' \quad v = C''
\]

where \( C'' = C - C^+ \). The result is

\[
I_2 = - \int_{X_m}^{X^+} (C - C^+) \, dx
\]

Thus, Equation 3 can be restated as,

\[
- \int_{X^-}^{X_m} (C - C^-) \, dx - \int_{X_m}^{X^+} (C - C^+) \, dx = 0
\]

(6)
The second integral of Equation 6 can be expressed as,

\[(x^+ - X_m) \cdot (c^+ - c^-) - \int_{X_m}^{X^+} (c - c^-) \, dx\]

Combining this expression with the first part of the Equation 6, we find

\[-x^+ \cdot (c^+ - c^-) + X_m \cdot (c^+ - c^-) + \int_{X^-}^{X^+} (c - c^-) \, dx = 0\]

Final rearrangement shows

\[X_m = x^+ - \int_{X^-}^{X^+} \eta \, dx\]  \hspace{1cm} (8)

where \(\eta = (C-C^-)/(C^+ - C^-)\).

Equation 8 is equivalent to that Carlson used to calculate the Matano interface [5]. But Equation 8 is simpler and more meaningful. After rearrangement, it also can be expressed as

\[X_m = x^- + \int_{X^-}^{X^+} (1 - \eta) \, dx\]  \hspace{1cm} (9)
2.3 DIFFUSIVITIES

To evaluate the diffusivities, the integral part of Equation 1,

\[ \text{Int} = \int_{C^{-}}^{C^{*}} (X - X_m) \, dC \]

can be rewritten in a similar manner,

\[ \text{Int} = \int_{C^{-}}^{C_m} (X - X_m) \, dC + \int_{C_m}^{C^{*}} (X - X_m) \, dC \quad (10) \]

\[ \int_{C_m}^{C^{-}} (X - X_m) \, dC + \int_{C^{-}}^{C^{*}} (X - X_m) \, dC' \]

Partial integration and using the relation found in Figure 5 gives,

\[ \text{Int} = -\int_{0}^{X_m-X^-} (C - C^-) \, dX' + (X - X_m)(C^* - C^+) \]

\[ -\int_{X_m-X^+}^{X^*} (C - C^+) \, dX'' \]

\[ = -\int_{X}^{X_m} (C - C^-) \, dX + \int_{X_m}^{X^*} (C^+ - C) \, dX + (X^* - X_m)(C^* - C^+) \]

\[ = -\int_{X}^{X_m} (C - C^-) \, dX + (X^* - X_m)(C^+ - C^-) - \int_{X_m}^{X^*} (C - C^-) \, dX \]

\[ + (X^* - X_m)(C^* - C^+) \quad (11) \]

Finally, we find

\[ \text{Int} = -\int_{X}^{X^-} (C - C^-) \, dX + (X^* - X_m)(C^* - C^-) \quad (12) \]
\[ \text{Int} = - \int_{X^-}^{X^*} (C - C^-) \, dx + (C^* - C^-) \int_{X_m}^{X^*} \, dx \]  

Figure 5 shows that areas abc and cdefg are equal according to the definition of \( X_m \). Consequently, Int represents the negative value of the area fgkj when \( X^* \) is greater than \( X_m \). As \( X^* \) is less than \( X_m \), Int is equal to the area abhi. This result is equivalent to that derived by Carlson; however, this equation is more general and efficient for computer coding.
Figure 5: The plot illustrates the equivalence of \( \text{Int} \) and the area \( \text{fgkj} \), and \( \text{Int} \) and the area \( \text{abhi} \)
2.4 FRAMES OF REFERENCE


In 1968 Guy et al [15] proposed a reference system, with volume fraction versus an ordinary space coordinate (cm), which is contradictory to Hartley's criterion for choosing a reference frame for Fick's second law. Recently Son et al [16] discussed the subject of the interdiffusion coefficient and the Matano interface, and Onishi et al [17]
published a work discussing the reference frame and the intrinsic diffusivity. Both of them presented in-depth mathematical support for their arguments which serve to unify the earlier papers. Summarizing these discussions, the common frames of reference for diffusion in a metallic system include:

(1) The Fick reference frame: the space coordinate is measured relative to a fixed point outside the diffusion zone, e.g., a diffusion cell wall.

(2) The volume-fixed reference frame: the concentration is measured in units of moles/cm$^3$, while the space coordinate is cm as usual. But the distance is measured relative to the center of volume of the system. When no total volume change occurs during diffusion, this reference frame is equivalent to the Fick reference frame.

(3) The mole-fixed reference frame (or number of moles fixed frame): The coordinates are defined as mole fraction $N_i$ versus $\xi_i$, where $\xi_i$ bears the unit of mole/cm$^2$. When the volume change of mixing is not zero during diffusion, this is a preferred reference frame.

(4) The lattice-fixed reference frame: This is the usual reference frame for intrinsic flow with an origin fixed on the crystal lattice that is proposed to move together with
inert markers. The movement of atoms relative to markers is termed the "diffusion flux" according to Darken's definition [3].

In addition to the above four reference frames, one may choose other coordinate systems provided that the governing diffusion equations conform with thermodynamic requirements such as the conservation of mass. For example, the center of mass also can be used as the reference plane in the case that one elects to employ weight fraction as the concentration unit, and cm/(specific volume) as the space coordinate. Recently Dayanada [18] suggested a reference plane which is relative to the zero-flux plane (ZFP) where the flux of the one constituent becomes zero. Its use for description of interdiffusion in a multi-component system needs more investigation. But with its characteristics of bypassing the direct determination of diffusivities this method may be relevant in the field of multi-component diffusion systems.

2.5 CONSISTENCY IN A REFERENCE FRAME

Among these reference frames, the most commonly used one is the Fick reference frame with an assumption of constant molar volume. This assumption enables the use of both the equations valid in a mole-fixed reference frame and the
Darken equations for intrinsic fluxes and the marker velocity equation as derived in the text [3]. In other words, the experimentally measured marker shift and the mole fraction can be incorporated into these equations directly. However if one is concerned about the intrinsic fluxes when the volume change of mixing is not negligible, a reference system must be specified since they are not interchangeable any more. To calculate the intrinsic flux one needs to know the way to measure the total displacement of the marker relative to the origin of the reference system specified. For a Fick reference the origin is on the cell wall outside the diffusion zone; a volume-fixed frame is the center of the volume; a mole-fixed frame is the plane with an equal amount of moles of solute on each side. These origins are moving relative to one another during the course of the interdiffusion. Therefore, whenever the assumption of a constant molar volume is not applicable, the use of equations has to be 'consistent' in that specified reference frame system.

A controversial issue about "the anomalous marker shift in Cu-Sn binary system" reported by da Silva and Mehl in 1951 [19] serves as an example of the effect of "inconsistency". In this controversy, Guy [20] and Oikawa [22] employed the Darken equations for marker velocity,

\[ \text{vm} = (D_2 - D_1) \left( \frac{\partial N_2}{\partial X} \right) \]  

(14)
to estimate the maximum marker shift by assuming \( D_1 = 0 \), and compared with the experimental values which were measured relative to the origin of a volume-fixed reference frame. Thus the maximum marker shift is

\[
X_{\text{max}} = 2 \ t \ D_2 \ \frac{\partial N_2}{\partial X}
\]  

(15)

On the basis of this equation, they found the actual marker shift is greater than the estimated values, and declared an agreement with da Silva et al finding of an anomaly for the marker shift in Cu-Sn binary system.

Instead of Darken's equations, Hoshino [23][21] utilized the equations in a volume-fixed reference which is valid provided that no dimension change occurs. These are

\[
v_m' = V_2 \ (D_2 - D_1) \ (\frac{\partial C_2}{\partial X})
\]  

(16)

\[
X_{\text{max}}' = 2 \ t \ D_2 \ V_2 \ (\frac{\partial C_2}{\partial X})
\]  

(17)

To compare \( X_{\text{max}} \) and \( X_{\text{max}}' \), \((dC_2/dX)\) can be converted by the substitution of

\[
\frac{\partial N_2}{\partial X} \left( \frac{V_1}{V_m^2} \right), \text{ then}
\]

\[
X_{\text{max}}' = 2 \ t \ D_2 \ V_2 \ (\frac{\partial N_2}{\partial X}) \left( \frac{V_1}{V_m^2} \right)
\]
In a Cu-Sn binary alloy with dilute tin, $V_m$ can be approximated by $V_1$, that is $V_{Cu}$; therefore,

$$X'_{\text{max}}/X_{\text{max}} = V_2/V_1/V_m^2 = V_2/V_1 = 1.8$$

because $V_{Sn}$ is about 1.8 times of $V_{Cu}$. Consequently, $X'_{\text{max}}$ estimated by Hoshino et al, which is consistent in a volume-fixed reference frame, is about two times greater than the values estimated by Guy et al. Accordingly, Hoshino et al. concluded that no anomaly exists in the Cu-Sn binary system with regard to the marker shift associated Kirkendall effect.

It is worth pointing out that the marker shift is a coordinate dependent term, while the intrinsic flux is coordinate independent. This can be realized by a review of the derivation of Equation 16 for marker velocity equation.

$$J_1 = j_1 + V_m C_1$$  \hspace{1cm} (18)

$$J_2 = j_2 + V_m C_2$$  \hspace{1cm} (19)

where $J_1$ is the interdiffusion flux, $j_1$ is the intrinsic flux, $V_m$ is the marker velocity relative to the origin of the reference frame in which the $J_1$ is measured, and $C_1$ is the concentration (moles/cm$^3$). In a volume-fixed reference frame,
\[ V_1 J_1 + V_2 J_2 = 0. \] Combining this and the relations of
\[ C_1 dV_1 + C_2 dV_2 = 0, \quad C_1 V_1 + C_2 V_2 = 1, \]
one can derive the marker velocity in a volume-fixed frame as:
\[ \nu_m = V_2 (D_2 - D_1) \frac{dC_2}{dX}. \]

For a mole-fixed reference frame, an equation \( J_1 = J_2 \) should be used to fulfill the requirement of the conservation of matter. It is clear that if one elects to employ the equations for the mole-fixed frame, he is obligated to use the marker velocity in this reference frame which is not experimentally measurable. It is invalid to use Darken's equation for a mole-fixed reference frame as Guy et al did in Cu-Sn binary system. An equation
\[ \nu_m = (D_2 - D_1) \left( \frac{\partial N_2}{\partial \xi} \right) \]
should be invoked if volume change of mixing is not negligible. Moreover a relative movement between two frames should be expected, and
\[ \nu_m' = V_m \cdot \nu_m - \Delta v, \]
where \( \Delta v \) is the relative velocity between two frames. In view of this controversy, the following section is devoted to the discussion of the formulae associated with each reference frame, and the justification of the choice of the appropriate reference frame.
2.6 FORMULAE ASSOCIATED WITH REFERENCE FRAMES

After Sauer and Freise [13], there were many variations of their expressions derived to permit the calculation of the interdiffusion coefficient in a binary system with a concentration dependent partial molar volume. Wagner [24] brought attention to an invariant of diffusion in a binary system, $v_1 - v_2$ [25], where $v_1$ and $v_2$ are the velocities of the constituent components. On the basis of a definition of interdiffusion coefficient by Jost [26],

$$\hat{D} = \frac{N_1 N_2 (V_1 - V_2)}{\frac{\partial N_2}{\partial X}} = \frac{V_m (N_2 J_1 - N_1 J_2)}{\frac{\partial N_2}{\partial X}}$$  \hspace{1cm} (21)

Wagner derived Equation 22 which is equivalent to that of Sauer and Freise,

$$D(N_2^*) = \frac{(N_2^+ - N_2^-) V_m(N_2^*)}{2 t \left( \frac{\partial N_2}{\partial X} \right)} \left\{ (1 - Y^*) \int_{X^-}^{X^*} \frac{Y}{V_m} \, dX + Y^* \int_{X^-}^{X^*} \frac{(1 - Y)}{V_m} \, dX \right\}$$  \hspace{1cm} (22)

where $Y = (N - N^-)/(N^+ - N^-)$. Later den Broeder [27] also derived a similar form of the SFW Equation 22 with the help of a plot of C vs X, shown in Figure 6. Upon examining both areas "between" curve and $C=C^+$ and $C=C^-$, we can equate,
Figure 6: The plot of $C$ vs $X$ used to derive the relation in Equation 23.
\[ B = \eta^* (B + C + D) \]
\[ A = \eta^* A + (1-\eta^*) A \]
\[ A + B = \eta^* (E + D) + (1-\eta^*) A \]

From the definition of \( X_m \), \((A+B+C)\) equals to \( E \), and
\[ \eta = (C - C^-)/(C^+ - C^-). \] With use of this equality, Equation 1 becomes
\[
\frac{1}{2} \left( \frac{\partial C}{\partial x} \right)_t \left\{ (1 - \eta^*) \int_{X^-}^{X^*} (C - C^-) \, dx + \eta^* \int_{X^-}^{X^*} (C^+ - C) \, dx \right\}
\]

(23)

This is an alternative form of the Boltzmann-Matano equation, and has the advantage of bypassing the procedure of locating the Matano interface. For the case of a binary system with limited solubility, one can easily employ the relation stated above in accordance with Figure 6 and Equation 23 via Figure 5 and Equation 13.

In the case that the partial molar volumes are not constant, den Broeder extended his argument starting from a modified form of Fick's second law for the "mole-fixed" reference frame [11],
\[
\left( \frac{\partial N}{\partial t} \right)_n = \left\{ \frac{\partial}{\partial \xi} \left[ \frac{\delta}{v_m} \left( \frac{\partial N}{\partial \xi} \right) \right] \right\}
\]

(24)
where, $N_i$ is the mole fraction, $d\xi = 1/V_m dX$ is the number of moles/cm$^2$ in an element $dX$, and $V_m$ is the molar volume (cm$^3$/mole).

Upon substituting $N_i$ for $C_i$, $\xi$ for $X$, $Y^*$ for $\eta^*$, and $D/V_m^2$ for $D$, into Equation 23, one can readily obtain the SFW equation with some rearrangement. Later Son [28] identified the term in Equation 24, $D/V_m^2$ as the interdiffusion coefficient defined in a "mole-fixed reference frame" in which the flux is defined as,

$$J_n = -D^m \left( \frac{\partial N}{\partial \xi} \right) = -\frac{\bar{D}}{V_m^2} \left( \frac{\partial N}{\partial \xi} \right)$$

(25)

where $J_n$ is the flux in mole-fixed frame and $\bar{D}$ is the interdiffusion coefficient in Fick's reference frame.

Up to this point, it is clear that these alternatives to the Boltzmann-Matano equation all conform with Fick's second law in the mole-fixed reference frame. In other words, when Fick's first and second law are valid in a certain reference frame, and given by

$$J_\xi = -\bar{D} \left( \frac{\partial N}{\partial \xi} \right)$$

$$\left( \frac{\partial N}{\partial t} \right) = \frac{1}{V_m} \left( \frac{\partial N}{\partial \xi} \right)$$

for instance in a mole-fixed reference frame, the interdiffusion coefficient can be calculated as follows:

$$D^m = \frac{1}{2} t \left( \frac{\partial Y}{\partial \xi} \right)^2 (1 - Y^*) \int_{\xi^-}^{\xi^+} Y d\xi + Y \int_{\xi^-}^{\xi^+} (1 - Y) d\xi$$

(26)
where \( Y = \frac{N - N^-}{N^+ - N^-} \),

\[
\frac{dY}{d\xi} = \frac{dN}{d\xi} \left( \frac{1}{N^+ - N^-} \right), \quad \text{and} \quad D_m^m = \frac{D}{V_m^2}.
\]

As pointed by Son [16] one can actually derive Equation 23 from the B-M equation by making use of Equation 12 and Equation 10, and substituting

\[
\eta = \frac{C - C^-}{C^+ - C^-}.
\]

This further proves that Equation 23 is the alternative form of the B-M method in a volume-fixed reference frame. Similar to the process for Equation 26, Equation 22 can be rewritten as,

\[
D^V = \frac{1}{2t} \left( \frac{d\eta}{dX} \right) \int_{X^-}^{X^+} \eta \, dX + \eta \int_{X^-}^{X^+} \left( 1 - \eta \right) \, dX
\]

As mentioned before, \( D^V \) is equal to \( \tilde{D} \) in the case that the volume change of mixing is zero. In other words, they are identical experimentally. The next table shows the reference frames that Son et al. suggested for use under different experimental conditions.

The definition of the Matano interface for a specific reference frame must conform with the reference frame employed. For instance, the equation used by Wagner

\[
\int_{-\infty}^{X_m} \frac{N_2}{V_m} - \frac{N_2}{V_m} \, dX + \int_{\infty}^{X_m} \frac{N_2}{V_m} - \frac{N_2}{V_m} \, dX = 0
\]
Table 1

The suggested choices of reference frames

<table>
<thead>
<tr>
<th>conditions</th>
<th>Reference Frame</th>
<th>( V_1 \neq V_2 ) &amp; ( V_1, V_2 = \text{cons} )</th>
<th>( V_1 \neq \text{constant} ) &amp; ( V_2 \neq \text{constant} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>coordinates</td>
<td>( X )</td>
<td>( \xi )</td>
<td></td>
</tr>
<tr>
<td>concentration</td>
<td>( C_i, \eta_i )</td>
<td>( N_i, Y_i )</td>
<td></td>
</tr>
<tr>
<td>diffusivity</td>
<td>( \tilde{D} )</td>
<td>( D^m )</td>
<td></td>
</tr>
<tr>
<td>diffusion fluxes</td>
<td>( J_{v,i} = - \tilde{D} \left( \frac{\partial C_i}{\partial X} \right) )</td>
<td>( J_{\xi,i} = - D^m \left( \frac{\partial N_i}{\partial \xi} \right) )</td>
<td></td>
</tr>
</tbody>
</table>

is nothing but the conservation law for the mole-fixed reference frame. Since the experimental data are usually plotted as mole fraction vs distance(cm) in the general literature, people usually ignore the underlying assumption of constant molar volume. As an example, the employment of the flux equation

\[ J_{\xi,i} = - \frac{\tilde{D}}{V_m} \left( \frac{\partial N_i}{\partial X} \right) \]  

(29)

is only valid in a mole-fixed reference frame while \( V_m \) is not constant. This can be easily verified as follows: Substituting \( d\xi = 1/V_m \ dX \), and \( dN = V_m \ dC + C \ dV_m \) into

\[ J_{\xi} = - \frac{\tilde{D}}{V_m^2} \left( \frac{\partial N}{\partial \xi} \right) \]
when \( V_m \) is not constant, one finds that \( J_\xi \) becomes

\[
J_\xi = - \frac{\overline{D}}{V_m} \left[ V_m \frac{dC}{dX} + C \frac{dV_m}{dX} \right] = J_V - \frac{D}{V_m} C \frac{dV_m}{dX}
\]

When \( V_m \) is constant, \( dC = dN/V_m \) and \( J_\xi \) relaxes to \( J_V \). Onishi et al., on the basis of Trimble's equations, derived the relation between two fluxes

\[
J_{V,i} = J_{\xi,i} - C_i \left( V_1 J_{\xi,1} + V_2 J_{\xi,2} \right) \quad (30)
\]

2.7 DIFFUSION BARRIER

A diffusion barrier is sometimes used for systems where interdiffusion can result in premature failure or breakdown of metallic systems such as metallization systems for semiconductor design, high temperature coating systems, etc. An effective diffusion barrier should meet many criteria in a particular application; however, in general, three basic properties are critical to its performance.

(i) the transport rate of components through the diffusion barrier should be small.

(ii) The diffusion barrier \( B \) should be thermodynamically stable with respect to the surrounding phases \( A \) and \( C \), Figure 7; in particular, there should be no rapid chemical reaction between either \( B \) and \( A \) or \( B \) and \( C \).
(iii) The adhesion of B to both A and C should be sufficiently sound to avoid the deterioration in the interface adhesion inherent to the original A/C system.

There are trade-offs among these properties in applications. For example, the absence of chemical reaction usually indicates poor adhesion. In other words, enhancing one property may possibly degrade another, and how to compromise among them, indeed, depends upon the particular application.

Most applications on metallization systems such as TiN in the metallization (beam lead metal) system [29] are thin film diffusion barriers with several hundred angstroms thickness. The thinness of the film is needed because of the requirements of miniaturization and low resistivity in integrated circuit systems. In contrast, the diffusion barriers applied beneath a high temperature coating are in the range of several micrometers thickness [30]. The application temperatures can range from above room temperature, to several hundreds, up to a thousand degrees Celsius. Because of the variety of environments for barrier applications, it is very difficult or nearly impossible to propose a universal model to interpret the behavior of diffusion barriers. For instance, in thin-film applications the high diffusivity paths such as grain boundaries may play a vital role [31]; however, bulk diffu-
Figure 7: Diffusion barrier with B between A and C
sion is usually the dominant failure mechanism for high temperature coatings. Defects in the barrier can provide another major source of failure. As such, the categorization according to kinetic behavior suggested by Nicolet [32] is appropriate for classifying the types of diffusion barriers. He distinguished three types of successful diffusion barriers:

(a) Stuffed Barrier: In this type of barrier, segregation of impurities such as oxygen or nitrogen along the high diffusion grain-boundary path can suppress rapid diffusion at low temperature. These impurities may be intentionally introduced during the formation of a diffusion barrier by sputtering in a vacuum contaminated with water vapor, air or oxygen.

(b) Passive Compound Barriers: This type of diffusion barrier is chemically inert with respect to the surrounding phases A and C. Such inertness can be achieved in materials which have negligible mutual solubilities and low diffusivities for A and C. This type of diffusion barrier inherently has poor adhesion to the parent phase, so is usually in the form of a compound [30], [33], [29], [34], [35]. For instance, TiN, with its high melting point, 2930 °C and low bulk resistivity, 22 \( \mu \Omega \text{m} \), has been studied as an ideal diffusion barrier for years. It was applied in both the
Ti/Pt/Au thin film metallization, known as the beam lead metal system, and the Al/Silicide/Si metallization system. In the beam lead metal system, TiN can suppress platinum penetration [29] and eliminate junction-shorting failure during the heat treatment after the metallization. In the second system, aluminum reacts with the silicide and eventually penetrates the silicide to cause failure. TiN was reported as an effective barrier up to 450 °C in this system.

(C) Sacrificial Barriers: [36],[37],[38],[39],[40] This type of barrier usually forms compounds with A and C in a uniform planar geometry. It is successful if the compounds grow slowly so that the barrier maintains the separation of A and C during the life of the application. An application exemplifying the sacrificial barrier is the use of Ti between aluminum and a silicide (PtSi or Pd$_2$Si). Ti reacts with aluminum to form a compound TiAl$_3$ during the heat treatment after the metallization of the silicon. Without a Ti diffusion barrier, aluminum would react with PtSi or Pd$_2$Si leading to the loss of the ohmic contact. In addition to Ti, some other thin metal films such as Ti(10wt%)W, Cr, or Mo may also be used as diffusion barriers during post-metallization annealing [36].
Most investigations of diffusion barriers emphasize aspects of the electrical or mechanical properties. Metallurgical characteristics are seldom presented except for the Auger spectra, Rutherford backscattering spectra, EPMA profiles, etc. Therefore the evolution of the diffusion-induced structural and morphological changes is a seldom explored field of diffusion barriers. Accordingly, an effort to study the interdiffusion behavior in Cu/(Sn-Ni)/Au system by Pinnel and Bennett [40] merits a detailed review.

The base material used by Pinnel et al was 1.55 mm thick OFHC copper with an ASTM grain size of 9. It was cleaned and electroplated on both sides with a 2.5, 5 or 12.5 um thick Sn-Ni alloy. Then a layer of 20 um thick pure gold was electroplated on the 5 um Sn-Ni alloy, while 100 um of gold was plated onto others. Actual thicknesses observed by the optical microscopy were 130 um, 20 um, and 70 um of gold on 2.5 um, 5 um, and 12.5 um Sn-Ni, respectively. Annealing temperatures were 100, 150, 200, 300, 400, and 500 °C for time periods ranging from 25 hours at the higher temperature to one year at the lower temperatures.

Back-scattered electron images, X-ray intensities determined by EPMA, and Auger electron spectra were presented in this study. At higher temperatures, the Sn-Ni layer disintegrated into fine discrete particles within 25 hours at
500 °C for the 12.5 um Sn-Ni barrier. Copper and gold apparently penetrated the Sn-Ni layer and formed a Cu-Au solid solution on both sides of the diffusion barrier.

Some Sn-Ni particles were separated away from the original layer into the copper-rich copper-gold solid solution. Tin rich wave-like stringers were found in the gold layer (Fig 3 in Pinnel's paper), and also at the gold surface. The total amount of Sn existing at the gold surface was greater for thicker Sn-Ni layers. Auger profiles showed that the oxygen signal tracked the Sn signal to as deep as 400 nm for samples annealed at 250 °C.

Pinnel et al presented a plausible mechanism of grain boundary diffusion to interpret the observation of rapid release of tin and rapid diffusion of Au and Cu through Sn-Ni. However, the breakdown of the planar interface through a morphological instability may have served as an accelerating factor for the disintegration of the Sn-Ni diffusion barrier. The AES oxygen signal found at a depth of 400 nm probably resulted from internal oxidation of Sn during annealing in air.

A non-planar interface developed between phases during diffusion at high temperatures is not uncommon in multi-phase, multi-component diffusion couple systems. Diffusion structures developing nonplanar morphologies have been reported in the systems Cu-Zn-Sn, Fe-Cr-Ni [41] and
Cu-Zn-Ni [42] during isothermal annealing. The stability of a planar interface is proposed to be dependent upon the terminal compositions of the couples.

In the system Cu-Zn-Ni, Sisson et al [43] found that the tendency for a non-planar morphology increases with increasing copper concentration in an alpha phase alloy which is interdiffused with the beta phase (Cu/Ni/Zn : 30.3/20.4/49.3 wt%). Diffusion for samples with planar interfaces exhibited slower rates than those with non-planar interfaces. Thus they suggested that the relative magnitudes of the diffusion fluxes of constituent components in adjacent phases should be taken into consideration when analyzing the problem of development of planar vs. non-planar interfaces in multi-component systems.

Wirtz and Dayananda [44] further studied the multiphase Cu-Ni-Zn couples of gamma vs alpha and gamma vs beta at 775 °C. Both the alpha/beta and beta/gamma interphases were observed to undergo transitions from planar to nonplanar configurations. Moreover, the interface compositions were consistent with equilibrium tie-lines for the planar interface case, and different from the tie-line compositions for the nonplanar cases. In addition, a transition from planar to nonplanar and a return to planar morphology were found at the gamma/beta interface as the composition of the beta terminal couple changed from the Cu-Zn binary side towards
the Ni-Zn binary side approximately parallel to the phase boundary.

They concluded that the deviation from tie-line compositions and the formation of nonplanar interfaces may depend upon the direction of individual component fluxes, the relative magnitudes of the fluxes, and the direction of interfacial movement.

One of the most detailed studies on the morphological stability in ternary multiphase diffusion was carried out by Coates and Kirkaldy [45]. They investigated a series of Cu-Zn (alpha) alloys coupled against beta alloys of varying nickel composition, and reported a higher tendency for morphological instability when the nickel concentration in the beta alloy increased in a direction approximately parallel to the alpha+beta/beta phase boundary. They claimed good agreement between the experimentally observed transition and the transition predicted on the basis of "linear perturbation theory" [46].

2.8 PERTURBATION THEORY

The perturbation theory of interface stability was first applied in the case of oxidation of alloys involving noble metals by Wagner [47] in 1956. In the period of 1963 to 1965, Mullins and Sekerka [48], [49], [50], and Voronkov [51]
also independently developed the perturbation theory as applied to the case of solidification. Later this theory was developed extensively and applied successfully to the case of solid-liquid interfacial morphology. Shewmon [52] also applied this theory to the solid-solid transformation for the decomposition of austenite. A detailed review of perturbation theory can be found in several of Sekerka's articles [53],[54],[55]. The following summarizes the general treatment of this theory according to Sekerka. The equations used for illustration will be for the case of a diffusion controlled solid-solid transformation, as shown in Figure 8.

The equations invoked are: Fick's second law in both the alpha and beta phases,

\[
\frac{\partial^2 C_\alpha}{\partial x^2} = \frac{\partial C_\alpha}{\partial t} \quad \frac{\partial^2 C_\beta}{\partial x^2} = \frac{\partial C_\beta}{\partial t} \quad (31)
\]

and the conservation of solutes at the interface,

\[
\hat{n} \left( C_\alpha - C_\beta \right) \hat{v} = \left( J_\alpha - J_\beta \right) \hat{n} \quad (32)
\]

\[
J_\alpha = - \hat{D}_\alpha \left( \frac{\partial C_\alpha}{\partial x} \right) \quad J_\beta = - \hat{D}_\beta \left( \frac{\partial C_\beta}{\partial x} \right) \quad (33)
\]

\( \hat{n} \): the normal unit vector to the interface.
Figure 8: The binary system with limited solubility, e.g., Cu-Ag
Some boundary conditions are also needed to solve problems in terms of perturbation theory; however, these conditions may vary from case to case, and are not listed here. The general treatment suggested by Sekerka consists of four steps [53]:

(i) An analytical solution for the unperturbed problem, e.g. a smooth interface for planar, spherical, cylindrical geometry, etc. For example assuming a quasi-steady-state solid-solid transformation,

\[
\frac{\partial^2 C}{\partial x^2} = 0
\]

is possible for the description of the diffusion behavior of a system. A typical analytical solution would be

\[
C(X,t) = C_0 + aX
\]

with the constraints

\[
C = C_0 , \quad ( \frac{\partial C}{\partial X} ) = a
\]

applicable at the interface. This solution is also valid in the vicinity of a moving boundary as long as the velocity times a characteristic structural length \( L \) is small compared to the diffusivity, that is \( VL/D \ll 1 \).

(ii) A perturbation, which can be expressed as a sinusoidal wave form,

\[
X = \delta(t) \sin(\omega y) + X_0
\] (34)
where \( \omega = \frac{2\pi}{\lambda} \), and lambda is the extent of the perturbation, is introduced. Since the boundary conditions imposed for this problem are all linear, a more complex perturbation can be built up by superposition of sinusoidal waves. The time derivative of Equation 34 can be compared with the amplitude at \( t=0 \), and defines the quantity

\[
\frac{\delta(t)}{\delta(t)} = \frac{\dot{X}(\omega,t)}{\dot{X}(\omega,t)} = f(\omega)
\]

Equation 36 can be obtained by the integration of Equation 35 from time equal to 0 to \( t \).

\[
X(\omega,t) = X(\omega,0) e^{t f(\omega)}
\]

Here, \( X(\omega,t) \) increases exponentially with positive \( f(\omega) \), and decreases with negative \( f(\omega) \).

(iii) For a perturbed interface the governing equation becomes,

\[
\frac{\partial^2 c_a}{\partial x^2} + \frac{\partial^2 c_a}{\partial y^2} = 0 \quad \frac{\partial^2 c_\beta}{\partial x^2} + \frac{\partial^2 c_\beta}{\partial y^2} = 0
\]

with the assumption of quasi-steady-state behavior, i.e. slow interface movement and a time-independent concentration profile. The boundary conditions can be set as follows,

\[
C(o,t) = C_o
\]
(B) \( \left( \frac{\partial c^\alpha}{\partial x} \right)_{x=0} = G^\alpha \); \( \left( \frac{\partial c^\beta}{\partial x} \right)_{x=0} = G^\beta \)

when \( x \rightarrow \infty \), that is, the perturbation gradually vanishes in the region away from the interface. To satisfy these boundary conditions, the trial solutions for Equation 37 may be chosen as,

\[
C^\alpha = C^\alpha_0 + G^\alpha X + A e^{-\omega x} \sin(\omega y) \tag{38}
\]

\[
C^\beta = C^\beta_0 + G^\beta X + B e^{-\omega x} \sin(\omega y) \tag{39}
\]

where \( A, B \) are constants; \( G^\alpha \) and \( G^\beta \) are gradients at the interface.

(iv) Particular boundary conditions, which may vary from case to case, are substituted into Equation 38 and Equation 39 so that one can solve for \( G^\alpha \) and \( G^\beta \) as in the case treated by Coates & Kirkaldy. Then \( A \) and \( B \) can be solved by plugging Equation 38 and Equation 39 into a equation describing the conservation of solute during diffusion-controlled interface movement, that is, an equation with the form [46],

\[
\vec{n} (c^\alpha - c^\beta) \vec{v} = -\vec{\nabla} \cdot \vec{D} \nabla \ln \tilde{N} \tag{40}
\]
Here $Ca$ and $Cb$ are the solubility limits, and $v$ is the velocity of the perturbed interface. We note that

$$\dot{v} = \frac{dX}{dt} = \delta(t) \sin(\omega_y) + v$$

and

$$X = \delta(t) \sin(\omega_y) + X_0$$

where $v$ is the velocity of the unperturbed interface. The above outlined procedures involve a great deal of algebraic manipulation which may vary from case to case. Some good examples are found in the early work done by Sekerka, Shewmon, and Kirkaldy [53],[46],[52]. However the final goal is always to obtain an expression for $\dot{\delta}/\delta$.

This can usually be achieved by equating $v$ to one of the expressions for the mass conservation equation Equation 32 after the constants in Equation 38 or Equation 39 have been evaluated. After gathering all the terms which involve $\sin(\omega x)$, one can equate the coefficients of $\sin(\omega x)$ to $\dot{\delta}$. Then the ratio of $\dot{\delta}/\delta$ can be examined and tested to deduce the conditions that cause $f(\omega)$ to be greater than zero, and hence cause a perturbation to grow into a morphological instability.
Chapter III
EXPERIMENT

3.1 SAMPLES

Two types of specimens were used, disks and foils. Copper and nickel disks, used as end couples, were cut from MARZ-grade zone-refined rods. Each measured 2 mm in thickness and 10 mm in diameter. Silver disks for barrier layers from 0.2 mm to 2 mm thickness were also cut from a MARZ-grade rod. The thinner silver 99.99% sheets for barrier layers were purchased from Alfa. Thin foils from 25 um to 100 um in thickness were cut from the sheets. Before diffusion annealing at the desired temperature of 760 °C, all separate parts of the samples were annealed in a 5% H$_2$/N$_2$ mixture of gases for 48 hours at 745 °C, 748 °C, and 960 °C for copper, silver, and nickel, respectively.
3.2 EQUIPMENT

The furnace system shown in Figure 9 was used for annealing the diffusion triples. The main body of the system consisted of the reaction chamber, heating furnace, temperature controller, and gas cleaning train. The reaction chamber was made up of a 23mm ID, 36 in long quartz tube enclosed in an open-ended mullite tube, 32mm in diameter. This reaction chamber was sealed with Pyrex ground joints on both ends. These two joints were mounted with Cajon Ultra-torr adapters, and tees. One of the tees was connected to the gas cleaning train, and another exhausted into the air. Adapters equipped with Viton O-rings allowed 3.2 mm metal sheathed K-type thermocouples to slide freely in and out without losing vacuum. Both ends of the reaction chamber were valve-controlled so that the gas cleaning train could be used to flush another reaction chamber.

The gas cleaning train was made up of Chemalog R3-11 catalyst deoxidizer, drierite, copper turnings, and Linde 4A molecular sieves. Of these substances, R3-11 and copper light turnings heated at 180 °C were used to deoxidize, drierite was used to demoisturize, and molecular sieves were used to adsorb larger gas molecules and for dehydration. The temperature controller was a Leeds & Northrup, model Electromax V current-adjusting proportional controller.
Figure 9: The furnace system for annealing diffusion triples
Other equipment used in this study included:

1. A Buehler Isomet slow-speed diamond saw used to cut the samples so as to reduce deformation as much as possible.

2. A JEOL JXA-35 X-ray microanalyzer equipped with an auto-stage system and an EDAX SW9100 computer system for on-line energy dispersive X-ray analysis.

3. A Syntron vibrating lapping machine made by FMC Corporation used to polish and remove the deformed layer on the sample surface.

4. Molybdenum sample holders, shown in Figure 10, used to hold the diffusion triple together during diffusion.
Figure 10: Molybdenum sample holder used for annealing diffusion triples
3.3 PROCEDURE AND MEASUREMENT

3.3.1 Sample Preparation

After a pre-anneal to relieve work hardening and obtain larger grains, the as-received sample rods were cut into desired sizes, e.g., 2 mm thick for copper and nickel, 1 mm thick for silver. These disks were mounted in a polishing holder shown in Figure 11 with Krazy glue; later they could be removed by immersion overnight in acetone.

The mounted samples were first ground on a 600 grit Buehler Carbimet paper, then polished with 1 μm diamond paste on the Syntron machine. The final polish was done on microcloth with 0.3 μm Linde B alumina powder. The polishing procedure was designed to make the sample surfaces as smooth and parallel as possible. This care ensured a good contact of the sample surfaces during diffusion. For silver foils, because of the difficulty in handling, only the 100 μm thick foils were polished with 1 μm diamond paste on a microcloth. During the diffusion annealing, diffusion triples with a silver layer sandwiched by copper and nickel disks were clamped together in the molybdenum holder shown in Figure 77. Copper, nickel and silver all have larger linear thermal expansion rates than molybdenum; consequently, they were forced into intimate contact. The
Figure 11: Polishing sample holder for members of diffusion triple.
diffusion could then proceed without retardation brought about by poor contact.

3.3.2 Diffusion Annealing

Before insertion of the sample holder the furnace was preheated to 760 °C, while a 5% H₂/N₂ mixture was flushed through the reaction chamber. Then the system was pumped to a low vacuum. This cycle was carried out three times; after the last cycle, about 2/3 atm of a 5% H₂/N₂ mixture gas was introduced into the system. Just before insertion of the diffusion triples, the gas mixture was pumped out, and prepurified argon gas was slowly backfilled into the chamber through the gas cleaning train. This pre-purified argon gas was maintained at a pressure slightly lower than 1 atm during the annealing.

In order to insert the sample holder without breaking the vacuum seal, the sample holder was placed inside the ground joint prior to the above procedure. An Inconel sheathed K-type chromel/alumel thermocouple passing through an Ultra-torr adapter was connected into a 3.2 mm hole at the bottom of the sample holder. A lubricated O-ring in the adapter allowed the sample holder, which was connected to the thermocouple, to be pushed into or out of the reaction chamber. Because the eutectic temperature of the
Cu-Ag binary system is about 779 °C, the insertion of the sample holder had to be done carefully to limit the temperature overshooting necessary to compensate for the temperature drop. This was made possible with a well-tuned Electromax V controller whose microprocessor combined the functions of reset, rate and proportional band, and was able to limit the overshooting to a maximum of 9 °C. Likewise, the temperature fluctuation during annealing could be controlled within ±0.5 °C.

The removal of the sample holder was done by a quick withdrawal of the thermocouple connected to it. To avoid damage to the O-ring, the thermocouple was withdrawn in two steps at an 1 min interval. A cooling fan was utilized to cool the Cajon adapter. The temperature of the sample holder dropped to 400 °C in about 1 min. After the temperature dropped to 50 °C, argon gas of one atm was admitted to the reaction chamber; then the tapered ground joints could be easily opened.

### 3.3.3 Measurement

Diffused triples were sectioned parallel to the diffusion path into halves after annealing. One half was mounted with Buehler Phenolic powder with the exceptions of run CAN-19 and run CAN-20. The diffusion triple of run CAN-19
was subjected to further diffusive annealing after each examination. CAN-20 was again sliced parallel to the Ag-Cu interface on the copper side so that the silver layer which was nearly perpendicular to the diffusion path could be examined.

A JEOL JXA-35 microanalyzer was used to examine sample morphologies, as well as to measure the concentration profile in the diffusion zone. In addition to secondary electron images, dot map X-ray images were also taken to verify the distribution of elements. Concentration profiles were measured perpendicular to the Ag-Cu interface. An autostage attached to the sample stage of the JXA-35 could move the stage by steps of 1 micrometer unit. The coordinates read from the autostage were fed into a BASIC program to compute the unit vector perpendicular to the Ag-Cu interface. Then the relative coordinates of each measured spot along the direction of concentration profile were calculated and entered into the stage table of the SW9100 system. These coordinates were chosen so that the spots were equally spaced with the intervals of 5 μm, 10 μm, and 20 μm, for the regions within 100 μm from the interface, between 100 μm and 200 μm, and between 200 and 300 μm, respectively. Consequently the EDAX SW9100 could be configured to record spectra automatically via a JOB mode. The interfacial compositions were not measured
directly, but instead extrapolated from the fitted data because the limit of the X-ray spacial resolution, resulting from the X-ray generation volume, is about 2 μm for Cu Kα in Cu [56].

Before starting each JOB of SW9100, the column alignment and beam alignment for the JXA-35 were adjusted. If further adjustment was necessary during the course of measurements, another set of the standard spectra would be taken for the rest of the unknown spectra. These spectra were stored in diskettes for later quantitative analysis.

This study primarily utilized the Conventional Standard Mode (CONV) of quantitative analysis available in the SW9100 system. This mode employs the FRAME on-line electron probe microanalysis software initially developed by Yokowitz et al at the National Bureau of Standards in 1973 [57]. Some of the profiles were checked by the non-standard mode (NOST). For the conventional mode, standard spectra were measured together with all unknown spectra of each profile.

The fluctuation of beam current is critical to the accuracy of the quantitative mode (QUAN). Because the JXA-35 is not equipped with a beam current monitor, the combination of the specimen current taken from the AEM meter, and the CPS counts from EDAX were used to monitor the stability of the beam current.
Chapter IV
DATA REDUCTION

The raw data for a concentration profile generated from EDAX inevitably had some irregular distribution resulting from the experimental and equipment errors. In addition, a function to describe the relation between concentration and penetration distance was necessary for later numerical calculations of diffusion coefficients and fluxes. A least-square method was used to fit the raw data of concentration with respect to the distance.

A concentration profile, $C$ vs $X$ is shown in Figure 12. This error function type curve is difficult to fit by a single low-order polynomial. Figure 13 shows a probability plot, where $Z$ is the argument of error function, and $X$ is the distance. The plot is obtained by converting $C$ into $Z$ in terms of a general equation,

$$
\frac{C - C^-}{C^+ - C^-} = \frac{1}{2} [1 - \text{erf}(Z)]
$$

This expression is applicable in the case that the diffusion coefficients are independent of concentration. When the diffusion coefficients depend upon both distance and
concentration, the curve could become very intricate. Even the probability plot could conceivably become a complicated curve. Fortunately, for the present studies the probability plot could be fitted piecewise [58] by a series of low-order polynomials. Thus fitting the probability plots was a more accurate procedure than fitting the original concentration profile.

Appendix (A) illustrates the major codes of the program DCHEM and FLUX. Some utility programs are not shown there: these may be obtained from the author on request. The following is merely intended as a brief discussion of the basic schemes employed in this work.

All the raw concentration data were converted to probability plots via a routine called ERFCON. It employs the Newton-Raphson method to iteratively solve the equation,

\[-0.5 + 0.5 \cdot \text{erf}(Z) = 0\]  

(42)

at each measured point X. Since the Z values fall into the range of ±2.5, an initial guess of Z equal to 1 always results in convergence in no more than 3 iterations. The regenerated data set of Z vs X were fed in turn into FITLOS, a least-squares curve-fitting routine. FITLOS is able to fit one data set with up to ten segmented subsets,
Figure 12: Typical Concentration Plot of C vs X
Figure 13: Typical Probability Plot
and smooth the curve at each spline joint point. It imposes the constraints of equal second and first derivatives at spline joints with the use of Lagrangian multipliers. The smooth curve thus obtained has the advantage of segmented curve fitting which enables later numerical calculation of diffusion coefficients and fluxes. Interested readers are referred to the documentations of FITLOS [58] for the detailed operations. This routine has been modified for being called from a main routine [5] by Carlson so that all parameters are passed via the argument list of the subroutine call.

The data for each phase, usually divided into two subsets, was fitted individually because of the discontinuities of the concentration profile at each phase boundary. Therefore each set of data for one phase was loaded through subroutine call of the FITLOS data-fitting program. The output from FITLOS was a set of polynomial coefficients, and corresponding spline joints, that defined the data subset boundaries. An example of output may be obtained from the author. The statistics of fitting can be found in the output. In this study all the spline joints are determined by the FITLOS subprogram that divides the data into two subsets with an equal number of data points. These polynomial coefficients provide subsequent numerical integrations and differentiations for the calculation of the diffusion coefficients and fluxes.
For the purpose of comparison, several subprograms such as DBOLT, DCURV, DETA, and DFUNVM, making use of different schemes were called to compute interdiffusion coefficients. The first routine DBOLT is a numerical translation of the Boltzmann-Matano method [3], [4]. Before calling DBOLT, the Matano interface $X_m$ was computed according to Equation 8 or Equation 9. Then $X_m$ was passed via the argument list. The integral part of Equation 1 as expressed in Equation 12 was evaluated through an intermediate function FAREA which, in turn, called a numerical integration subprogram - QUANC8. Because of the nature of the curve-fitting program FITLOS, integrations were done for each fitted segment individually, and finally totaled.

QUANC8, quadrature adaptive Newton Cotes' 8-panel, was introduced by Forsythe et al [59]. It must be supplied with a external function $\text{FUN}(x)$ for the integrand $f(x)$ in QUANC8, the lower and upper limits of integration $A$ and $B$, and the absolute and relative error tolerance. Roughly speaking, $f(x)$ is the function for which some derivative $f^k$ of $x$ with $k \leq 10$ neither is unbounded nor fails to exist. It is based on a piecewise polynomial approximation, and hence is not designed to handle certain kinds of integrals. Apart from these restrictions, QUANC8 is fast and suitable for fitting the curves encountered in this work.
The slope \(\frac{dC}{dX}\) at \(X_{\text{STAR}}\) was calculated from the polynomial functions fitted by FITLOS. Taking the derivative of Equation 41, \(\frac{dC}{dX}\) can be expressed as

\[
\frac{dC}{dX} = \frac{(C^+ - C^-)}{\sqrt{\pi}} \exp(Z^2) \frac{dZ}{dX}
\]

Since \(Z(x) = a + bX + cX^2 + dX^3\) in one subsegment of the curve of \(C\) vs \(X\), the derivative of \(Z(X)\) is

\[
\frac{dZ}{dX} = b + 2cX + 3dX^2.
\]

Substituting \(\frac{dZ}{dX}\) in Equation 43 gives the slope at \(X = X^*\)

\[
- \frac{(C^+ - C^-)}{\sqrt{\pi}} \exp(Z^2) \left( b + 2cX + 3dX^2 \right)
\]

The second subprogram called is DCURL which used the SFW equation to calculate the diffusivity in a volume fixed reference frame. It must be pointed out that \(C_{\text{MIN}}\) and \(V_{\text{MIN}}\) in the program are always declared as the concentration and molar volume at the minimum \(X\) \((X = X^-)\) position. This is the left-most position of the concentration profile in the copper phase in our work. On the other hand, \(C_{\text{MAX}}\) AND \(V_{\text{MAX}}\) are the quantities at \(X = X^+\). In this way, the SFW equation can handle both the cases when the concentration profile is ascending or descending with increasing \(X\).
However, for the descending case, the reduced concentration $Y$ is different from the usual definition and becomes $Y' = (C - C_{\text{max}})/(C_{\text{min}} - C_{\text{max}})$ which is $(1-Y)$ for the usual case. DETA used the formula of Equation 27 to calculate the chemical diffusivity in the volume-fixed frame so it should be equivalent to the result obtained from DCURL. The last subprogram utilized the method employed in DBOLTZ but with the concentration $C$ vs $X$ instead of $N$ vs $X$. This routine should serve to provide an estimation of the error arising from the assumption of constant molar volume when calculating the chemical diffusivities.

A slightly modified DCURL can be used to compute the fluxes for each component according to the equations introduced by Kirkaldy [60],[61] The program FLUX was thus formulated by using the equation,

$$J_i = -\frac{1}{t} \left[ \frac{1}{2} \int_{X-}^{X+} (1 - Y) \, dX + Y \int_{X-}^{X+} (1 - Y) \, dX \right] (45)$$

and used to estimate the fluxes of each component, i.e. Cu, Ag, Ni in this study.
Chapter V
RESULTS AND DISCUSSIONS

This section is divided into four major parts. Part one is the chemical diffusivity measurement for the Cu-Ag binary system, part two includes the morphological observations and concentration profiles, part three discusses the experimental results, and part four presents a proposed model for the breakdown of the Ag blocking layer.

5.1 DIFFUSIVITY MEASUREMENT

5.1.1 Test of the DCHEM program

Before presenting the experimental results, the program DCHEM used to calculate the chemical diffusivities was tested. To test the reliability of DCHEM, Carlson's original data for the Ti-V binary system were used as dummy data input [5]. The output of DCHEM presented in Figure 14 were, then, compared with the Carlson's results. In particular, the effect of varying molar volume was studied. Vegard's law was assumed for calculating the molar volume.
There is only about a 3% difference in the diffusivities calculated with or without the assumption of constant molar volume in this system. However, the Matano interfaces, XBM and NBM, calculated by DCHEM were found to differ significantly. Specifically NBM, equal to 489 μm, is the Matano interface calculated for a Fick reference with the assumption of constant molar volume, while XBM, equal to 442 μm, is the Matano interface calculated for a volume-fixed reference. The Matano interface EBM, for a mole-fixed reference frame with N vs $\xi$, is 52.988 (μm mole/cm$^3$).

From Figure 15, the plot for converting $\xi$ to X (cm), the Matano interface EBM corresponds to 479 μm in the X coordinate.

The difference of NBM and EBM is 10 μm which is barely significant. Darken's analysis, used by Carlson to compute the intrinsic diffusivities, employed the equations which are applicable in a mole-fixed reference frame. Consequently, one can expect that ignoring the molar volume change in this system will be insignificant to the values of intrinsic diffusivities as well.

This might appear confusing, since there is a large discrepancy between XBM and NBM, but the following is a rationalization for this point. Firstly, there is a relative movement between the mole-fixed frame and the volume-fixed frame. Secondly, the equations used to
Figure 14: The output data of DCHEM program. The input input data was selected from Carlson's report.
Figure 15: The plot for conversion of ξ to X.
compute intrinsic diffusivities in a volume-fixed frame are different from those used in the mole-fixed reference frame. The former equations are those for the marker velocity $v_m'$,

$$v_m' = V_2 (D_2 - D_1) \left( \frac{dC_2}{dx} \right)$$

and the chemical diffusivity $D$,

$$D = C_2 V_2 D_1' + C_1 V_1 D_2'$$

If a constant molar volume $V_1 = V_2 = V_m$ is assumed, then

$$D = C_1 V_m D_1' + C_2 V_m D_2' = N_1 D_2' + N_2 D_1'.$$

This equation is equivalent to Darken's equation. On the other hand, a varying molar volume would result in a relation,

$$D_1' = V_m/V_2 D_1$$

where $D_1$ is the intrinsic diffusivity in the mole-fixed reference frame, and $D_1'$ is the intrinsic diffusivity in the volume-fixed reference frame. In other words, different intrinsic diffusivities would be expected.

On the basis of Equation 46 and Equation 47, we can calculate the intrinsic diffusivities in a volume-fixed reference frame. According to Carlson's data, the marker plane was located at 426 μm; the annealing time was 86400 seconds. The data acquired from DCHEM are:
the marker plane concentration equals 0.38009 molar fraction;
the marker velocity \( v_m' = \frac{\Delta X}{2t} \), and hence
\[ v_m' = \frac{(426-442) \times 10^{-4}}{2 \times 86400} = -9.25 \times 10^{-9} \text{ cm/sec}; \]
\[ D = 0.1048 \times 10^{-7} \text{ cm}^2/\text{sec}; \]
\[ V_v (\text{partial molar volume for vanadium}) = 8.35 \text{ cm}^2/\text{mole}; \]
\[ V_{Ti} = 10.6 \text{ cm}^3/\text{mole}; \]
slope \( \frac{dC}{dX} = -0.9546 \text{ mole/cm}^4. \]

Solving the Equation 46 and Equation 47 simultaneously as follows:

\[ -9.25 \times 10^{-9} = 8.35 \times (D_v' - D_{Ti}') \times (-0.9546) \]
\[ 0.1048 \times 10^{-7} = 0.3256 D_{Ti} + 0.6744 D_v' \]
\[ 1.1605 \times 10^{-9} = D_v' - D_{Ti}' \]
\[ 3.2187 \times 10^{-8} = D_{Ti}' + 2.0712 D_v' \]

we obtain \( D_v' = 1.086 \times 10^{-8} \) and \( D_{Ti}' = 0.920 \times 10^{-8} \) cm\(^2\)/sec.

By using the relations between intrinsic diffusivities, we can further calculate \( D_v \) and \( D_{Ti} \) as follows:

\[ D_v = D_v' \times \left( \frac{V_{Ti}}{V_m} \right) \]
\[ = 1.086 \times 10^{-8} \times 10.6/(0.32 \times 8.35 + 0.68 \times 10.6) \]
\[ = 0.1165 \times 10^{-7} \text{ cm}^2/\text{sec}, \text{ and} \]

\[ D_{Ti} = D_{Ti}' \times \left( \frac{V_v}{V_m} \right) \]
\[ = 0.92 \times 10^{-8} \times (8.35/9.88) \]
\[ = 0.7775 \times 10^{-8} \]

From Carlson's results,
$D_V'' = 0.12242 \times 10^{-7}, \quad D_{Ti}'' = 0.79781 \times 10^{-8}$.

As can be seen, the difference between $D_V$ and $D_V''$ is less than 3% which is within the experimental error.
Figure 16: The plot for diffusivities in Cu-Ni binary alloy system. The figure shows the dependence of diffusivity on copper concentration for Cu-Ni binary system. [19]
5.1.2 Diffusivity Measurements

The Cu-Ag and Cu-Ni binary systems both are well investigated. The chemical diffusivities in the Cu-Ni solid solutions have been studied in the temperature range from 710 °C to 1066 °C [19],[62] across the entire composition range. These data, shown in Figure 16 and Figure 17, demonstrate a significant dependence on copper concentration. This is conceivably caused by the large difference in tracer diffusivities for Cu in Ni and Ni in Cu, which are \(8.81 \times 10^{-14} \text{ cm}^2/\text{s}\) and \(3.00 \times 10^{-12} \text{ cm}^2/\text{s}\) at 760 °C, respectively [19]. In Figure 17 the chemical diffusion coefficients increase more rapidly at higher copper contents, greater than 60 at%, because of an increase in solid solution lattice energy [62].

There have been many investigations of interdiffusion coefficients in the Cu-Ag binary system. Discrepancies among them, particularly in the dependence of interdiffusion coefficients on Ag concentration, indicate that further investigations are needed. Two pure copper and silver disks held in a traditional sandwich type diffusion couple were used for this purpose. After diffusion annealing for 2 days, 4 days, and 6 days, concentration profiles were acquired by using the EDAX SW9100 system. The computer program DCHEM, discussed before, was employed to compute the chemical diffusivities. The results are shown
Figure 17: The plot for diffusivities in Cu-Ni binary alloy system. The figure shows the rapid increase of the dependence of the diffusivity on copper concentration for Cu-Ni binary system. [62]
in Figure 18 and Figure 19, accompanied by the previous results [19].

The trend of the concentration dependence is in agreement with the results by Oikawa et al [63] on the Cu-rich side. The unreliable experimental data near the phase boundary were replaced by the extrapolated data. The data are apparently scattered within a range; nevertheless, the average values of the chemical diffusivities agreed with the values commonly used [64]. Since the Cu-Ag binary phase diagram exhibits a miscibility gap, the solubility limits being 4 at% Ag in Cu and 87 at% Ag in Ag, the diffusion couples always have a large discontinuity gap in the concentration profile. The diffusivity measurement for this kind of system, an incremental diffusion couple with small composition difference, is considered more appropriate than for the diffusion couples consisting of the pure end members [7]. This can be realized when one considers the dimensional change of the system caused by the abrupt change of molar volume in the vicinity of the Ag-Cu interface. The use of the pure end couples may account for the scattering of the data with respect to the concentration in this study. An incremental diffusion couple may reduce the scattering induced by experimental errors.
Figure 18: The interdiffusion coefficients for copper-rich phase.
Figure 19: The interdiffusion coefficients for Ag-rich phase.
5.2 CONCENTRATION PROFILE AND MORPHOLOGICAL OBSERVATIONS

For those samples with a silver layer of 400 μm thickness, copper is still undetectable near the Ag-Ni interface after annealing for 10 days. The silver layer of run CAN-11M then was reduced to 200 μm, and the diffusion triple was annealed at 760 °C for 4 days. About 3.2 at% of copper was found in the Ni phase at the Ag-Ni interface. However, the morphology remained unchanged, with sharp interfaces maintained as originally, except that the Ag-Cu interface moved towards the Cu phase and the Ag layer was thickened accordingly. Therefore, Ag foils of 100 μm and 25 μm thickness were chosen as the intermediate layers between Cu and Ni end members for studies of the concentration profiles and the morphology. These samples were annealed at 760 °C for time periods ranging from 12 hours to 31 days. Table 2 and Table 3 summarize the heat treatment histories of these samples.

The morphologies of the intermediate layers were observed in the SEM using the secondary electron image, while the concentration profiles were measured with the EDAX SW9100 system. For the EDAX measurement, the specimen current was about $2.0 \times 10^{-10}$ amp, the rate setting was about 3000 CPS for the pure silver standard, the total counting (life) time was set at 200 sec. X-ray maps were taken to check the distribution of elements for some of the samples.
Table 2

The Heat Treatment History for 100 μm Sample

<table>
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<th>Annealing</th>
<th>Conc</th>
<th>Pictures</th>
</tr>
</thead>
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<td></td>
<td>Thickness(μm)</td>
<td>Time (Days)</td>
<td></td>
<td>Profile</td>
</tr>
<tr>
<td>CAN-19-1</td>
<td>99.1</td>
<td>1 day</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>CAN-19-2</td>
<td>99.1</td>
<td>2 days</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>CAN-19-3</td>
<td>99.1</td>
<td>3 days</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>CAN-19-4</td>
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<td>No</td>
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<td>CAN-12M</td>
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<td>5 days</td>
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<td>Yes</td>
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<td>CAN-13M</td>
<td>101.6</td>
<td>6 days</td>
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</tr>
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* Pre-annealing: Ag : at 748°C for 48 hours.
  Ni : at 960°C for 48 hours.
  Cu : at 745°C for 48 hours.
Table 3
The Heat Treatment History for 25 μm Sample

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<td>CAN-33M</td>
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<td>CAN-20-4</td>
<td>30.0</td>
<td>4 days</td>
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<td>No</td>
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<tr>
<td>CAN-34M-5</td>
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<td>30.0</td>
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<td>CAN-34M-5</td>
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<td>CAN-27M</td>
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<td>CAN-31M</td>
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<td>15 days</td>
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</table>

* Pre-annealing: Ag : at 748°C for 48 hours.
  Ni : at 960°C for 48 hours.
  Cu : at 748°C for 48 hours.

5.2.1 Ag Layer of 100 μm Thickness

After annealing for 1 day, the composition of copper at the Ag-Ni interface in run CAN-19-1 reached 6 at% as indicated in Figure 20. But there was no detectable copper found in the Ni phase. The morphology given in Figure 21 shows clear, sharp interfaces for run CAN-19-1, and there were no morphological changes except for the thickening of silver layer and the shift of the 1 μm Al₂O₃ markers towards the Ag phase relative to the Ag-Cu interface. The markers remained approximately at the estimated B-M interface.
because of the small difference of the intrinsic diffusion coefficients and short annealing time. The movement of the Ag-Cu interface is the consequence of the larger flux from the Ag phase across the interface. The shift rate of the Ag-Cu interface in a finite geometry has been studied by Tanzilli and Heckel [64]. They found a reversal of the movement after the concentration gradient in the finite geometry become lower than a threshold value.

For run CAN-19-2, a 2-day sample, about 30 at% Cu was found in the Ni phase, and 8 at% Cu in the Ag phase at the Ag-Ni interface, as shown in Figure 22. The values for the limiting concentration of copper at the Ag-Ni interface were extrapolated by the equations fitted by FITLOS.

In Figure 23, the morphology for run CAN-19-2 is similar to the case of run CAN-19-1, and both interfaces remained clearly planar. In Figure 24 the compositions of copper at the Ag-Ni interface for run CAN-19-3, which had been annealed for 3 days, were found to be about 8 at% Cu in Ag and 60 at% Cu in Ni. However, the planar interface of the Ag-Ni interface developed a degree of instability for this diffusion triple as can be seen in Figure 25. A few ripples were found at the Ag-Ni interface, while the Ag-Cu interface still remained planar.

For samples annealed less than 3 days, the Ag layers were thickened by the movement of the Ag-Cu interface. The
Figure 20: The profile for sample with 100 μm Ag treated at 760 °C for 1 day.
Figure 21: The morphology of 100 μm Ag sample treated at 760 °C for 1 day. The interface remains clearly planar.
Figure 22: The profile of Cu for the 2-day 25 μm Ag sample treated at 760 °C.
Figure 23: The morphology of 100 μm Ag sample treated at 760 °C for 2 days.
Figure 24: The profile of Cu for 100 µm Ag sample treated at 760 °C for 3 days.
Figure 25: The morphology of 100 μm Ag sample treated at 760 °C for 3 days. It demonstrates a rippled Ag-Ni interface.
rate of movement can be estimated by a finite-difference simulating program developed for this study. This program may handle the case of the diffusion triple with varying diffusivities if the dependence of the diffusivities upon concentration is known and the interface remains planar. As copper arrives at the Ag-Ni interface, a ternary system is introduced in the vicinity of the interface. However, the program only considered the copper flux because it was the only mobile species at the interface. This may slightly simplify the situation; nevertheless, additional diffusivities, the off-diagonal terms, are still needed in order to calculate the fluxes at the interface for the ternary system. The program utilized a scheme similar to that employed by Johnson, Lanam and Heckel [65] [66], as initially introduced by Murray and Landis [67] in 1959.

In Figure 26, some protruding fingers from the Ni phase in addition to a wavy Ag-Ni interface were first observed for run CAN-19-4, which had been annealed for 4 days. Figure 27 shows the morphology of the Ag-Ni interface of CAN-12M which was also annealed for 4 days. It exhibits a morphology similar to those found for run CAN-19-4. The concentration profile of copper for run CAN-12M in Figure 28 shows about 9 at% Cu in Ag and 70 at% Cu in Ni at the Ag-Ni interface.
Figure 26: The morphology of 100 μm Ag sample treated at 760 °C for 4 days. The protrusions can be observed at the Ag/Ni interface.
Figure 27: Another sample with 100 μm Ag layer treated at 760 °C for 4 days.
Figure 28: The profile of Cu for 100 µm Ag sample treated at 760 °C for 4 days.
Figure 29: The sample with 100 μm Ag layer treated at 760 °C for 5 days. The sidewise growth of finger-like protrusions was observed in the sample.
In Figure 29, after an anneal for 5 days, the finger-like protrusions found for run CAN-19-5 demonstrate an obvious sidewise growth which left some patches of Ag enclosed by protrusions. These Ag patches were found to be enclosed by the fingers of the Cu-Ni solid solution. Figure 30 shows the X-ray map for silver at the Ag-Ni interface for run CAN-19-5, providing evidence that the white patches in Figure 31 are the silver phase. Figure 32 shows the concentration profile of copper and demonstrates a further buildup of copper in the Ni phase at the interface. The limiting concentrations were about 8 at% Cu in Ag and 80 at% Cu in Ni.

Figure 33 shows sample CAN-13M which was annealed for 6 days. The fissures behind the Ag-Ni interface were identified as the 1 um Al₂O₃ markers placed at the Ag-Ni interface before annealing. The markers have obviously moved towards the Ni-side relative to the Ag-Ni interface but have a locus following the contour of the non-planar Ag-Ni interface as shown in Figure 34. Figure 35 is the concentration profile of copper for run CAN-13M, with limiting concentrations of 9 at% Cu in Ag and 87 at% Cu in Ni.

After an 8-day anneal, some apparent Cu-Ni islands with an average composition of about 80 at% Cu were developed along the Ag-Ni interface. The concentration profile is shown in Figure 36. Apparent islands were observed, as
Figure 30: The silver X-ray map for the sample shown in Figure 31.
Figure 31: The SEM image taken at the same area as Figure 30.
Figure 32: The profile of Cu for the sample treated at 760 °C for 5 days.
Figure 33: The morphology of the sample treated at 760 °C for 6 days. More finger-like Cu-Ni protrusion found at the Ag-Ni interface.
Figure 34: An enlarged view of markers outlining the non-planar Ag-Ni interface
Figure 35: The profile of Cu for 100 μm Ag sample treated at 760 °C for 6 days.
illustrated in Figure 37, and occupied some areas in front of the Ag-Ni interface. These apparent islands are associated with the Ni phase via a 3-dimensional continuous network of Cu-Ni solid solution, and they are merely the extensions of the initial finger-like protrusions. After a 15-day anneal, the morphology shown in Figure 38, similar to that of the 8-day sample, was observed. But it appears that more apparent islands were formed. Figure 39 presents the concentration profile of copper for this specimen.

The apparent islands shown in the figures represent only part of the tortuously developed 3-dimensional branches of the Cu-Ni solid solution. Initially the finger-like protrusions grew forward; these branches later were forced to swing sidewise. A similar development took place everywhere along the Ag-Ni interface so that many mushroom-like protrusions were formed 3-dimensionally on the Ag-Ni interface at a later period. Accordingly, these discrete islands are merely the 2-D display of the 3-D network of these protruded Cu-Ni alloy branches rooted at the Ag-Ni interface.

Upon further annealing of the triples for 20, 25 and 31 days, the basic morphology and concentration profiles appeared more or less the same, e.g., tortuously developed fingers with some apparent islands, and average interface compositions of about 11 at% Cu in Ag and 85 at% Cu in Ni.
Figure 36: The profile for 100 μm Ag layer treated at 760 °C for 8 days.
Figure 37: The sample of 100 μm Ag layer treated at 760 °C for 8 days. The morphology shows the apparent islands formed in Ag phase.
Figure 38: Sample with 100 μm Ag was treated at 760 °C for 15 days. More apparent islands formed in the sample.
Figure 39: The concentration profile of Cu for 15-day, 100 μm Ag specimen.
From observations of these apparent islands, it appeared that every apparent island is connected to others or to the Ni phase through a necked root. The average distance from the protrusion to the Cu phase became shorter.

Figure 40 to Figure 48 show typical morphologies and the corresponding concentration profiles for these samples. The copper concentration profile traversing one protrusion, given in Figure 43, is compared with another, shown in Figure 44, which plainly traverses in the Ag phase. The average concentration of the protrusion is about 78 at% Cu. The slope of the former profile is greater than the latter one, which does not across a protrusion.

Figure 40 and Figure 46 are the enlarged views of the sidewise-grown protrusions. In Figure 40 the stems of the apparent island from the Ag-Ni interface cannot be observed in this cross section, while in Figure 46 the stems are clearly seen connecting to the Ag-Ni interface and branching sidewise into the Ag phase. One branch even tortuously grew and touched the Ag-Ni interface. A similar mechanism may take place repeatedly along the Ag-Ni interface as discussed above. Therefore, we can depict a 3-D picture of this development as having a resemblance to mushrooms rooted on the Ag-Ni interface.

Figure 47 and Figure 48, respectively, are the concentration profiles which were measured with or without encom-
Figure 40: Sample of 100 μm Ag treated at 760 °C for 20 days.
Figure 41: The profile for triple with 100 µm Ag treated at 760 °C for 20 days.
Figure 42: Sample of 100 µm Ag treated at 760 °C for 25 days.
Figure 43: The profile 1 for triple with 100 µm Ag treated at 760 °C for 25 days. The profile of Cu traversing across the apparent island.
Figure 44: The profile 2 for triple with 100 μm Ag treated at 760 °C for 25 days. The concentration profile of Cu is plainly in the Ag phase.
Figure 45: Sample of 100 μm Ag treated at 760 °C for 31 days.
Figure 46: Sample of 100 μm Ag treated at 760 °C for 31 days. An enlarged view for one of the apparent islands.
passing an protrusion for the 31-day specimen. The limiting copper concentrations shown in Figure 47 reached values as high as 12 at% Cu in Ag and 94 at% Cu in Ni. However, the copper composition at the interface is only about 70 at% as presented in Figure 48. This lower value is believed to arise from the fact that the profile is the continuity of the one across the apparent island. This apparent island is so close to the interface that it actually connects to the Ni phase via a hidden connection underneath this cross-section.

Accordingly, the concentration gradient of Cu favors a flux from the planar portion of the interface to the perturbed portion where protruding branches are formed. This also implies that the buildup of copper content at the unperturbed part was eased by this flux at the interface. This extra flux of copper may also enhance the growth of the protrusions since it supplies Cu atoms from the Ni-phase side.
Figure 47: The profile 1 for 100 μm Ag sample treated at 760 °C for 31 days. The concentration profile of Cu encompasses one apparent island.
Figure 48: The profile for 100 μm Ag sample treated at 760 °C for 31 days. The concentration profile of Cu is plainly in the Ag phase.
5.2.2 Intermediate Layer of 25 μm Ag Foil

Thin Ag foils with a 25 μm to 30 μm thickness were used for the study of morphological changes developing from the initial interface instability observed in the case of the 100 μm intermediate silver layer. With 12 hours annealing at 760 °C, the diffusion triple of run CAN-35M started developing the rumpled interface depicted in Figure 49. This is similar to the case found for the 100 μm Ag layer after 3 days of annealing at 760 °C. Although the Ag-Cu interface also showed a wavy configuration, its development of protrusion was probably suppressed by a surface tension effect so that the Ag-Cu interface remained planar. After 1 day of annealing the Ag-Ni interface in Figure 50 started to show many finger-like protrusions similar to those found in the 4-day, 100 μm Ag specimen.

Further annealing caused the fingers to develop into apparent islands and eventually the islands grew and reached the Ag-Cu interface. The 4-day sample shown in Figure 51 had several finger-like stems linked to the Ag-Cu interface, and some widespread apparent islands in the Ag phase. This morphology manifests the onset of the total breakdown of the silver intermediate layer, i.e., the diffusion barrier. The Al₂O₃ markers were placed at the Ag-Cu interface of CAN-34M before annealing. After a 5-day anneal, these markers shifted towards the Ag phase as
**Figure 49:** Sample of 25 µm Ag layer treated at 760 °C for 12 hours. The rippled interface has been developed in the diffusion triple.
Figure 50: Sample of 25 μm Ag layer treated at 760 °C for 1 day. Finger-like protrusions have been observed.
can be seen in Figure 52. The Ag-Cu interface was wavy only at a few spots, but the interface as a whole was still moving in a planar manner. Figure 53 depicts the usual findings that the markers placed at the Ag-Cu interface contour the Cu-Ni protrusions. This phenomenon results from the earlier growth of the protrusions which caused the markers to be pushed away from the Cu-Ag interface by means of the mechanism of Nabarro-Herring creep which results in the deposition of Ag on the Ag-Cu interface. Therefore, the markers in the Ag phase are observed to reside closer to the Ag-Ni interface at locations where no or fewer protrusions developed. This observation is similar to that found in Figure 34 at the Ag-Ni interface where markers had been placed before annealing. These markers, inside the Ni phase, at the valley of the perturbed interface, were also pushed by the deposited Ag because of the Nabarro-Herring creep mechanism.

The sample CAN-20-6, annealed for 6 days, was sliced parallel to the interfaces in the Cu phase near the Ag-Cu interface. The sliced sample was then mounted and polished to reveal a tapered section of the Ag layer. The picture shown in Figure 54(a) is such a section of the Ag layer nearly perpendicular to the diffusion path. It depicts the 3-dimensional links between the Cu-Ni apparent islands distributed in the Ag phase. Figure 54(b) gives the corre-
**Figure 51:** Sample of 25 µm Ag layer treated at 760 °C for 4 days. Some apparent islands were found in this sample.
Figure 52: 5-day sample with 25 μm Ag layer shows markers.
Figure 53: Sample with 25 μm Ag treated at 760 °C for 5 days. The wavy marker plane was observed.
sponding X-ray map of silver in Figure 54(a). This X-ray map demonstrates the growth of the Cu-Ni protrusions tortuously through the Ag-rich phase from the original Ag-Ni interface to the Ag-Cu interface. One may find a few discrete aggregates of Cu-Ni alloy in these pictures. Similar to the cases of the cross-sectional pictures for the Ag layer, this is only the projection of the 3-D Cu-Ni protrusion, so these discrete aggregates are actually linked by some hidden connections.

Further annealing of CAN-34M led to a dramatic change at the Ag-Ni interface. The sample of run CAN-34M-8, annealed for 8 days, demonstrated the breakdown of the Cu-Ag interface. Many "stems" rooted at the Cu-Ag interface were observed as shown in Figure 55. Figure 56 illustrates the origin of these stems. As shown in Figure 56, the stems from the Ag-Cu interface are connected to one long apparent island in the Ag phase. Thus, the last stage of the growth of these peninsular protrusions is believed to have ended in a growth of branches emanating from each peninsula. These peninsula-rooted fingers in turn grew until they touched the Ag-Cu interface.

After a 10 day anneal, as shown in Figure 57, the sample CAN-27M developed a structure consisting completely of intermixed Cu-Ni protrusions in an Ag phase. At this stage, the Cu can diffuse through these Cu-Ni bridges, and
Figure 54: Sample with 25 µm Ag layer treated at 760 °C for 6 days. The morphology and X-ray map for the tapered section of the Ag layer.
Figure 55: Sample with 25 μm Ag layer treated at 760 °C for 8 days. Shows the links to Cu-Ag interface.
Figure 56: Morphology for 25 μm Ag sample treated at 760 °C for 8 days. The stems connected to one long peninsula are rooted at Ag-Ni interface.
the thickening of the Ag layer was slowed. A concentration profile across one of the bridges is presented in Figure 58. About 1.5 at% Ag is found in the Cu-Ni solid solution protrusion when the Cu composition reaches 75 at%. With a higher copper composition the silver content also increases. However, the copper concentration always drops off beyond a distance of about 30 μm deep into the Ni phase from the Ag-Ni interface. The X-ray maps of the sample CAN-20-12 shown in Figure 59 depict the distribution of these elements. In Figure 59(c) and (d), the boundary between the Cu-Ni solid solution and the Ni substrate appear at a depth of about 25 μm in the Ni phase.

Figure 60 shows the morphology of sample CAN-31M which was annealed for 15 days. The thickness change of the Ag layer appears to have stopped. The total disintegration of the Ag layer became more evident. Figure 61 presents the concentration profile of copper across one of the bridges. The slope found is less than that for the profile of the 10-day sample, as shown in Figure 58. However, the penetration depth is still only about 40 μm, regardless of the rising Cu composition at the Ag-Ni interface. This can be attributed to the large difference of diffusivities in the copper and nickel phases, as presented in Figure 78, and the dramatic change in the dependence of diffusivities upon copper composition when copper reaches about 65 at% in
Figure 57: The sample with 25 µm Ag was treated at 760 °C for 10 days. The morphology shows intermixed Cu-Ni alloy bridges.
The concentration profile across one bridge.

- X: Cu profile
- +: Ni profile
- *: Ag profile

**Figure 58:** The 25 µm Ag sample was treated at 760 °C for 10 days. The concentration profile of Cu was measured across one bridge.
Figure 59: The X-ray map for the sample with a 25 μm Ag layer treated at 760 °C for 12 days.
a Cu-Ni solid solution, is also shown in Figure 17. This large difference and dramatic change in the dependence result in a buildup of copper at the Ag-Ni interface, and the attendant limited penetration of copper into the Ni phase. Apart from the above reason, copper also tends to diffuse from the high concentration sites to the low concentration region, as found in Figure 47 and Figure 48, where the protrusions have been formed. Therefore the growth of the Cu-Ni protrusions was subjected to the Cu flux entering not only from the front, but also from the stem because of this Cu composition gradient.
Figure 60: The 15-day sample with 25 μm Ag layer was treated at 760 °C.
The sample with 25 μm Ag was treated at 760 °C for 15 days. The concentration profile of Cu across one of the bridges.
5.3 DISCUSSION OF EXPERIMENTAL RESULTS

5.3.1 The interface concentration

The interface concentrations of copper were found to increase with annealing time until about 8 days; thereafter, the concentrations remained constant at about 12 at% Cu in Ag and 90 at% Cu in the Ni phase. Figure 62 plots the limiting interface concentrations of Cu with respect to annealing time. No silver was found in the Cu-Ni solid solution adjoining the Ni phase until the copper content reached about 65 at% at the interface.
Figure 62: The limiting interface concentration of Cu vs annealing time.
5.3.2 A tentative ternary partial phase diagram for the Cu-Ag-Ni system at 760 °C

From the data for interfacial compositions presented in Figure 58 and Figure 61, a tentative partial ternary phase diagram for the Cu-Ag-Ni ternary alloy system at 760 °C is proposed as schematically illustrated in Figure 63. Along the Cu-Ni binary, the Ag concentration is undetectable by EDAX in the Cu-Ni solid solution, e.g. lower than about 0.5 at%, until the copper concentration becomes greater than about 65 at%. Then the silver concentration increases considerably. As the nickel content drops to zero, the silver concentration reaches about 4 at% which is the Ag solubility limit for the Cu-Ag binary alloy system. The available data for this ternary system [68] also agree with these observations.
Figure 63: A tentative ternary partial phase diagram for Cu-Ag-Ni system.
5.3.3 The onset of interface instability

In the diffusion triple of the Cu-Ag-Ni ternary system, copper atoms are the mobile diffusing species in the Ag to the Ag-Ni interface. The development of the non-planar Ag-Ni interface was not observed until the copper concentration reached about 10 at% in the Ag phase and 75 - 80 at% in the Ni phase. The arrival of copper atoms is believed to play a role in the interface breakdown. However, the instability may not be so simple as treated by Coates and Kirkaldy [46], although they have invoked the constraints of tie-line compositions into the perturbation theory for the morphological stability.

The earlier studies of morphological stability were performed for either diffusion controlled precipitation or solidification processes. All relevant properties were assumed to be isotropic, and stress accumulation was ignored. As suggested by Sekerka [69], a modified theory for solid-solid transformation should include all the possible anisotropic properties such as inhomogeneous strain, departure from local equilibrium at the moving interface, diffusion flux coupled with phase transformation strain, and interactions among the centers of growth.

Coates and Kirkaldy [45][46] suggested a criterion for interface stability in ternary systems. The boundary conditions they proposed are the tie-line compositions
which are maintained because of the thermodynamical considerations. These local equilibrium boundary conditions, however, may not be sufficient for some systems with large size misfit and high surface energy or large differences of shear modulus. For example, the atomic volumes for Ni and Ag are 6.1 and 10.6, and the shear moduli are 9.47*10^{10} \text{ Pa} and 3.38*10^{10} \text{ Pa} [70], respectively. Therefore, neglect of the anisotropic properties may lead to biased conclusions.

Realizing that other factors are involved in morphological instabilities during solid-solid transformations, in some cases one must consider that the factors contribute to this phenomenon other than the constraints imposed by the tie-line compositions. In other words, the transport mechanism may simply provide a means, but not necessarily a cause, for the morphological change.

In this study, the extent of the perturbation (see review of perturbation theory) or the wavelength lambda of the perturbations are hardly measurable. However, we can assume that a value predicted by Mullins and Sekerka's theory [49] [50], or Coates and Kirkaldy's criterion [45] [46] is the lower bound of the value for instability because the theories ignores the effect of anisotropy, e.g. in strain fields, in surface energy etc.

According to Shewmon [52], a criterion which involves interface energy is formulated as follows:

\[ \omega_o = \left( \frac{G}{C_o} \cdot \Gamma \right)^{1/2} \]
\[ \Gamma = (v \cdot Y / R \cdot T), \quad \omega_0 = 2 \cdot \pi / \lambda_0 \] is wave number, \( G \) is the gradient in front of the interface, \( C_0 \) is the equilibrium solubility, \( \gamma \) is the surface energy, and \( V \) is the atomic volume. Substituting appropriate values:

- \( G \approx 0.8 \times 10^5 \) at\%/cm, \( C_0 = 12 \) at\%, \( V = 10.3 \) cm\(^3\)/g-atom,
- \( R = 8.314 \times 10^7 \) erg/g-atom \( \cdot \) K, \( \gamma \approx 750 \) erg/cm\(^2\), \( T = 1033 \) K,

then we obtain \( \omega_0 = 2.7 \times 10^5 \) and \( \lambda_0 = 0.23 \) micrometer. This value is much smaller than the average grain size, which is about ASTM number 5 corresponding to 50 \( \mu \)m, for the annealed Ag foil.

Recently Alexander, Sekerka, Iwan and Leo [72] made a first attempt to incorporate the transformation induced stresses into considerations of the morphological stability of an interface during a precipitation process. They calculated the elastic fields for an inclusion with shapes that are slightly perturbed from a circular cylinder [71] and a sphere [72]. The shear moduli were allowed to be different in the inclusion and the matrix. Two different boundary conditions were employed. However, the effects of surface stress and surface free energy were still neglected. They proposed that further developments of their latest work should include: introducing surface stress into the model, examining the role of various reasonable interface boundary conditions and formulating
constitutive relations for diffusion. According to their calculation, an elastic field could affect the diffusion flux, and hence the morphological stability of the interface.

In our case, the size misfit and the difference of shear moduli, $3.38 \times 10^{10}$ Pa for Ag and $9.47 \times 10^{10}$ Pa for Ni [70], possibly affect the stability of the Ag-Ni interface in an early stages of reaction. After the buildup of copper in the Ni phase, the interface becomes perturbed because of the flux of copper atoms across the interface. The rippled interface remained stable as a whole until either the value of lambda for the perturbation exceeds the lower bound, or else other factors such as size misfit offset the stabilizing forces. The finger-like protrusions were observed in this work after about 3 days for 100 um and 1 day for 25 um Ag blocking layers.
Figure 64: A typical picture for Videoplane measurement. Channel 0: Reference width; Channel 1: Dotted area; Channel 2: Dotted area + Hatched area.
5.3.4 The thickening of the Ag layer

In order to trace the thickness change for the intermediate Ag layer, a software Videoplane was used. It is run under CP/M operating system on a CARL ZEISS computer equipped with a digitizing pad. The pictures taken on the SEM for each sample were reproduced and enlarged for this purpose. A typical picture is shown in Figure 64. Three perimeters were traced, by use of the digitizing pad for each picture, and stored in the memory. The reference perimeter corresponding to a known width was stored as channel 0; the perimeter enclosing the entire silver layer was stored as channel 1; the sum of each perimeter for individual apparent island and finger-like protrusions was stored as channel 2. These perimeters were then used to estimate the areas enclosed by each perimeter via the internal calculation of the Videoplan. For each sample, 2 to 4 pictures were taken with magnifications varying from 80x to 600x, and for each picture at least 3 sets of perimeters were calculated. These areas were compared with the reference areas, stored in channel 0, and subsequently the thicknesses were estimated on the basis of the reference width. The perimeter for the channel 1 was always traced by following the natural contour along the interfaces. As shown in Figure 64, the trace enclosing the dotted area cuts the sharper protrusions by connecting the ends with a smooth contour line.
Figure 65 and Figure 66 present the thickness change of the Ag layer with respect to annealing time. In addition, the equivalent thicknesses, which was obtained by comparing the total areas of the apparent islands and fingers in the Ag layer with the reference area, are also presented. From the plot for the 100 μm Ag layer, the rate of thickening increases dramatically after about 3 days and levels off after 8 days. From Figure 62 one can observe a noticeable correspondence of buildup of copper concentration and the accelerating thickening of the silver layer, and therefore conclude that copper plays an important role in the breakup of the Ag layer.

For the 25 μm barrier, the data are somewhat scattered; nevertheless, one can still observe the general trend. For times shorter than 12 hours, the data are lacking, but they are probably follow a similar trend to that observed in Figure 65 for times less than 3 days. After the initial thickening of the Ag phase via Cu uptake by diffusion with planar interfaces, the barrier thickening mechanism gradually shifts to a creep controlled one (discussed later). In this latter stage, the rate may follow a linear rate law.

The final stage begins after the total penetration of the blocking layer, i.e., after about 10 days annealing for the case of the 25 μm Ag intermediate layer. As shown in
Figure 65: The thickness change of Ag layer for 100 μm sample vs time.
Ag Original Thickness ≈ 25~30μm

- □ Thickness Change of Entire Ag Layer
- ○ Equivalent Thickness of Cu-Ni Protrusions

**Figure 66**: The thickness change of Ag layer for 25 μm sample vs time.
Figure 66, the thickening rate actually decreases or even becomes negative at large annealing times. This change is understandable since after the breakdown of the Ag layer, the copper atoms diffuse through the Cu-Ni bridges while the Ag atoms diffuse into the Cu phase and the Cu-Ni alloy branches. Furthermore, the copper concentration gradient in the Ag phase became smaller because of the finite geometry effect. The finite geometry effect was fixed by these apparent islands whose limiting Cu content at the interface is 12 at%. Thus the gradient from the Ag-Cu interface to the advancing front decreased with time. Whereupon, the Ag-Cu interface can reverse its direction of movement, the Ag layer may start shrinking. Eventually, the Ag layer is expected to dissipate into the Cu-Ni solid solution branches.

5.4 THE MECHANISM OF HIGH TEMPERATURE CREEP CONTROLLED THICKENING

As mentioned in the earlier chapter, Ag has a very limited solubility in Ni. In addition, according to the experimental data of this study, Ag was undetectable until the Cu content reached about 65 at% in the Cu-Ni solid solution. Therefore, one may raise a question: 'How does the Ag barrier layer accommodate the volume change resulting from
the growth of the Cu-Ni alloy protrusions? The answer may not be simple; however, a stress driven vacancy diffusion, analogous to the mechanism of high temperature creep, is the most probable mechanism for the redistribution of the Ag atoms during the growth of Cu-Ni protrusions.

5.4.1 Creep calculation

If one assumes that the thickening resulting from the copper flux is totally compensated by creep, the following equations are obtained:

\[ J_{Cu} = - D_v \frac{C_{Cu}}{k \xi_x} \left( \frac{\Delta \mu}{\xi_x} \right) \]  
(52)

\[ J_{Cu} V_{Cu} = - \left( \frac{d\xi_x}{dt} \right) = \xi_x \dot{\xi}_x \]  
(53)

where \( J_{Cu} \) is the copper flux, \( D \) is the diffusivity of copper in silver, \( \Delta \mu \) is the chemical potential drop for copper across the Ag layer, \( \xi_x \) is defined in Figure 67, \( V_{Cu} \) is the atomic volume of copper and \( \dot{\xi}_x \) is the strain rate for creep in the Ag layer. Figure 67 illustrates schematically the growth of branches from the Ag-Ni interface. These protruded branches are schematically shown as a form of square wave with an equal spacing of lambda. The hatched areas stand for the silver rejected from the growing front and deposited onto the Ag-Ni interface by the
Figure 67: The schematic diagram for creep calculation. The square wave form is assumed for the protrusions with an equal spacing of lambda.
creep process. We further assume that at $t=0$, $\xi_x = \xi_y = \xi$ and $\xi_x + \xi_y = 2 \xi$ when $t>0$, where $\xi$ is the original thickness of Ag layer. For a quasi-steady-state, illustrated in Figure 68, the chemical potential gradient of copper can be given by a straight line, and be expressed as $\Delta \mu / \xi_x$. Delta $\mu$ can be evaluated by means of the following equation,

$$
\Delta \mu = ( \mu_{Cu,Ag} - \mu_{Cu}^0 ) - ( \mu_{Cu,Ni} - \mu_{Cu}^0 )
= \mu_{Cu,Ag} - \mu_{Cu,Ni}
$$

(54)

The second term of Equation 54 can be evaluated from Equation 55,

$$
\mu_{Cu,Ni} - \mu_{Cu}^0 = RT \ln a_{Cu}
$$

(55)

The data used in Equation 55 are the activity of copper $a_{Cu} = 0.8$ at a copper concentration $N_{Cu}$ equal to 0.75 mole fraction in the Ni phase [73], the temperature $T= 1033 \, ^{0}\text{K}$, and the gas constant $R=1.987$. Inserting these values we obtain

$$
\mu_{Cu,Ni} - \mu_{Cu}^0 = -1914.52 \times 10^{-7} \, \text{erg/g-atom.}
$$

The data required for the evaluation of the first term of Equation 54, the chemical potential of copper in the Ag phase with a concentration of 10 at% copper, are presented in Figure 69. The values employed are the tabulated data at about 779 $^{0}\text{C}$ [1]. From the common tangent method, the chemical potential for copper is estimated to be about $-105 \, \text{cal/g-atom}$, corresponding to $-438.9 \times 10^{-7} \, \text{erg/g-atom}$. 
Figure 68: The chemical potential of Cu in the diffusion triple. A quasi-steady-state is assumed in the Ag barrier layer.
Figure 69: The integral free energy vs Cu concentration. A common tangent method is used to estimate the partial molar free energy of Cu in silver.
There are two candidates for control of the silver flow by this mechanism: dislocation creep and Nabarro-Herring creep, in the temperature range spanned in the experiments. The constitutive equation for the strain rate of dislocation creep [74] is

\[ \varepsilon_x = A \frac{D'}{kT} \left( \frac{\sigma}{u} \right)^n \]  

(56)

where \( A = 2.30 \times 10^6 \), \( D' = 3.5 \times 10^{-10} \) cm²/sec at 760 °C, \( u = 2.64 \times 10^{11} \) dyne/cm², \( b = 2.89 \times 10^{-8} \) cm, \( kT = 1033 \times 1.38 \times 10^{-16} \) erg and \( n = 5.3 \) for silver. Equating Equation 56 to Equation 53 and substituting in all the values,

\[ 16.723 \left( \frac{\sigma}{u} \right)^5.3 = \frac{1}{(2\xi - \xi_x) \xi_x} \]  

(57)

in which \( \xi = 25 \) μm is the thickness of the Ag layer. Solving Equation 57 for \( \Sigma \) by substituting values of \( \xi_x \) from \( 0.01\xi \) to \( 1.0\xi \), we can get the estimated ratios of \( (\Sigma V_{Ag}) \) with respect to \( (\Delta \mu) \), where \( V_{Ag} \) is the atomic volume of Ag, \( \Sigma \) is the stress needed for dislocation creep and \( \Delta \mu \) is the available chemical potential for the system. The ratio found is as high as \( 1.0 \times 10^3 \) at time=0 when \( \xi_x = \xi \), while for \( \xi_x = 0.99\xi \) the ratio even becomes \( 0.4 \times 10^4 \). In other words, the dislocation creep is impossible to occur with regard to the chemical potential driving force that could be supplied in this system.

The constitutive equation for Nabarro-Herring creep is
\[ e_x = 14 \ D_v \ \sigma \frac{V_{Ag}}{kT} \frac{1}{d^2} \]

where \( d \) is taken as the thickness of Ag. Similarly, by equating Equation 58 to Equation 53 and solving the following equation with \( \xi \) from 1.0*\( \xi \) to 0.01*\( \xi \),

\[ \text{ratio} = \left(25 \times 10^{-4}\right)^2 \times 7.1/14 \times 0.10/9.98 \times 1/\xi^2 \]

where \( \text{ratio} = \sigma \frac{V_{Ag}}{\Delta \mu} \), we find that the equivalent ratios range from 0.510*10^-2 at \( t=0 \) to 510*10^-2 when \( \xi = 0.01 \).

As shown in Figure 70, a plot of the ratio vs \( 1-(\xi_x/\xi) \) suggests that the stress needed for Nabarro-Herring creep becomes significant only during the last 10% growth of the protrusions. Therefore we propose that Nabarro-Herring creep is a possible mechanism for the thickening of the silver layer during the non-planar movement of the Ag-Ni interface. In other words, the silver rejected during the growth of the protrusions can be accommodated by Nabarro-Herring creep with little effect on the kinetics. Only in the final stages of breakdown of the blocking layer does the Nabarro-Herring creep process provide some limitation to the rate of reaction.

Figure 71 illustrates the process of N-H creep. The silver atoms rejected at the growing interface build up a gradient of compressive stress, which favors the annihilation of the vacancies at the corners of the growing front. Hence a gradient of vacancy concentration is built up,
Figure 70: The result of Nabarro-Herring creep calculation.

Nabarro-Herring Creep Calculation

$x$ for 25 um Ag layer
$+$ for 100 um Ag layer

\[
\text{Ratio} = \frac{(\text{Stress} \cdot \text{Atomic volume})}{\text{Chemical potential}}
\]

At time $= 0$; \( x = \xi \)

$1 - \left( \frac{\xi_x}{\xi} \right)$
which serves as the driving force of the Nabarro-Herring creep process.

As a result, the silver flow emanates from the corners, with lower vacancy concentrations, to vacancy sinks such as the grain boundaries, dislocations, the protrusion-Ag phase interfaces, the Ag-Ni interface, or the Ag-Cu interface. However, with an annealing temperature as high as 760 °C, which is only 19 °C lower than the eutectic temperature and is about four-fifths of the melting point of pure Ag, bulk diffusion should dominate. Therefore, it is reasonable to expect that most of the silver atoms plate onto the Ag-Ni and Ag-Cu interfaces which have large available areas.

According to observations of the evolution of the morphologies, we propose that the silver atoms are deposited onto the Ag-Ni interface in the early stage of reaction. Later, the silver atoms will be rejected and deposited onto both the Ag-Cu and Ag-Ni interfaces roughly adjacent to the area opposite to the front of the protrusions. This may account for the observed marker contour that followed the shape of the islands as shown in Figure 53. The markers, which are not directly in front of the island, are pushed towards the Ni side by the silver atoms that were deposited via the high temperature creep mechanism during the early stage. Therefore, these markers opposite to the growing protrusions moved slower towards
Figure 71: The schematic diagram for Nabarro-Herring assisted growth.
the Ni side and fell behind the rest of the markers after the onset of the instability.

5.4.2 Sidewise growth of the protrusions

The sidewise growth of those fingers can be attributed to the "depletion of Cu" in Ag at the growing front of the protrusions. This effect is slightly different from the 'point effect' referred to by Sekerka and Marinis [69], and Shewmon [52] because of the geometric effect at the interface. In the case of precipitation, which requires a long range diffusion field, the isoconcentration profile become more dense in front of the protrusion and more sparse in front of the recessed boundary. Therefore the point effect can enhance the growth of the protrusions.

In this study, on the other hand, the diffusion path from the copper phase to the protrusion is comparable in dimension with the size of the protrusions. This would introduce a inhomogeneous diffusion field along the perimeter of the protrusions. Furthermore, the limiting Cu concentration is about 12 at% at the growing front of the protrusions. Therefore, the depleted region must be saturated with 12 at% Cu so that the growing front can advance forward again. As a result, the protrusions tend to grow laterally following the isoconcentration line until the depleted region saturated again.
The sidewise growth is retarded as the edges of these protrusions experienced mutual interaction, i.e., solute draining the same volume. The sidewise growth then slows down and forward growth dominates again. These sidewise growth and forward growths would occur alternatively during the annealing until the branches reached the Ag-Cu interface. Then the final breakdown by combination of the interdiffusion and the creep process occurs.

5.4.3 Model for the breakdown of the diffusion barrier

The breakdown of the Ag diffusion barrier can be separated into four stages, as illustrated in Figure 72, in terms of the thickness change of the silver layer vs annealing time.

1. STAGE 1: THE PLANAR INTERFACE MOVEMENT

a. Stage 1a: Stable planar interface movement

In this stage, as shown in Figure 73a, copper atoms have not reached the Ni side. The thickening of the Ag layer results from a purely diffusion-controlled process. The Cu-Ag interface moves towards the Cu side, and the markers placed at the Ag-Cu interface are left behind in the Ag phase. The Ag-Ni interface is immobile at this early period.
Figure 72: Stages for the growth of Cu-Ni protrusions in terms of the thickness change of Ag layer.
Stage Ia: The Planar Interface Movement; The Ag Phase Thickened by the Interdiffusion of Cu through the Ag-Cu Interface.

Stage Ib: The Initiation of the Planar Instability Was Observed at the Ag-Ni Interface.

Figure 73: Stage I: Planar interface movement prevails.
b. **Stage 1 b: The transient stage from planar to non-planar movement**

After copper atoms reach the Ag-Ni interface, the limiting Cu concentration builds up very rapidly, but is still below about 10 at% in Ag and 75 at% in the Ni phase. Only a few points on the Ag-Ni interface start rumpling, as depicted in Figure 73b, but otherwise the interface remains planar. The surface energy is believed to be the stabilizing force for the planar movement brought about by the copper atom flux into and across the interface.

2. **STAGE 2: COOPERATIVE NABARRO-HERRING CREEP AND INTERDIFFUSION**

In this stage, the Ag-Cu interface is still moving as a consequence of the interdiffusion flux at the interface. The copper concentration in the Ni phase increases more slowly than previously. In addition, the Ag-Ni interface become unstable and non-planar movement initiated because of the transformation induced stresses and other factors. The Nabarro-Herring creep in the Ag phase accommodated the growth of the copper-rich finger-like protrusions. In Figure 74a, the finger-like protrusions formed and the Al$_2$O$_3$ markers moved towards the Ni phase. The Ni
atoms preferably diffused to the protrusions. The silver rejected by the finger-like protrusions deposited onto the Ag-Ni interface. No apparent islands can yet be found for the silver phase, but sidewise growth caused by the "Cu reactant depletion" can be observed for those protrusions near the Ag-Ni interface. As observed in Figure 46 since the Ag-Ni interface also grows outward, the sidewise grown Cu-Ni alloy fingers may touch the Ag-Ni interface and enclose Ag-Cu alloy patches. The Nabarro-Herring creep of Ag at the Ag-Ni interface results in a gradually increasing the thickening rate of the Ag layer.

3. STAGE 3: NABARRO-HERRING CREEP DOMINATES THE GROWTH

The copper concentration continuously increases until it reaches about 12 at% Cu in Ag and 90 at% Cu in Ni at the Ag-Ni interface. More apparent islands formed and grew into the Ag phase. The silver rejected by the Cu-Ni branches started depositing onto the Ag-Cu interface. Nabarro-Herring creep gradually became rate controlling in the thickening of the Ag layer although it was accompanied by the series diffusion mechanism occurring at the Ag-Cu interface. The thickening rate of the Ag layer increases rapidly because the Nabarro-Herring assisted growth dominates. Figure 75a illustrates the growth of these peninsulae.
Figure 74: Stage 2: Cooperative Nabarro-Herring creep and interdiffusion.
Figure 75: Stage 3: Nabarro-Herring creep dominates the growth.
Finally this stage ends up with many branched finger-like protrusions emanating from each protrusion. In the later period, as shown in Figure 75b, the apparent islands were so close to the Ag-Cu interface that the growing front was subjected to more intensive copper flux which can saturate the depleted region within a short time. Therefore, the forward growth of these branches from the protrusions is more favored.

4. **STAGE 4: BRIDGE FORMED - TOTAL PENETRATION OF THE AG LAYER**

The branches of the Cu-Ni protrusions reach the Ag-Cu interface, as shown in Figure 76 and this high diffusion path permits copper to diffuse freely through the bridge instead of through the silver phase. The thickening of the Ag layer slows, and the silver layer may even be dissolved by means of the interdiffusion of silver into the Cu-Ni alloy branches and through Ag-Cu interface. The Ag-rich layer will eventually dissipate into the Cu-Ni solid solution.
Stage IV: Cu-Ni Bridges Formed - Total Penetrated Ag Barrier Layer

**Figure 76:** Stage 4: Bridges formed - total penetration of the Ag barrier layer.
Chapter VI
SUMMARY AND CONCLUSION

(1) A computer module DCHEM was developed to study the effect of a variable molar volume on diffusivity calculations in a mole-fixed reference frame, a volume-fixed reference frame, and the Fick reference frame with the assumption of constant molar volume. This program is particularly useful when a large difference of the partial molar volumes exists in a binary alloy system such as the Cu-Sn binary.

(2) According to the data generated in this work, a tentative ternary phase diagram of Cu-Ag-Ni system was suggested.

(3) The breakdown of a Ag diffusion barrier results from the planar instability at the Ag-Ni interface after the local copper composition had reached about 10 at% in Ag and 75 at% in Ni at the interface. The instability of the planar interface can be attributed to the size misfit and large difference of the shear moduli between Ag and Ni. The subsequent growth of Cu-Ni solid solution protrusions
through the Ag layer from the Ag-Ni interface results in the total penetration of the blocking layer.

(4) On the basis of experimental observations, a model based on Nabarro-Herring creep, needed to assist the deformation of the Ag barrier by the Cu-Ni alloy protrusions, is presented to interpret the failure of the diffusion blocking layer in a Cu-Ag-Ni diffusion triple.

Although there are other factors may cause the instability of the interface, the solubility limits at both interfaces, the difference of the Cu diffusion coefficients in the Ag phase and the Ni phase certainly play vital roles of the breakdown. Therefore, this is an undesirable type of diffusion barrier for the practical application. Since the instability of the interfaces can cause a premature failure of the diffusion barrier, how to stabilize the interfaces can be an important issue for the future study in this field.

(5) The technique of studying a diffusion triple can be used to investigate the stability of a thin film diffusion barrier while the thickness of the Ag layer is scaled down to the range of several hundred angstroms. The interdiffusion behavior may be different between thin film and bulk materials. However, the morphological observation for the thicker diffusion barrier could still supply valuable
informations to interpret the failure mechanism. For instance, Coble creep could dominate the Ag redistribution mechanism during the interdiffusion for thinner diffusion barriers where grain boundary diffusion could become important. The mechanism of failure for Pinnel's work may be interpreted by the early instability of the interfaces similar to the observations found in this study.
Appendix A

APPENDIX (A) COMPUTER PROGRAM DCHEM

A.1 The list of computer program - DCHEM:
The list of "DCHEM" program begins on the next page. The utility programs, FITLOS and QUANC8, are not listed here. The FITLOS may be replaced by a code which is capable of doing the multi-sectional polynomial fitting. The QUANC8 may be substituted by a module such as Newton-Cotes formulae, or Simpson's rule. However, both of FITLOS and QUANC8 are recommended for their unique features.
C *** THIS IS MAIN ROUTINE OF 'DCHLM' SAVED AS 'PUNP9' ***

C THIS MAIN PROGRAM USES 'OCHEM5'

C THE FOLLOWING IS THE DESCRIPTION OF SYMBOLS >>>>>

C TITLE : THE DESCRIPTION OF THIS DATA SET

C NPTS : TOTAL NUMBER OF DATA POINTS

C MM1 : THE DEGREE OF POLYNOMIAL USED TO FIT ZNEW(I) VS. X(I) BY

C 'FITLOS'.

C MM1 : M-1

C MP1 : M+1

C X(I) : THE DISTANCE (MICROMETER) OF THE # ITH POINT

C CONC(I) : THE CONCENTRATION (ATOM FRACTION) AT ITH POINT

C RCONE(I) : THE REGENERATED CONC(I) BY SUBROUTINE 'ERFCON'

C Y(I) : THE NORMALIZED CONC (Y=(CONC-MIN)/(CMAX-MIN)) AT ITH PT

C RELERR : RELATIVE ERROR OF Y(I) WITH RESPECT TO Y(I)

C Z(I) : THE ARGUMENT OF ERROR FUNCTION IN Y(I)= 0.5*1-ERF(Z(I))

C WHERE Z IS A FUNCTION OF X TO BE FITTED WITH 'FITLOS'

C ZNEW(I) : THE FITTED VALUE OF Z(I) BY ROUTINE 'FITLOS'.

C CMAX : MAX VALUE OF CONC(I)

C CMIN : MIN VALUE OF CONC(I)

C XBT : ARRAY USED BY 'FITLOS' FOR SPLINE JOINT IN EACH PHASE

C NBT : THE NO. OF SPLINE JOINTS IN EACH PHASE

REAL TITLE(3),X(200),CONC(200),RCONE(200),Y(200),RY(200)
REAL XBI(11),XI(4),XST(4),XEP(4),NB
DOUBLE PRECISION ZNEW(200),A(10,4),C(4,10),U,J0
LOGICAL LREPIT,TRANX,TRANY,HILLOW,DCHEM
COMMON CMAX,CMMIN,NFUN,HILLOW,MAXC,MINC/PARAC/C,M,NST
COMMON /PARAEP/XB/PARAVM/VMAX,VMIN,VM1,VM2
EXTERNAL CFUN,DEN,DYM,ETA

DCHEM=.TRUE.
VM1 = 10.3
VM2 = 7.1
IXM = 10
INX = 200
ILIM = 10
KMIN = 2
KINC = 2
READ(5,10) TITLE
10 FORMAT (3A4)
READ(5,*)NPTS,M1NC.MAXC,TITLE
WRITE(6,20)TITLE,TIME
20 FORMAT (11,' CHEMICAL DIFFUSIVIES CALCULATION OF SAMPLE ',
      11,3A4,E15.4)
WRITE(6,25)NPTS,TIME
25 FORMAT (13,E15.4)
WRITE(6,30)
30 FORMAT (11,' 1','**',' 2','**',' 3','**',' 4','**',' 5','**',' 6','**',' 7','**',' 8','**',' 9','**',' 10','**',' 11','**',' 12','**',' 13','**',' 14','**',' 15','**',' 16','**',' 17','**',' 18','**',' 19','**',' 20','**',' 21','**',' 22','**',' 23','**',' 24','**',' 25','**',' 26','**',' 27','**',' 28','**',' 29','**',' 30','**',' 31','**',' 32','**',' 33','**',' 34','**',' 35','**',' 36','**',' 37','**',' 38','**',' 39','**',' 40','**',' 41','**',' 42','**',' 43','**',' 44','**',' 45','**',' 46','**',' 47','**',' 48','**',' 49','**',' 50','**',' 51','**',' 52','**',' 53','**',' 54','**',' 55','**',' 56','**',' 57','**',' 58','**',' 59')

Y(I) = (CONC(I)-MIN)/(CMAX-MIN)

166
CALL ERFCON(Y(I),RY(I),Z(I))
RCONC(I) = RY(I)*(MAXC-MINC) + MINC
IF(Y(I) .NE. 0.) KERR = (RY(I)-Y(I)) / Y(I)
IF(Y(I) .EQ. 0.) KERR = (RY(I)-Y(I)) / RY(I)
IF(KOUNT .LE. 2) GO TO 50
KOUNT = 1
WRITE(6,20) TITLE,TINT
WRITE(6,60)
WRITE(6,30)
WRITE(6,60) XI(I),Z(I),CONC(I),RCONC(I),Y(I),RY(I),KERR
FORMAT(4,F5.0,5X,E15.6,130,F8.4,T45,F8.4,T60,F8.4,T75,
1 F8.4,T90,E15.6)
KOUNT = KOUNT + 1
WRITE(8,35) XI(I),CONC(I)
FORMAT(2F10.9)
CONTINUE
THE FOLLOWING CODES ARE TO FIT Z(I) VS. XI(I) BY 'FITLOS'

C NO : THE NO. OF PHASES, NO-1 IS THE NO. OF DISCONTINUITIES
C OF CONCENTRATION PROFILE.
C NSP : THE NO. OF SECTIONS IN EACH PHASE FOR 'CURVE FITTING' BY
C SUBROUTINE 'FITLOS'.
C IBASE : THE FIRST INDEX IN EACH PHASE OF X, AND Z ARRAYS.
C JBASE : THE STARTING SECTION INDEX IN EACH PHASE.
C IS : THE INDEX OF DISCONTINUITIES.
C X(IN) : THE POSITION OF DISCONTINUITIES.
C NX : THE NO. OF POINTS IN A PHASE.
C NSP : THE NO. OF SECTION TO BE FITTED IN EACH PHASE.
C NS : TOTAL NO. OF SECTIONS.

C ***************************************************************
READ(5,*1) ND
IF(ND .NE. 0) READ(5,75) (XI(I),I=1,NO)
75 FORMAT(4F6.1)
X(ND) = X(NPTS)
C
IBASE = 1
JBASE = 1
NS = 0
C
DO 60 LS=1,NC
60 IS = IBASE
JS = NPTS
KS = (IS+JS)/2
IF(XI(LS) .LE. X(KS)) JS = KS
IF(XI(LS) .GT. X(KS)) IS = KS
IF(JS .GT. IS+1) GO TO 61
IF(JS .EQ. NPTS) IS = NPTS
READ(5,90) LREFIT,TRANX,TRANY
90 FORMAT(3L10)
READ(5,*) NSP,NBT,MM1,1CL
IF(NSP .EQ. 0) AND. NBT .EQ. 0 GO TO 1000
IF(NBT .NE. 0) GO TO 101
READ(5,*) (XI(LS),L=1,NO)
C
ENTRY = 0
M = MM1+1
NX = (IS-IBASE) + 1
CALL FITLOS(X(1:BASE),Z(1:BASE),N,XS,NSP,MM1,NBT,NF,TRANX,TRANY,
**FORTRAN 77 Source Code Translation**

```fortran
120. IREFIT, TOL, IENTRY, ZNEW, IBASE, XBT, A, ZIFS
121. IBASE = IS * 1
122. NS = NS * NS
123. C NSPP1 = NS + 1
124. DO 100 J=1,NSPP1
125. 'XB(I*JBASE-1) = X0(I*J-1)
126. IF(J.EQ.NSPP1) XB(J*JBASE-1) = X1(J)
127. 100 CONTINUE
128. DO 110 J=1,NS
129. DO 110 I=1,NS
130. C(J+JBASE-1) = AI(I,J)
131. 110 CONTINUE
132. JBASE = JBASE + NS
133. DO 130 I=1,NPTS
134. XB(I) = X(I)
135. WRITE(6,105) (XB(I),I=1,IXM)
136. 105 FORMAT('X',15.4)
137. 115 CONTINUE
138. C WRITE(6,120)
139. 120 FORMAT(//' 0 1 , ' 'X',T15,'CONC',T32,'CNEW',T50,'RELEER',)
140. 120 FORMAT('TITLE,TIME')
141. KOUNT = 1
142. DO 150 I=1,NPTS
143. IF(X(I) .GT. XB(I)) NST = 1
144. 140 CONTINUE
145. CNST = CFUN(X(I))
146. IF(CONC(I) .NE. 0.) RELERR=(CNEW-CONC(1))/CONC(I)
147. 150 CONTINUE
148. C CNST = CNST + 1
149. KOUNT = 1
150. WRITE(6,120) X(I), CONC(I),CNEW, RELERR
151. 160 FORMAT('TITLE,TIME')
152. WRITE(6,160)
153. 160 FORMAT(//' 0 1 , ' 'X',T15,'CONC',T32,'CNEW',T50,'RELEER',)
154. 160 FORMAT('TITLE,TIME')
155. KOUNT = 1
156. WRITE(6,140) X(I), CONC(I), CNEW, RELERR
157. 160 FORMAT('TITLE,TIME')
158. WRITE(6,160)
159. 160 FORMAT('TITLE,TIME')
160. 160 FORMAT('TITLE,TIME')
161. 160 FORMAT('TITLE,TIME')
162. 160 FORMAT('TITLE,TIME')
163. 160 FORMAT('TITLE,TIME')
164. 160 FORMAT('TITLE,TIME')
165. 160 FORMAT('TITLE,TIME')
166. 160 FORMAT('TITLE,TIME')
167. 160 FORMAT('TITLE,TIME')
168. 160 FORMAT('TITLE,TIME')
169. 160 FORMAT('TITLE,TIME')
170. 160 FORMAT('TITLE,TIME')
171. 160 FORMAT('TITLE,TIME')
172. 160 FORMAT('TITLE,TIME')
173. 160 FORMAT('TITLE,TIME')
174. 160 FORMAT('TITLE,TIME')
175. 160 FORMAT('TITLE,TIME')
176. 160 FORMAT('TITLE,TIME')
177. 160 FORMAT('TITLE,TIME')
178. 160 FORMAT('TITLE,TIME')
179. 160 FORMAT('TITLE,TIME')
180. 160 FORMAT('TITLE,TIME')
181. 160 FORMAT('TITLE,TIME')
182. 160 FORMAT('TITLE,TIME')
183. 160 FORMAT('TITLE,TIME')
184. 160 FORMAT('TITLE,TIME')
185. 160 FORMAT('TITLE,TIME')
186. 160 FORMAT('TITLE,TIME')
187. 160 FORMAT('TITLE,TIME')
188. 160 FORMAT('TITLE,TIME')
189. 160 FORMAT('TITLE,TIME')
190. 160 FORMAT('TITLE,TIME')
191. 160 FORMAT('TITLE,TIME')
192. 160 FORMAT('TITLE,TIME')
193. 160 FORMAT('TITLE,TIME')
194. 160 FORMAT('TITLE,TIME')
195. 160 FORMAT('TITLE,TIME')
196. 160 FORMAT('TITLE,TIME')
197. 160 FORMAT('TITLE,TIME')
198. 160 FORMAT('TITLE,TIME')
199. 160 FORMAT('TITLE,TIME')
200. 160 FORMAT('TITLE,TIME')
201. IF (.NOT. DCHEM) STOP
202. C *** THE FOLLOWING CODES ARE DESIGNED TO CALCULATE CHEMICAL ***
203. C *** DIFFUSIVITIES AT EACH POINT ***
204. C
205. NST = 1
206. CMIN = CFUN(IBASE)
207. WMIN = VMX(IBASE)
208. NST = NS
209. CMAX = CFUN(IBASE+1)
210. WMAX = VMX(IBASE+1)
```

**Description:**

The presented code is a FORTRAN 77 program segment, likely part of a larger computational chemistry or physical chemistry application. The program appears to be calculating and outputting data related to chemical concentrations and their diffusivities at each point in a grid or dataset. The code includes standard FORTRAN routines for data manipulation and output, indicating that it might be used for simulation or analysis tasks in a scientific computing environment. The use of array indices and loops suggests that the program processes multidimensional data, possibly in a two-dimensional grid format, to calculate and output chemical concentrations and their diffusivities. The presence of comments like `C *** THE FOLLOWING CODES ARE DESIGNED TO CALCULATE CHEMICAL ***` is typical of well-documented scientific code, aiming to provide clarity on specific sections of the program.
THE SYMBOLS USED IN THIS PROGRAM ARE DEFINED AS FOLLOWS:

WHERE NST IS THE INDEX OF THE SECTION OF THE PROBABILITY PLOT WHICH IS DESCRIBED BY THIS FUNCTION.

WHERE NST IS THE INDEX OF THE FUNCTIONS TO BE INTEGRATED BY USING THE WAGNER'S EQUATION TO CALCULATE THE INTERDIFFUSIVITY, NFUN = 1 : F(J) = (1 - Y(J)) / VM

NFUN = 2 : FUN(J) = Y(J) / VM

CONCIXI IS THE ATOMIC FRACTION AT X.

X IS THE DISTANCE RELATIVE TO THE ONE END OF THE SPECIMEN.

VM : THE MOLAR VOLUME

XBINJ : THE POSITION OF THE JOINT POINT OF TWO SECTIONS.

CMAX, CMIN : MAX. & MIN CONCENTRATIONS AFTER FITTING.

NFUN : THE INDEX OF THE SECTION CALCULATED.

NB M : MATANO INTERFACE IN N-X SYSTEM

EBM : MATANO INTERFACE IN N-SAI SYSTEM (MOLAR FIXED SYSTEM)

NBM : MATANO INTERFACE IN C-X SYSTEM (VOLUME FIXED SYSTEM)

AREAT = 0.0

AREAT = AREAT + FAREA(XBINSTJ, XBXINS+1, WVE) / VM

CONTINUE

AREAT = AREAT + FAREA(XBINSTJ, XBINS+1) / VM

CONTINUE

AREAT = AREAT + FAREA(XBINSTE) / VM

CONTINUE

AREAT = AREAT + FAREA(XBINSTJ, XBINS+1) / VM

CONTINUE

AREAT = AREAT + FAREA(XBINSTJ, XBINS+1, ETA)

CONTINUE
IF (KOUNT .LE. 50) GO TO 258

WRITE(6,256)
KOUNT = 1
DO 1257 I=1,4
   XSTAR = XSTAR + 2.
   XP(I) = EP(XSTAR(I))
1257 CONTINUE
IF (XSTAR .LE. XMIN + 1.01) GO TO 257

WRITE(6,259) (XSTAR(I), XP(I), I=1,4)
KOUNT = KOUNT + 1
IF (XSTAR .GT. XBU + 1.1) IXB = IXB*1
KOUNT = KOUNT + 1
XSTAR = XMIN

WRITE(6,270)
KOUNT = KOUNT + 1
XSTAR = XMIN

WRITE(6,370)
KOUNT = KOUNT + 1
IF (XSTAR .GT. XBU + 1.1) IXB = IXB*1
XSTAR = XMIN
CSTAK = CFUNVM1 (XSTAK)
WRITE (8, 460) XSTAR, CSTAR, DBOLTZ, DINTER
460 FORMAT (2F10.4, 2E15.5)
KOUNT = KOUNT + 1
XSTAK = XSTAR * XINC
IF (XSTAK .GE. XB(NST + 1)) XB = 1XH + 1
IF (IXB .GT. NST) IXB = NST
IF (XSTAK .LE. XB(NS + 1)) GO TO 300
C
C
C
C
I X J = 1
DO 460 I = 1, NS
IF (XMIN .GT. XB(I)) .AND. XMIN .LE. XB(I + 1) IXB = I
C
C
C
C
460 CONTINUE
KOUNT = 1
XSTAK = XMIN
C
C
C
C
WRITE (6, 470)
470 FORMAT ('/11', *XSTAR', OX', *CSTAR', 6X', 'CFUNIX', 11X', 'SLOPE', 10X,
*ARAX', '8X', 'DFC-AX')
480 NST = IXB
IF (KOUNT .LE. 25) GO TO 490
WRITE (6, 470)
KOUNT = 1
CALL DFUNVX (XSTAR, TIME, XB, IXB, XB, DBOLTZ)
490 CALL DFUNVX (XSTAR, TIME, XB, IXB, XB, DBOLTZ)
C
C
C
C
NST = IXB
CSTAR = CFUN1 (XSTAR)
WRITE (8, 500) XSTAR, CSTAR, DBOLTZ, DINTER
500 FORMAT (2F10.4, 2E15.5)
KOUNT = KOUNT + 1
XSTAK = XSTAR * XINC
IF (XSTAK .GE. XMIN(NST + 1)) IXB = 1XH + 1
IF (IXB .GT. NST) IXB = NST
IF (XSTAK .LE. XB(NS + 1)) GO TO 480
C
C
C
C
STOP
1010 WRITE (6, 1011)
1011 FORMAT ('0', ' >>>>>>> JOB FAIL DUE TO EOF ENCOUNTERED DURING ',
'I'INPUT OF DATA'/', ' >>>>>>> CHECK THE INPUT VALUE OF NPTS')
STOP
1000 WRITE (6, 1001)
1001 FORMAT ('0', ' >>>>>>> JOB FAIL DUE TO FORBIDDEN Nb=0 & Ns=0')
STOP
END
C
C
C
C
FUNCTION VM FOR COMPUTING CONCENTRATION
C
C
C
C
FUNCTION ETA FOR X-L SYSTEM
C **FUNCTION ETA(X)**
360. REAL*8 C(4,10)
361. REAL XB(11)
362. LOGICAL HILO
363. COMMON CMAX,CMIN,NFUN,HILUH/PAKAC/C,M,NS,NST/PARAEP/XB
364. COMMON CMAX/VMMAX,VMMIN,VM1,VM2
365. C **EXTERNAL VM,CFUN**
366. ETA = (CFUN(X)/VM(X) - CMIN/VMMIN)/(CMAX/VMMAX - CMIN/VMMIN)
367. C RETURN
368. END

C *** FUNCTION WYE FOR ETSILON-N SYSTEM ***
370. FUNCTION WYEVMIX)
371. REAL*8 C(4,10)
372. REAL XB(11)
373. COMMON CMAX,CMIN/PARAC/C,M,NS,NST/PARAEP/XB
374. WYEVM = (CFUN(X) - CMIN/(CMAX - CMIN)/VM(X))
375. C RETURN
376. END

C *** FUNCTION WYE IN WYE-TSAI SYSTEM ***
378. FUNCTION WYEIX)
379. REAL*8 C(4,10)
380. REAL XB(11)
381. COMMON CMAX,CMIN/PARAC/C,M,NS,NST/PARAEP/XB
382. C WYE = (CFUN(X) - CMIN)/(CMAX - CMIN)
383. C RETURN
384. END

C *** THE CORRESPONDING EP OF XEP WILL BE CALCULATED.***
386. C *** EP(I+1) = INTEGRAL OF DEN(X) FROM 0 TO XEP. THUS, AT ***
388. C *** EACH XEP(I), EP(I) WILL BE CALCULATED. ***
389. FUNCTION EP(XEP)
390. REAL*8 C(4,10)
391. REAL XB(11)
392. COMMON /PARAC/C,M,NS,NST/PARAEP/XB
393. EXTERNAL DEN
394. IXB = 1
395. DO 180 J=1,NS
396. IF(XEP.GT.XB(J)) AND. XEP.LE.XB(J+1) IXB=J
397. 180 CONTINUE
398. IE = 0.0
399. DO 190 NST=1,IXB
400. IF(NST.IQ. IXB) IE = IE + FAREA(XB(NST),XEP,DEN)
401. IF(NST.NQ. IXB) IE = IE + FAREA(XB(NST+1),XEP,DEN)
402. 190 CONTINUE
403. EP = IE
404. DO 190 NST=1,IXB
405. IF(NST.IQ. IXB) IE = IE + FAREA(XB(NST),XEP,DEN)
406. IF(NST.NQ. IXB) IE = IE + FAREA(XB(NST+1),XEP,DEN)
407. 190 CONTINUE
408. EP = IE
409. GO TO 190
C ************************************************************
C *** THIS IS THE SUBROUTINE LIBRARY OF 'OCHEM' SAVE AS 'OCHEMS' ***
C ************************************************************
SUBROUTINE CBOLT(XSTAR, TIME, XB, XBM, DBOLTZ)

REAL XB(10), MAXC, MINC
REAL *8 AREA, U, DU, DC, C(4,10)
LOGICAL HILOW

COMMON CMAX, CMIN, NFUN, HILON, MAXC, MINC, PARAC/C, M, NS, NST
EXTERNAL U, DU, CFUN

OC(X) = MAXC-MINC)*(OC(X)+U(X)**2)*U(X)/1.772453

C IF XSTAR .GE. XBM GO TO 30
AREA = 0.000
NFUN = 1
GO TO 10

IF(INST .EQ. 1) AREA = AREA + FAREA(XBM, XSTAR, CFUN)
IF(INST .NE. 1) AREA = AREA + FAREA(XB(INST), XB(INST+1), CFUN)
GO TO 10

AREA = AREA + FAREA(XSTAR, XSTAR, CFUN)

NST = IXB
AREA = CMIN*(XSTAR-XB(1)) - AREA + (XBM-XSTAR)*(CMIN-CFUN(XSTAR))
GO TO 50

C *** NFUN = 2; THE SECTION TO THE RIGHT OF BOUNDARY
C
30 AREA = 0.000
NFUN = 2

DU = D20 NST=IXB, NS

IF(NST .EQ. IXB) GO TO 1

IF(NST .EQ. IXB) AREA = AREA + FAREA(XSTAR, XB(NST+1), CFUN)
IF(NST .NE. IXB) AREA = AREA + FAREA(XB(NST), XB(NST+1), CFUN)

GO TO 20

AREA = AREA + FAREA(XSTAR, XB(NST+1), CFUN)

GO CONTINUE

NST = IXB

AREA = (CFUN(XSTAR)-CMIN)*(XSTAR-XBM) + AREA - (XB(INST+1)-XSTAR)*CMIN

C *** IXB IS THE SECTION WHERE XSTAR LOCATED
C
50 NST = IXB
SLOPE = DC(XSTAR)
CSTAK = CFUN(XSTAR)
UX = U(XSTAR)
YSTAR = (CFUN(XSTAR)-CMIN)/(CMAX-CMIN)

C
DBOLTZ = -AREA/(2.*SLOPE*TIME**1.1E-B

WRITE(6,13) XSTAR, CSTAR, YSTAR, SLOPE, AREA, DBOLTZ

FORMAT(3*,F4.2,3X,F8.5,3X,F12.5,3X,F12.5,3X,F12.5,3X,F12.5)

RETURN
END
SUBROUTINE OCUKL1YSTAK, XSTAK, TIME, X0, IXB, 01, NICR)
REAL XDd'JI , MAXC, MINC
REAL * 8 DXB, (LI4, 10), AREA(2), U, DU, UC
LOGICAL HILOW
COMMON C MAX, CMIN, NFUN, HILow, MAXC, MING/PARAC/L, MNS, NST
EXTERNAL

FD(X) = -(MAXC-MINC)*DEXP(-U(X)***2)*DU(X)/1.772453
NST = IXB
SLOPE = DC(XSTAR)
YSTAR = (LFUN(XSTAR)-CMIN)/(CMAX-CMIN)

C

NFUN=1: THE FUNCTION TO BE INTEGRATED IS '*WYE(X)/VM(X)'

NFUN = 1
AREAFUN = 0.
U = 10 NST = 1, IXB
IF IIXB .EQ. 11 GO TO 11

C
IF(IIXB .EQ. 11) AREA(NFUN) = AREA(NFUN) + FAREA(XB(1), XB(2), FUN)
IF(NST .EQ. IXB) AREA(NFUN) = AREA(NFUN) + FAREA(XB(IXB),
XSTAR, FUN)
1 XSTAR, FUN
IF(NST .NE. IXB) AREA(NFUN) = AREA(NFUN)
1 FAREA(XB(INST), XB(INST+1), FUN)
GO TO 10
11 AREA(NFUN) = AREA(NFUN) + FAREA(XB(1), XSTAR, FUN)
CONTINUE
10

C

NFUN=2: THE FUNCTION TO BE INTEGRATED IS '*WYE(X)/VM(X)'

NFUN = 2
AREAFUN = 0.
U = 10 NST = 1, IXB, NS
IF (NST .EQ. IXB) GO TO 21.

C
IF (NST .EQ. IXB) AREA(NFUN) = AREA(NFUN) + FAREA(XSTAR,
XSTAR, FUN)
1 XSTAR, FUN
IF (NST .NE. IXB) AREA(NFUN) = AREA(NFUN)
1 FAREA(XB(INST), XB(INST+1), FUN)
GO TO 20
21 AREA(NFUN) = AREA(NFUN) + FAREA(XSTAR, X3(NS+1), FUN)
CONTINUE
20

C

INTER = (CMAX-CMIN)*VM(XSTAR)*(YSTAR*AREA(2)+11.-YSTAR)*AREA(1)) /
2.*TIME*SLOPE*1.E-8

C

WRITE(6,30) AREA(1), AREA(2), DINTER
30 FORMAT(*,,159,3X,12.5,3X,12.5,3X,12.5)
RETURN
END

C

*******************************************************************************
FUNCTION CFUN(X)
  REAL*8 C(4,10),U
  REAL MAXC,MINC
  COMMON CMAX,CMIN,NFUN,HILW,HILU,MAXC,MINC/PARAC/C,M,NS,NST
  EXTERNAL U
  CFUN = MINC + (MAXC-MINC)*DL(1-DERF(U*X))
  RETURN
END

FUNCTION FAREA(A,B,FUN)
  REAL*8 C(4,10)
  COMMON CMAX,CMIN,NFUN/PARAC/C,M,NS,NST
  RELERR = 1.0E-6
  ABSERR = 1.0E-6
  CALL QUANCa!FUN,A,B,ABSEKk,RELERR,RESULT,ERROR,RESULT,FLAG)
  IF(FLAG .NE. 0.01 WRITE(6,10) FLAG
  10 FORMAT(*' WARNING: ..RESULT MAY BE UNRELIABLE. RESULT',I2,F9.2)
  FAREA = RESULT
  RETURN
END

FUNCTION U(X)
  REAL*8 C(4,10),U
  COMMON /PARAC/C,M,NS,NST
  U = 0.
  DU = 1.
  I = M+1
  U = U*X + C(I1,NST)
  CONTINUE
  RETURN
END

FUNCTION DU(X)
  REAL*8 C(4,10),DU
**FUNCTION DEN(X)**

**EXTERNAL VM**

**RETURN**

**END**

**FUNCTION DETAIL(XSTAR,TIML,XXB,IXB,DCHEM)**

- REAL XB(10),MAXC,MINC
- REAL*8 DXB(14,10),AKLAL(2),U,DU,DC
- LOGICAL HILLOW

**COMMON CMAX,CMIN,NFUN,HILLOW,MAXC,MINC/PARAC/C,M,NS,NST**

**COMMON /PARAVM/VMMAX,VMMIN,VHI,VVM2**

**EXTERNAL ETAFUN**

**DC(X) = -(MAXC-MINC)*EXP(-U*X)**2)*DU(X)/1.772453**

**NST = IXB**

**SLOPE = DC(XSTAR)/VM(XSTAR) - CFUN(XSTAR)/(VM1-VM2)*DC(XSTAR)/VM(XSTAR)**

**ETASTA = ETAFUN(XSTAR)**

**FUNCTION NFUN=1; THE FUNCTION TO BE INTEGRATED IS \* \* W(X)/VM(X)**

**C**

**NFUN = 1**

**AREA(NFUN) = 0.**

**DO 10 NST = 1,IXB**

**IF(INB .EQ. 1) GO TO 11**

**IF(NST .EQ. IXB) AREA(NFUN) = AREA(NFUN) + AREA(XB(IXB)).**

**1 XSTAR,ETAFUN**

**IF(NST .NE. IXB) AREA(NFUN) = AREA(NFUN) + AREA(XB(NST),ETAFUN).**

**10 CONTINUE**

**FUNCTION NFUN=2; THE FUNCTION TO BE INTEGRATED IS \* \* (1-W(X))/VM(X)**

**C**

**NFUN = 2**

**AREA(NFUN) = 0.**

**DO 20 NST = IXB,NS**

**IF(NST .EQ. IXB) GO TO 21**

**IF(INB .EQ. IXB) AREA(NFUN) = AREA(NFUN) + AREA(XB(NST),ETAFUN).**

**10 CONTINUE**
IF(INST.NE.1XB) AREAINFUN = AREAINFUN + AREA(INFUN)
1 AREAI(KBNST),KBNST+11,EATAFUN)
GO TO 20

AREA(INFUN) = AREAINFUN + AREAI(XSTAR),XSTAR+11,EATAFUN)
20 CONTINUE
NST = 1XB
CFUNX = CFUNVM(XSTAR)
VMX = VMXSTAR
C
DCHEM = (CMAX/VMMAX-CMIN/VMMIN)*(ETASTA*AREA(2+11.-ETASTA)*
1 AREA[I]/12.*TIME*SLOPE)*1.E-8
C
ETAFUN = ETAFUNCX
RETURN
C
FUNCTION ETAFUNCX

REAL*8 C(A,10),U,DU
REAL MAXC,MINC
LOGICAL HILOW
COMMON CMAX,CMIN,NFUN,HILOW,MAXC,MINC
COMMON /PARAC/C,K,NS,NS1/PARAVM/VMMAX,VMMIN
FUNX = (CFUNVM(XSTAR) - CMIN/VMMIN)/(CMAX/VMMAX - CMIN/VMMIN)
GO TO (1,2) . NFUN
ETAFUN = 1. - FUNX
RETURN
ETAFUN = FUNX
RETURN
END

FUNCTION CFUNVM(X)
C
FUN VM = CFUN(X)/VM(X)
RETURN
END

SUBROUTINE DFUNVM(XSTAR,TIME,XB,IXB,XBM,DBOLTZ)
REAL*8 AREA,U,DU,DU.DC,C(A,10)
LOGICAL HILOW
COMMON CMAX,CMIN,NFUN,HILOW,MAXC,MINC/PARAC/C,M,NS,NS1/PARAVM/VMMAX,VMMIN

DC(X) = -(MAXC-MINC)*JCXP(-UX)*21*DUX/X1.772*53
IF(XSTAR .GE. XBM) GO TO 30
AREA = 0.000
NFUN = 1
DO 10 NST=1,IXB
   IF(IXB.EQ.11) GO TO 11
   IF(INST.EQ.IX), AREA = AREA + FAREA(XB(IX),XSTAR,CFUNVM)
   IF(INST.NE.IX), AREA = AREA + FAREA(XB(NST),XB(NST+1),CFUNVM)
   GO TO 10
11 AREA = AREA + FAREA(XB(11),XSTAR,CFUNVM)
10 CONTINUE
NST = IXB
AREA = CMIN/VMMIN*(XSTAR-X3(I) - AREA*(X3(I)-XSTAR)*CMIN/VMMIN
1 -CFUNVM(XSTAR))
GO TO 50
C *** NFUN = 2; THE SECTION TO THE RIGHT OF BOUNDARY
30 AREA = 0.000
NFUN = 2
DO 20 NST=IXB,NS
   IF(INST.EQ.IX) GO TO 21
   IF(INST.NE.IX) AREA = AREA + FAREA(XSTAR,XB(NST+1),CFUNVM)
   GO TO 20
21 AREA = AREA + FAREA(XSTAR,XB(NST+1),CFUNVM)
20 CONTINUE
NST = IXB
AREA = CFUNVM(XSTAR)-CMIN/VMMIN*(XSTAR-X3(I)) + AREA-(X3(I)-XSTAR)
1 *CMIN/VMMIN
35 C *** IXB IS THE SECTION WHERE XSTAR LOCATED
C NST = IXB
SLOPE = DC(XSTAR)/VM(XSTAR) - CFUN(XSTAR)*VM1-VM2)*DL(XSTAR)/VM(XSTAR)**2
CFUNX = CFUN(XSTAR)
CSTAR = CFUN(XSTAR)
C DBOLTZ = -AREA/2.*SLOPE*TIME*1.E-8
C WRITE(6,13) XSTAR,CSTAR,CFUNX,SLOPE,AREA,DBOLTZ
13 FORMAT(9*F9.2,3X,F6.5,3X,E12.5,3X,E12.5,3X,E12.5,3X,E12.5)
RETURN
END
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