Interdiffusion in the Al-Cu System*

By Yasuhiro Funamizu** and Katsuya Watanabe**

Interdiffusion in the aluminum–copper system was investigated in the temperature range of 400° to 535°C with diffusion couples of pure aluminum and copper metals.

In the aluminum–copper equilibrium phase diagram there are five intermediate phases in this temperature range, namely \( γ_2 \), \( δ \), \( ζ_2 \), \( ζ_1 \) and \( θ \). Electron probe micro line analysis of specimens studied indicated that all of these phases were located in the diffusion layer.

It appears that the layer growth of each phase is controlled by the process of volume diffusion since the rate of layer growth obeys the parabolic law. From the temperature dependency of the rate constants of layer growth, the activation energies of the individual phases were obtained.

The interdiffusion coefficient for each intermediate phase was calculated by the method introduced by Heumann, and the values obtained were consistent with those derived from Kidson's equation for the \( δ \), \( ζ_2 \) and \( ζ_1 \) phases.

Aluminum oxide powder was used for the measurement of the Kirkendall effect. It is clear from this measurement that diffusion in the multilayer system is controlled by the vacancy mechanism and that aluminum diffuses more rapidly than copper.

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I. Introduction

With the recent development of the electron probe microanalyzer, experimental studies on the diffusion of the multilayer alloy systems have extensively been investigated by many researchers.

These studies have shown that the intermediate phases are formed in many different ways in a diffusion zone. It has been reported quite frequently that some of the intermediate phases which are clearly seen in an equilibrium phase diagram are not detectable at all, while in other cases all the phases predicted from the diagram are found in the diffusion zone(1)–(4). And several observers have found intermediate phases which are not equilibrium ones(4). As one of the most extreme cases, it has been recently reported that the formation of intermediate phases is not found in the interdiffusion couple of pure metals at all(5).

An attempt to explain the factors controlling the growth of the various phases above mentioned has been made from the viewpoints of formation energy, crystal structure and diffusion rate in the intermediate phase. Kidson(6), Gibbs(7) and others have developed a theoretical analysis of the growth rate of intermediate phases, with successful achievements on some of the special systems.

In the study of polyphase diffusion, many researchers recently stimulated interest in the determination of the factors controlling the occurrence and growth rate of the phases. But at present, it seems fairly difficult to theoretically explain the complex experimental results because of the limited basic data in this field. So, this problem is in need of further investigations.

The purpose of the present research work was to investigate the interdiffusion of the Al–Cu system in connection with the formation and growth of intermediate phases in the polyphase diffusion. The formation behaviors and temperature dependencies of growth rates of five intermediate phases (shown below) in this alloy system were observed, and the activation energies and interdiffusion coefficients for each phase were obtained. The study on the Kirkendall effect was also performed with an aim to discuss the mechanism of interdiffusion in the system.

Figure 1 represents the equilibrium phase diagram of the Al–Cu system(8). The temperature range studied was 400° to 535°C, and there are five intermediate phases in the range. They are as follows:

- \( γ_2 \) phase (Cu₃Al₄) 69.2 at% Cu;
- \( δ \) phase (Cu₅Al₆) 60.0 at% Cu;
- \( ζ_2 \) phase (Cu₅Al₆) 57.1 at% Cu;
- \( ζ_1 \) phase (CuAl) 50.0 at% Cu;
- \( θ \) phase (CuAl₂) 33.3 at% Cu.

As is widely known and can easily be seen from the phase diagram, the compound phases have an extended phase range. In this case, for the sake of convenience, their molecular formulas and chemical compositions at the stoichiometry are presented.

In Table 1 crystal structures and lattice parameters of these phases obtained by Bradley and his co-workers(9) (10) are summarized and reproduced.

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Fig. 1 Equilibrium phase diagram of the Al-Cu system.

Table 1 Crystal structure of intermediate phases in the Al-Cu system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Chemical composition</th>
<th>Crystal structure</th>
<th>Lattice parameter</th>
<th>Atoms per unit cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \tau )</td>
<td>Cu₃AI</td>
<td>( \gamma )-brass type</td>
<td>( a = 8.70 \AA )</td>
<td>36 Cu, 16 Al</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Cu₂Al₂</td>
<td>( \gamma )-brass type</td>
<td>( a = 8.69 \AA )</td>
<td></td>
</tr>
<tr>
<td>( \zeta )</td>
<td>Cu₄Al₃</td>
<td>Monoclinic</td>
<td>( a = 7.66 \AA ), ( b = 4.07 \AA ), ( c = 10.00 \AA ), ( \beta = 90.38^\circ )</td>
<td>12 Cu, 9 Al</td>
</tr>
<tr>
<td>( \eta )</td>
<td>CuAl</td>
<td>Body-centered orthorhombic</td>
<td>( a = 6.88 \AA ), ( b = 4.08 \AA ), ( c = 9.87 \AA )</td>
<td>10 Cu, 10 Al</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Cu₃Al₂</td>
<td>C-16 type</td>
<td>( a = 6.07 \AA ), ( c = 4.87 \AA )</td>
<td>4 Cu, 8 Al</td>
</tr>
</tbody>
</table>

Up to the present, the results of several investigations have been reported in this system. Bückle(11) determined the coefficient of interdiffusion in Al solid solution over the temperature range of 500° to 550°C. Murphy(12) also determined the coefficient in this solid solution over the concentration range of 0–0.5 wt% Cu by a spectrophotometric method. da Silva and Mehl(13) reported on the diffusion in Cu solid solution. Eifert and his co-workers(14) investigated the conditions prevailing for phase transformation at the interface between the two phases in a Cu–Al diffusion couple and compared the concentration at the interface with those associated with the thermodynamic equilibrium between the two phases. No information, however, is available on the multilayer diffusion in the whole concentration range of the Al–Cu system.


II. Experimental Procedure

In this study, diffusion couples of pure Al (99.99%) and oxygen free Cu (99.99%) metals were used. Al disks of 12 mm diameter and 5 mm thickness were machined from an aluminum ingot, and Cu plates of 15 mm square and 1 mm thick were cut from a copper sheet. In order to obtain big grain sizes, Al disks and Cu plates were annealed in a vacuum of 10⁻⁴ mm Hg for 48 hr at 500°C, and 72 hr at 800°C respectively. The grain sizes obtained were about 2 mm for Al and 1 mm for Cu specimens. The surfaces of the disks and plates were ground metallographically to receive flat and smooth planes. Then a Cu plate was sandwiched between two disks of Al and this pile was pressed with a spring so as to have a tight contact, and then thermally welded in an evacuated electric furnace. A very thin layer of the diffusion zone, less than 5 μ wide, was formed during the welding treatment. Aluminum oxide powder was used as a marker for the measurement of the Kirkendall effect. The powder was scattered at the two interfaces of the sandwiched couple and then welded.

The diffusion couple was sealed in an evacuated glass capsule and diffusion-annealed over the temperature range of 400° to 535°C which was controlled within ±1°C. After the annealing, the glass capsule was quenched in cold water, and the couple in the capsule was cut, polished and analyzed on the plane parallel to the direction of diffusion.

Concentration-penetration curves were established using the electron probe microanalyzer with CuKα radiation. An accelerating voltage of 25 kV was employed. The concentration of copper in the diffusion zone was obtained from the relative intensity of CuKα radiation. Figure 2 represents the calibration curve for the quantitative analysis determined experimentally using specimens chemically analyzed.

III. Experimental Results

1. Behavior of the diffusion zone

Photo. 1 shows a typical micrograph of the diffusion zone of the couple which was diffusion-annealed at
535°C for 80 hr. Figure 3 is a typical concentration-penetration curve obtained from the recorded chart of the electron probe microanalyzer. As shown in Fig. 3, all the five intermediate phases existing in the phase diagram appeared in the diffusion zone. In this study, the five phases were detected at all annealing temperatures. In the diffusion zone the Al solid solution phase extended widely, while the thickness of Cu solid solution was less than 5μ under all the experimental conditions.

Figure 3 Typical concentration-penetration curve for Al-Cu couple diffused at 495°C for 56 hr.

2. Layer growth of intermediate phase

Figure 4 shows the layer width of the five intermediate phases plotted against the square root of the diffusion time at 515°C. It is clear in the figure that the linear relation between the width and the square root of the time is attained, and the relation is expressed as

\[ W = k \sqrt{t}, \]  

where \( W \) is the width of an intermediate phase layer, \( t \) is the time of diffusion and \( k \) is a rate constant. It turned out distinctly that the parabolic law was upheld for the layer growth, suggesting that the layer growth is controlled by the process of volume diffusion.

Figure 5 shows the temperature dependencies of the rate constant obtained from Fig. 4. Again the linear relation was obtained between the rate constant squared and the reciprocal absolute temperature. From this relation, eqs. (2) to (6) are calculated using the least square method.

\[ \gamma_2 \text{ phase} : k^2 = 3.2 \times 10^{-2} \times \exp(-31600/RT), \quad (2) \]
\[ \delta \text{ phase} : k^2 = 2.6 \times 10^{-1} \times \exp(-33500/RT), \quad (3) \]
\[ \gamma_2 \text{ phase} : k^2 = 2.7 \times 10^{-6} \times \exp(-61200/RT), \quad (4) \]
\[ \gamma_2 \text{ phase} : k^2 = 1.7 \times 10^{-6} \times \exp(-19600/RT), \quad (5) \]
\[ \theta \text{ phase} : k^2 = 9.1 \times 10^{-6} \times \exp(-29300/RT), \quad (6) \]
where $k^2$ is the squared rate constant (cm$^2$/sec), $R$ is the gas constant (cal/mol·°K) and $T$ is the absolute temperature (°K).

3. Interdiffusion Coefficient

Generally the interdiffusion coefficient ($D$) for binary alloys is obtained by Matano’s method as follows:

$$D(c) = -\frac{1}{2t} \int_0^c x dc$$  \hspace{1cm} (7)$$

with $x dc = 0$, if the total concentration range within the diffusion zone extends from zero to $C_0$. Where $D(c)$ is the interdiffusion coefficient of the alloy phase of concentration $c$, $x$ is a distance from the initial interface and $t$ is the time for diffusion.

When intermediate phases are formed in the diffusion zone, however, one cannot always apply eq. (7) directly to the system. From Matano’s equation, Heumann derived an equation which is valid for diffusion in an intermediate phase under the condition that the concentration profile is approximately kept linear in the phase from end to end. The equation is

$$D_i = -\frac{W_i}{2tD_i} \int_0^{c_{i/2}} x dc$$  \hspace{1cm} (8)$$

where $D_i$ is an interdiffusion coefficient, $W_i$ is a layer width, $DC_i$ is a concentration difference between both ends, $C_{i/2}$ is a middle point with regard to the concentration profile within the phase and the suffix $i$ means an intermediate layer of $i$th. $x$ and $t$ have the same meaning as in eq. (7). Following Heumann, $D_i$ is regarded as an average value of the diffusion coefficient in an $i$th intermediate phase.

In the present study calculations were made on the molar volume change with the concentration in the system concerned by referring to the study of Bradley and his co-workers (1952,1953) on the lattice parameters. It became clear from the calculation that the molar volume changes largely from $7.1$ cm$^3$/mol of pure copper to $10.0$ cm$^3$/mol of pure aluminum, but the change was almost linear with the concentration. When there is a large volume change within the diffusion zone, a factor of volume change must be added to the equation for the interdiffusion coefficient.

Balluffi derived an equation which is valid for the diffusion with a volume change, that is,

$$D = -\frac{1}{2t} \left( \frac{\partial x}{\partial C_a} \right) \left( 1 - C_a V_a \right) \left( \int_0^{C_{a(-\infty)}} x dc \right) + V_a C_a \left( \int_0^{C_{a(-\infty)}} \frac{V_a}{V_b} x dc \right)$$  \hspace{1cm} (9)$$

where $V_a/V_b$ denotes a partial molar volume of the element $a$ ($b$), and $C_a/C_b$ is a concentration of the element $a$ ($b$) expressed in mol/cm$^3$. Equation (9) indicates that calibration of the volume change factor is not necessary for the calculation of $D$ when the ratio of $V_a/V_b$ is kept constant even if a volume change is existing as a whole. For the present system, as mentioned above, the author’s calculation showed that the ratio is almost constant for the whole range of concentration. Then the molar volume factor was disregarded in the present study and Heumann's method was employed to calculate the interdiffusion coefficient indicating the concentration as mol/cm$^3$.

The temperature dependence of the interdiffusion coefficient thus obtained is represented in Fig. 6. The coefficients of $\zeta_2$ and $\gamma_2$ phases at 400°C and 425°C were not calculated. The reason was that the erroneous result was indispensable for the determination of concentrations because the layer thickness was too narrow at these temperatures to obtain a reliable analytical value with the electron probe micro analyzer. And the calculation of $D$'s of the other phases were carried out assuming proper values for the concentrations of $\zeta_2$ and $\gamma_2$ phases at the temperatures. The error coming from this assumption might affect the determination of Matano’s interface within the accuracy of less than one per cent which is a negligibly small value.

As shown in Fig. 6, the linear relation is held between $D$ and $1/T$, and from the relation, the temperature dependence of interdiffusion coefficients is determined by the least square method for each layer.

These are

$$\gamma_2 \text{ phase: } D_{\gamma_2} = 8.5 \times 10^{-11} \exp(-32500/RT),$$  \hspace{1cm} (10)$$

$$\delta \text{ phase: } D_\delta = 2.1 \times \exp(-33000/RT),$$  \hspace{1cm} (11)$$

$$\zeta_2 \text{ phase: } D_{\zeta_2} = 1.6 \times 10^6 \exp(-55100/RT),$$  \hspace{1cm} (12)$$

$$\eta_2 \text{ phase: } D_{\eta_2} = 2.2 \times \exp(-33500/RT),$$  \hspace{1cm} (13)$$

$$\theta \text{ phase: } D_\theta = 5.6 \times 10^1 \exp(-30500/RT).$$  \hspace{1cm} (14)$$

Frequency factors and activation energies for the layer
growth and interdiffusion of each phase are summarized in Table 2.

4. Kirkendall effect

The Kirkendall effect was measured in order to investigate the diffusion mechanism of the Al-Cu system. The marker shift was determined as the distance between the marker and Matano’s interface. It was observed that the marker moved toward the aluminum side with respect to Matano’s interface. In Fig. 7 the marker shift is plotted with the square root of diffusion time, and a linear relation substantially holds between them. This result suggests that the diffusion is controlled by a vacancy mechanism and that the aluminum diffuses more rapidly than the copper in the system.

IV. Discussion

The observation by the electron probe microanalyzer showed that the diffusion layer of the copper solid solution was very narrow in contrast to a wide diffusion layer of aluminum solid solution. It also showed that the aluminum concentration in the copper solid solution was lower than that of equilibrium. The reason why the copper solid solution layer was very narrow compared with that of aluminum can be explained by the difference in diffusion rate between primary solid solutions of aluminum and copper. The interdiffusion coefficient in the aluminum solid solution and the self-diffusion coefficient of copper in aluminum were both determined by some researchers as about \(5 \times 10^{-13} \text{cm}^2/\text{sec}\) at 500°C (18)-(19). In the present study the values of the interdiffusion coefficient and the self-diffusion coefficient of aluminum in the copper solid solution were evaluated from the extrapolation of available data in the literature (18)-(20). The coefficients thus obtained were about \(1 \times 10^{-13} \text{cm}^2/\text{sec}\) at 500°C. From the comparison of those diffusion coefficients, it is evident that the diffusivity in the aluminum solid solution is much greater than that in the copper solution.

The equilibrium phase diagram of the Al-Cu system proposed by Hansen (8) (Fig. 1) shows that there is a two-phase region between the \(\tau_2\) and \(\delta\) phases. But Bradley et al. (10) reported that the two-phase region did not exist. In the present investigation, the presence of the two-phase region was clearly observed with the electron probe microanalyzer. Of course the present specimens were diffusion annealed and not equilibrated at the experimental temperatures, but the observation of the two-phase region might be helpful for arguments in regard to the pertinence of the diagram.

Some investigators have given theoretical analysis for the layer growth of intermediate phases in the diffusion zone. Baird (22), in discussing a formation of alloy layers, listed Seith’s criteria: a layer will grow more rapidly

(a) the greater the diffusion coefficient,
(b) the less the coefficient in the adjoining phase,
(c) the greater the homogeneity range of the phase, and
(d) the smaller the concentration range of the adjoining two-phase areas in the diagram.

Kidson (6) derived the following equation from Fick’s second law assuming the material balance set up at the phase boundaries.

\[
W_j = 2\left[ \frac{\left( \frac{dC}{dx} \right)_{j+1}-\left( \frac{dC}{dx} \right)_{j+1}}{\left( \frac{dC}{dx} \right)_{j+1}-\left( \frac{dC}{dx} \right)_{j+1}} \right]^{\sqrt{t}} = k_j \sqrt{t}
\]  

where \(W_j\) is a layer thickness of the \(j\)th phase, \(C_{j+1}\) is the concentration, \(K_{j+1}\) is \(\sqrt{t} \left( \frac{dC}{dx} \right)_{j+1}\), and the suffix \((j+1)\) represents an interface between \(j\)th and \((j+1)\)th phases in the \(j\)th phase.

Gibbs (7) developed Kidson’s analysis and described the layer growth in terms of the interdiffusion coefficient and concentration of each phase.

From the results of these analysis, it is seen that the growth of the intermediate phase is complicatedly affected by the diffusion rate, miscibility gap and \(K\) value and so it is not simple to determine essential factors controlling the behavior of layer growth.

The results of the present study suggest, as one might

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presume phenomenologically from Fig. 6 and Fig. 7, that the layer growth depends to a considerable extent on the interdiffusion coefficient in this system.

As shown in Fig. 3, all five intermediate phases existing in the phase diagram are detected under all the experimental conditions. This sort of observation has seldom been reported. A conclusive explanation has not yet been proposed for the genesis of these phases. They have a similar crystal structure which arises from the CsCl type, suggesting that they constitute a genetic sequence. Each crystal phase could grow from the preceding one without wasting much of the energy that would be involved in the nucleation and in the formation of an interface.

Equation (15) shows that $D$ for each intermediate phase can be obtained by solving the $(j-2)$ simultaneous equations of first degree for $D$, if the values of $D$ and $K$ of solid solutions of aluminum and copper are known respectively. The interdiffusion coefficients thus obtained ought to be essentially consistent with those obtained by other methods so far as those methods are based on Fick’s law. The comparison must be valuable in supporting the justification of the equation deduced by Kidson. Unfortunately, $D$ and $K$ of both solid solutions were not obtained in this study on account of a very low concentration of the aluminum solid solution and a very narrow width of the copper solid solution layer. But those of $\delta_2$ and $\theta$ phases were obtained. Hence the values of diffusivities of $\delta$, $\zeta_2$, and $\eta_2$ were calculated by solving the three simultaneous linear equations. The values were compared with the values of diffusivities determined by Heumann’s method.

From eq. (15), the following equation was obtained:

$$
\frac{W_j}{2 \sqrt{t}} = \frac{(C_{j+1} - C_{j+1,2} - C_{j+1,2} - C_{j+1})K_j}{(C_{j+1} - C_{j+1,2}) (C_{j+1} - C_{j+1})} D_j + \frac{K_{j+1}}{K_{j+1}} \frac{D_j}{D_{j+1} + (C_{j+1} - C_{j+1,2})} D_{j+1}
$$

The values of $D_\delta$, $D_{\zeta_2}$ and $D_{\eta_2}$ at 515°C obtained from the simultaneous linear equations derived from eq. (16) are represented in Table 3 together with the values determined by Heumann’s method.

The result shows that the interdiffusion coefficients calculated from Kidson’s equation coincide well with those obtained by Heumann’s method, giving a strong support to the validity of Kidson’s equation to determine the interdiffusion coefficients of the intermediate phases in polyphase diffusion.

In Table 2, the activation energy of the layer growth $(Q_k)$ is compared with that of interdiffusion $(Q_D)$. With respect to $\eta_2$, $\delta$ and $\theta$ phases, the values of $Q_k$ are almost equal to the values of $Q_D$ respectively. But for $\eta_2$ and $\zeta_2$ phases, there is a difference between the values of $Q_k$ and $Q_D$. It is generally known that the value of $Q_k$ is not always equal to that of $Q_D$, and it is difficult to quantitatively explain the origin of the difference by reason of the complexity of the temperature dependence of $K$ in eq. (15). In this study, it was observed that the composition range of $\eta_2$ phase was most dependent on temperature and that of $\zeta_2$ phase was the next among the five phases. And the temperature dependence of the miscibility gap between $\eta_2$ and $\zeta_2$ phases was fairly large, while that of the gaps between other phases was very small. Therefore, it seems that the difference between the values of $Q_k$ and $Q_D$ of $\eta_2$ and $\zeta_2$ phases originates from the large temperature dependency of concentration of the two phases.

V. Summary

The results of the present investigation can be summarized as follows:

1. Interdiffusion between aluminum and copper was studied in the temperature range of 400°C to 535°C. In this temperature range, all of the five intermediate phases existing in the equilibrium phase diagram were formed in the diffusion zone.

2. The layer growth of each phase obeyed the parabolic law and was controlled by the process of volume diffusion.

3. From the temperature dependence of rate constant, the activation energy for each layer growth was determined.

4. The interdiffusion coefficient of each phase was obtained by Heumann’s method and from their temperature dependencies, the activation energy for the interdiffusion of each intermediate phase was determined.

5. Interdiffusion coefficients for $\delta$, $\zeta_2$ and $\eta_2$ phases were calculated with Kidson’s equation, and the values obtained were coincident with those derived from Heumann’s method. This result must support the validity of Kidson’s equation to determine the interdiffusion coefficients of the intermediate phases in polyphase diffusion.

6. The measurement of the Kirkendall effect indicated that the diffusion was controlled by the vacancy mechanism, and that aluminum diffuses more rapidly than copper in this system.

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