Analysis of Two-Dimensional Diffusion of Zn in the Lamellar Eutectic Al-CuAl₂

When zinc diffuses into the aligned lamellar eutectic αAl-9CuAl₂, a complicated interaction occurs — a ternary phase γAl₂ZnCu₃ forms at the Zn-8 interface. The ternary phase is richer in Cu and leaner in Al than is the γ from which it forms. The phase transformation and growth of the products follow the reaction γ + γ → γ resulting from diffusion into γ of Zn and rejection of Al. Nearly coherent α–γ eutectic interfaces are replaced by incoherent α–γ interfaces. Rapid boundary-enhanced diffusion occurs, and zinc reaches α from both γ and the Zn layer. An understanding of the measured compositional profiles requires the problem to be considered in terms of two-dimensional diffusion.

Crank has shown that analysis of the two-dimensional diffusion process can be accomplished by using the finite difference methods of Schmidt. Simulation of diffusion of Zn in the Al-CuAl₂ eutectic, using a two-dimensional finite difference approach, provides a method for rapidly surveying the influence of platelet width, time of diffusion, diffusion coefficient of Zn in α, and diffusion temperature. An unexpected independence of platelet width and γ + γ reaction rate is explained by the analysis. A comparison of calculated and measured compositional profiles also leads to an estimation of the dislocation density in α.

The computer simulation involves establishment of a grid of points in the α-phase for finite difference compositional calculation. The Zn-eutectic interface is perpendicular to the eutectic platelet boundaries. The program initializes each point in the grid and allows the accumulation of an increment of diffusion time. The growth of γ during the increment is then calculated. The interface compositions are recalculated based on equilibrium compositions, and compositions for the remainder of the grid are calculated by the finite difference method. Diffusion time is incremented again, and the process is repeated until the diffusion time of interest is accumulated. A complete description of the concentration gradients within the α-phase results.

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ANALYSIS OF TWO-DIMENSIONAL DIFFUSION OF Zn IN THE LAMELLAR EUTECTIC Al-CuAl₂

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INTRODUCTION

Diffusion experiments which are undirectional in nature allow the use of equations of the form:

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1) \]

where \( c \) is concentration of the diffusing species, \( t \) is the time of diffusion, \( D \) is the lattice diffusion coefficient, and \( x \) is the distance away from the original diffusion couple interface. (1) Although grain boundary enhanced diffusion is a two-dimensional problem, frequently it can be treated in a nearly one-dimensional manner. Fisher's analysis (2) of the problem describes the phenomenon in terms of undirectional diffusion perpendicular to the grain boundary. The boundary has a high diffusivity \( D_B \). Although the analysis developed to describe boundary enhanced diffusion has the appearance of two-dimensionality, diffusion in the boundary is completely independent of diffusion perpendicular to the boundary. The analysis is valid for temperatures where \( D_B/D_A \) is greater than 5 to 10⁴. (3) For most metals the analysis is a good approximation below 0.83 \( T_m \), where \( T_m \) is the melting point. (4) At higher temperatures diffusion from both the boundary and the diffusion couple interface must be considered.

Under certain conditions the boundary enhanced solution will be inappropriate at temperatures well below 0.83 \( T_m \). When the width of the grain is small enough that diffusion fields from adjacent boundaries overlap, then lattice diffusion in both \( x \) and \( y \) directions must be considered. Boundary enhanced diffusion in an aligned eutectic is such a case. In a study of zinc diffusion in the aligned lamellar Al-CuAl₂ eutectic, a true two-dimensional diffusion analysis was required to explain measured composition gradients. (5, 6) A brief description of the observations is necessary before the analysis is developed. The details of the experiment have been discussed previously. (5, 6)

EXPERIMENTAL OBSERVATIONS

Sheets of Zn were bonded to a lamellar eutectic consisting of alternating platelets of Al (99.5 w/o Al, 0.5 w/o Cu) and 8%CuAl₂ (45.5 w/o Al, 53.5 w/o Cu) (Ref. 7). The Zn-eutectic interface was perpendicular to the boundaries between the platelet phases. The solubility of Zn in \( \theta \) is small (~1 w/o) and Zn-\( \theta \) couples result in the formation of a ternary phase \( \tau \)-Al₁ZnCu₃ (Ref. 8). When \( \tau \) and \( \alpha \) are in contact, the equilibrium composition of \( \tau \) is nearly independent of temperature and is 32 w/o Al, 58 w/o Cu, 10 w/o Zn.

Atomic mismatch at the \( \alpha-\theta \) eutectic interface produces a dislocation network with a \( \sim 1000 \) A spacing. (9) However, as Zn diffuses into the eutectic, the \( \theta \) transforms to \( \tau \), and the eutectic interface is replaced by an incoherent \( \alpha-\tau \) phase boundary, as seen in Fig. 1 (Refs. 5, 6). These interfaces act as paths for rapid diffusion of Zn to the advancing \( \tau \) growth front. Diffusion of Zn also occurs laterally into \( \alpha \) to maintain interfacial equilibrium. However, penetration of Zn into \( \alpha \) is greater than would be predicted for lattice diffusion because of the short distances for lateral diffusion from the interface into \( \alpha \). Penetration of Zn into \( \theta \) to cause transformation to \( \tau \) is less than was seen for Zn-\( \theta \) diffusion couples, because some of the Zn diffuses into the \( \alpha \)-phase that would otherwise go in the \( \theta-\tau \) transformation. The parameters \( \lambda \), distance from the Zn layer to the \( \tau \) growth front, and \( \lambda \), distance from the Zn layer to the position where Zn x-ray intensity in \( \alpha \) is twice the background intensity (0.3 w/o Zn), are shown in Fig. 1. The value of \( \lambda \) varies paradoxically with time, but \( \lambda \) does not. The value of \( \lambda \) is always greater than \( \lambda \), but the difference between them depends on the time and temperature of diffusion and on the lamellar spacing, \( \lambda \).

There is no observed dependence of \( \lambda \) on \( \lambda \), but there is for \( \lambda \). Table 1 shows the experimentally determined values of \( \lambda \) and \( \lambda \).

The observed independence of \( \lambda \) and \( \lambda \) is unexpected. More \( \tau \) should be produced as \( \lambda \) is increased. This is because larger distances for lateral diffusion into \( \alpha \) should result in less \( \alpha \) volume being saturated with Zn. More Zn should be available for \( \tau \) formation. Values for \( \lambda \) studied were 2 to 6 μm. Because of the apparent inconsistency between the observed and expected behavior, a two-dimensional analysis was considered.

TWO-DIMENSIONAL DIFFUSION ANALYSIS

Simultaneous diffusion in two directions is described by:

\[ \frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) \quad (2) \]

Crank (10) has shown that analysis of the diffusion process can be accomplished by using the finite difference methods of Schmidt. A grid of squares of side \( h \) is superimposed on the diffusion couple and the composition at the grid point \( x=nh, y=nh \) is \( c_{j,k} \). In Crank's treatment, the infinitesimal "\( \Delta \)" terms are replaced by incremental "\( \Delta \)" terms. At point \( (j,k) \):

\[ D \left( \frac{\partial^2 c_{j,k}}{\partial x^2} + \frac{\partial^2 c_{j,k}}{\partial y^2} \right) = \]

\[ \frac{\Delta x}{2} \left[ \frac{c_{j+1,k}-2c_{j,k}+c_{j-1,k}}{(\Delta x)^2} + \frac{c_{j,k+1}-2c_{j,k}+c_{j,k-1}}{(\Delta y)^2} \right] \quad (3) \]
and $\frac{\partial C_j}{\partial t} = (C^+_j - C^-_j) \Delta t$.  

The term $C^+_j$ is the concentration of $(j, k)$ after an increment of time $\Delta t$. Equating Eqs. (3) and (4) and solving for $C^+_j$:

$$C^+_j = C^-_j + \frac{D}{\Delta t} \left[ C_{j+1,k} + 2C_j + C_{j-1,k} \right]^{2/2} + \frac{C_{j+1,k+1} + 2C_j + C_{j-1,k-1}}{\Delta y^2}$$

TABLE I
A Compilation of Diffusion Distances for Zn-Eutectic Diffusion Couples

<table>
<thead>
<tr>
<th>Initial</th>
<th>Final</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.0</td>
<td>0.5</td>
</tr>
<tr>
<td>2.0</td>
<td>3.0</td>
<td>1.0</td>
</tr>
<tr>
<td>3.0</td>
<td>4.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Once initial and boundary conditions are specified, $C^+_j$ can be calculated for each point $(j, k)$ for any number of time increments $\Delta t$.

For third-element diffusion in a two-phase eutectic, initial and boundary conditions for the two phases would make the solution difficult. However, if two-dimensional diffusion in one phase can be ignored, the problem is much simpler. This is the case for Zn diffusion in the $\alpha$-Zn eutectic. The transformation of $\theta$ to $\tau$ is rapid compared to Zn diffusion in $\alpha$, so that this transformation can be considered to be one-dimensional. Diffusion in $\alpha$ occurs both from the Zn surface and from adjacent transformed $\theta$ platelets.

The grid arrangement in the $\alpha$-phase used for the two-dimensional finite difference analysis is illustrated in Fig. 2. As above, $j$ is measured in the $x$ direction and $k$ is in the $y$ direction. For each point, the equilibrium ternary phase diagram (Fig. 2(b)) is used to establish initial and boundary conditions. (6) At $(0, 0)$ and $(10, 0)$, $\alpha$ is in contact with both $\tau$ and $\eta$(Zn), so that for all diffusion times these points are fixed at $C^\alpha(\tau, \eta)$ as defined by the three-phase $\alpha$-$\tau$-$\eta$ field. The nine points $(0, 0)$ to $(9, 0)$ have compositions in the two-phase $\alpha$-$\tau$ field. However, for simplicity, these will also be set at $C^\alpha(\tau, \eta)$. Initially, all other points in the grid are at $C^\alpha = 0$. Initial conditions for $(j, k, t=0)$ are:

$$C(j, 0, 0) = C^\alpha(\tau, \eta), 
\frac{C(j, k, 0)}{C(j, k, 1)} = 0$$

Growth of $\tau$, as measured by $\lambda$, is given by:

$$\lambda = p \sqrt{t}$$

where $p$ is a proportionality constant, dependent upon temperature. At the $\tau$ growth front, $\alpha, \tau$, and $\delta$ co-exist, so that the composition is fixed at $C^\alpha(\alpha, \tau, \delta)$, as given by the phase diagram. (8) Points in $\alpha$ at the $\alpha$-$\tau$ interface are assumed to have compositions that vary linearly with distance between $\alpha$ and $C^\alpha(\alpha, \tau, \delta)$.
At infinite distance in y, all points contain zero Zn. For \( t > 0 \):

\[
C(j, 0, t) = C_a(\tau, \eta),
\]

\[
C(0, L, t) = C(a, 0, t).
\]

\[
C(j, \alpha, t) = 0, \quad (8)
\]

\[
C(0, 0 < k < L, t) = C(10, 0 < k < \tau, t),
\]

\[
= C_a(\tau, \eta) + \left( C_a(\tau, \eta) - C_a(\tau, \eta) \right) \frac{(\tau - k)}{\tau}.
\]

With the specification of initial and boundary conditions in Eqs. (6) and (8), Eq. (5) can be used to determine the grid \( C^S_{j, k} \) after an increment \( \Delta t \). The actual operation of the computer simulation is as follows. First, the user is asked to establish equilibrium compositions at \( \alpha-\gamma \) and \( \alpha-\delta \) junctions, lamellar spacing, diffusivity of Zn in \( \alpha \), total time for diffusion, the proportionality for \( \gamma \) growth, and the number of points in the x and y directions of the grid illustrated in Fig. 2. For stability to be achieved in the computer simulation, at least eleven points across the platelet were necessary. Since \( \alpha \) is 50 v/o of the eutectic, the spacing \( \Delta x \) is 0.051. The spacing \( \Delta y \) is chosen equal to \( \Delta x \), and the number of grid points in \( y \) is adjusted so that points farthest from the Zn layer satisfy the boundary conditions. The increment of diffusion time is chosen to be the smaller of either 0.01 of the total time or one quarter of the square of the grid spacing divided by the diffusivity. Again, the choice ensures stability of the simulation. The program then establishes the specified initial conditions at all points in the grid. Time is incremented and the growth of \( \gamma \) is calculated using the proportionality constant. Values of \( C^S_{j, k} \) are calculated with Eq. (5) for all grid points within the \( \alpha \) phase, but not at a boundary. The calculation proceeds down each column of points, then increments to the next column. The points at the \( \alpha-\gamma \) boundary and the \( \alpha-\gamma-\delta \) junction do not change in composition throughout the simulation. The composition of the \( \alpha-\gamma-\delta \) junction does not change in composition, but the junction moves as the \( \gamma \) growth front advances. The compositions for points at the \( \alpha-\gamma \) interface are calculated as varying linearly from the \( \alpha-\gamma-\delta \) junction to the \( \alpha-\gamma-\delta \) junction. The final compositional calculation is for points along the \( \alpha-\delta \) interface. In Eq. (5), there is a term \( C_j \). Since there is no grid point to the left of the \( \alpha-\delta \) interface \((0, y)\), the term \( C_{j-1, k} \) is assumed to be equal to \( C_{j+1, k} \), only for the \( \alpha-\delta \) interface. The assumption is reasonable since the adjacent \( \delta \) phase has near-zero solubility for Zn, and will not act as a sink. The calculation continues with another incrementing of diffusion time and a new calculation of \( C^S_{j-1, k} \), using the most recent \( C^S_{j+1, k} \) as the C grid for Eq. (5). When the total diffusion time is accumulated, the simulation ends. Different diffusivity temperatures were modeled by using the proper isothermal section of the ternary phase diagram in choosing \( C_a(\tau, \eta) \) and \( C_a(\gamma, \delta) \). The value of \( D \), the diffusion coefficient of Zn in \( \alpha \), can be varied independently.

COMPARISON OF MODEL AND EXPERIMENT

For a given diffusion temperature, the composition at each grid point can be calculated as a function of time. Isoconcentration lines can be drawn in the \( \alpha \)-phase connecting regions with the same calculated composition. It is shown in Fig. 3 that, with increasing time, \( \gamma \) increases and the location and shape of the isoconcentration lines shift. Concentration gradients as measured by electron microprobe analysis for the two diffusion times, shown in Fig. 3(b), are determined as follows. Each contour intersects the \( \alpha-\gamma \) or \( \alpha-\delta \) boundary at a maximum value of \( \gamma \), and crosses the middle of the \( \alpha \)-phase at a minimum value of \( \gamma \). It is assumed that the composition of the contour would be measured in electron microprobe analysis at a position that is the average of the minimum and maximum values of \( \gamma \). The volume from which x-rays are counted in microanalysis may be several microns wide, so that -- in a chemical gradient -- microanalysis yields an average composition of the region. The concentration profiles in Fig. 3(b) are derived in this way from the isoconcentration lines in Fig. 3(a).

Isoconcentration lines are shown in Fig. 4(a) for two different assumed diffusivities, \( 5 \times 10^{-14} \) and \( 5 \times 10^{-12} \) cm²/sec. Contours are flatter for higher diffusivity values. The actual measured profile in Fig. 4(b), for the same values of \( \lambda, T \), and \( t \). Best agreement is for \( D = 5 \times 10^{-14} \) cm²/sec. Lattice diffusivity for this temperature is much lower.
2.8 \times 10^{-14} \text{ cm}^2/\text{sec}, (12) and use of the lattice diffusivity in the computer simulation did not produce as good agreement. If the value 5 \times 10^{-12} \text{ cm}^2/\text{sec} is used to describe isoconcentration contours for \lambda's actually used [Fig. 5(a)], then the resulting concentration profiles can be compared with measured profiles [Fig. 5(b)]. The agreement of experimental and predicted concentration profiles indicates the diffusivity of 5 \times 10^{-12} \text{ cm}^2/\text{sec} is reproducible, and that the iso-concentration contours are nearly planar for diffusion at 240°C for 1.6 \times 10^5 \text{ seconds}, independent of \lambda for the spacings studied (\lambda \leq 0.2 \mu m). For each \lambda, the \alpha-phase is nearly saturated laterally with Zn. The two-dimensional analysis predicts that the same amount of Zn is absorbed by \alpha for each value of \lambda, which explains the observed independence of \lambda and \lambda.

At higher diffusion temperatures (287°C), a saturation with Zn is even less dependent upon \lambda. At lower diffusion temperature (193°C), isoconcentration contours are more curved with increasing \lambda. Thus, \lambda is measured (see Table I) and is predicted by the model to decrease with increasing \lambda. Differences in the amount of Zn absorbed by the \alpha-phase for different values of \lambda are too small for any variation in \lambda with \lambda to be measured.

By comparing experimental and calculated concentration profiles, as in Figs. 4(b) and 5(b), Zn diffusivity in \alpha can be determined as a function of temperature. The values are compared to bulk lattice diffusivities (12) in Table II.
TABLE II
Comparison of Values of Diffusivity

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Lattice Diffusivity, $D_L$ (12)</th>
<th>Apparent Diffusivity, $D_A$</th>
<th>$D_A/D_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>193 (0.5 $T_m$)</td>
<td>$1.7 \times 10^{-14}$ cm²/sec</td>
<td>$1.9 \times 10^{-12}$ cm²/sec</td>
<td>6</td>
</tr>
<tr>
<td>240 (0.55 $T_m$)</td>
<td>$2.8 \times 10^{-13}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>287 (0.6 $T_m$)</td>
<td>$1.0 \times 10^{-13}$ cm²/sec</td>
<td>$1.1 \times 10^{-10}$</td>
<td>34</td>
</tr>
</tbody>
</table>

DISCUSSION

The two-dimensional analysis presented here is similar in approach to Fisher's grain boundary enhanced diffusion solution. (2) The transformation of $\theta$ to $\tau$ produces a high-diffusivity path similar to the grain boundary slab. However, a two-dimensional analysis simplifies the geometry of the solution, as the grain boundary model would require that care be taken to avoid diffusional "leakage" across $\alpha$ platelet midplanes. More important, the grain boundary model would require assumptions about the composition along the $\alpha$-boundary, the $\alpha$ growth front. Because there is no evidence that the $\alpha$ boundary is acting as a high diffusivity path, any assumptions about composition along the boundary would be arbitrary. In the two-dimensional analysis, the Zn concentration in $\alpha$ ahead of the $\tau$ growth front is a natural consequence of the analysis. The present analysis may serve as a model of boundary enhanced diffusion above 0.63 $T_m$.

For the particular temperatures, times and lamellar spacings studied, the diffusivities are great enough that nearly complete diffusion occurs across the $\alpha$ platelets for the largest $\lambda$'s studied. The growth of $\tau$ from $\theta$ is independent of $\lambda$ for the $\lambda$'s studied because the amount of Zn supplied to $\alpha$ is nearly independent of $\lambda$. However, for lower temperatures, shorter times or much larger spacings, the gradients of Zn in $\alpha$ will be more severe and relatively less Zn will need to be supplied across the $\tau$-$\alpha$ interface. For the case where $\alpha$ is unsaturated in Zn, less Zn goes to $\alpha$, so that more is available for $\tau$ formation, and the growth rate of $\tau$ will increase, and in the limit will equal the growth of $\tau$ in Zn-$\theta$ couples (Fig. 1).

The ratio of apparent diffusivity to lattice diffusivity (Table II) is approximately 6 at 193°, 8 at 240°, and 34 at 287°. According to Hart, (13) a random distribution of dislocations will result in an apparent diffusivity greater than the lattice diffusivity, such that

$$D_A = D'L + D' \cdot (1-g).$$

where $D'L$ is the diffusivity in the dislocation core and $g$ is a dimensionless parameter (a ratio of the time an atom spends in the dislocation core to the time it spends in the lattice) equal to $10^{-14}$ cm²/dislocation lines times $\rho_\parallel$, the dislocation density. Equation (10) can be rewritten as:

$$\left(\frac{D_A}{D_L} - 1\right) \frac{D_L}{D'} \times 10^{14} \frac{\text{dislocation lines}}{\text{cm}^2} \approx \rho_\parallel (10)$$

An approximation of the dislocation pipe diffusivity results in values of $\rho_\parallel$ given in Table III.

TABLE III
Dislocation Pipe Diffusivity Results

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$\frac{D_A}{D_L} - 1$</th>
<th>$D_L/D'$</th>
<th>$\rho_\parallel$ (Dislocation Lines/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>193</td>
<td>5</td>
<td>$1.5 \times 10^{-8}$</td>
<td>$7.5 \times 10^{6}$</td>
</tr>
<tr>
<td>240</td>
<td>17</td>
<td>$7.8 \times 10^{-8}$</td>
<td>$1.3 \times 10^{8}$</td>
</tr>
<tr>
<td>287</td>
<td>33</td>
<td>$3.1 \times 10^{-7}$</td>
<td>$1.0 \times 10^{6}$</td>
</tr>
</tbody>
</table>

A density of $10^6$ to $10^9$ lines/cm² is within the range estimated from transmission electron micrographs of the Al-CuAl₂ eutectic. (9) Thus diffuson of Zn in the $\alpha$-phase of the eutectic can be understood in terms of a two-dimensional diffusion process enhanced by an adjacent phase transformation ($\theta \rightarrow \tau$) and by a high density of dislocations within the $\alpha$ platelets.

SUMMARY

Computer simulation of two-dimensional diffusion of Zn in the lamellar eutectic, Al-CuAl₂, can be accomplished using the finite difference method. The analysis predicts experimental observation and explains the independence of lamellar spacing and phase growth. The influence of diffusion time, temperature, and coefficient also are treated in the simulation.

The present analysis may serve as a detailed description of boundary enhanced diffusion. This could be accomplished by replacement of the $\tau$ growth region by an equation relating to the diffusion gradient within the grain boundary slab.

REFERENCES


