Interdiffusion Coefficient in Cu–Zn Alloys Determined by a Volatilization Phenomenon of Zinc

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Interdiffusion coefficients $D$ in Cu–Zn alloys have been determined by using diffusion couples consisting of pure copper wire as vapor absorbent and the alloy having 15 and 30 at% Zn from which zinc atoms volatile and by annealing the alloy having 15 at% Zn in an evacuating furnace. The values of $D$ thus obtained coincide with each other, but, they are 2–5 times larger than those obtained previously by use of the usual solid-solid diffusion couples in a dilute region while they are almost equivalent in a highly concentrated region. The reasons have been considered in relation to the vacancy flux which comes from the surface into the alloy specimen.

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I. Introduction

Since Balluffi et al.\(^{(1,2)}\) have shown a method for determination of the interdiffusion coefficients in binary alloys by use of vapor-solid type diffusion couples, this method has been frequently used by many investigators\(^{(3)}\). However, the above studies dealt with the diffusion from a vapor source into a solid metal having a negligible vapor pressure and not with the case where a volatile element diffused out from a solid alloy specimen. On the basis of the surface fixed frame of reference, the present authors\(^{(4)}\) previously presented an analysis to determine the interdiffusion coefficients in a solid alloy from which the volatile component diffuse out. In this paper interdiffusion coefficients in a brass from which zinc atoms volatile have been determined experimentally. The interdiffusion coefficients thus obtained are compared with those obtained previously by the use of the usual solid-solid type diffusion couple\(^{(5)}\). The difference between these interdiffusion coefficients has been considered.

II. Experimental Procedure

Pure copper wires of about 99.98% purity and $1.7 \times 10^{-4}$ m in diameter were degassed in vacuum of $3 \times 10^{-2}$ Pa at 1073 K for 10.8 ks for preparation of the zinc vapor absorbent.

Cu–Zn alloys respectively having 15 and 30 at% Zn were prepared by melting copper of 99.99% purity and zinc of 99.99% purity. The chemical compositions of the alloys are shown in Table 1. The ingots of the alloys were rolled and then cut to the form of about $7 \times 7 \times 6$ mm. The alloy specimens were sealed along with chips of the alloy and annealed at 1073 K for 10.8 ks to yield crystal grain growth. The chips were used in order to prevent dezincification of the alloy specimens. The crystal grains thus obtained were about 900 μm in diameter. The surfaces of each specimen were ground by a waterproof abrasive paper and polished on a buff with fine alumina paste about 0.1 μm in diameter. All of specimens were then weighed and the size of each specimen was measured as a procedure to obtain the mass loss per unit area.

Table 1: Chemical composition (at%) of Cu–Zn alloys.

| Designation | Cu     | Pb     | Fe     | Zn |
|-------------|--------|--------|--------|----|
| 15          | 84.9   | 0.01   | 0.01   | bal.|
| 30          | 70.2   | 0.01   | 0.01   | bal.|

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The wires and a solid specimen were sealed in an evacuated quartz capsule in such a way as to avoid contacts between the specimen and the wires. The combination of the wires and the 15 at% Zn–Cu alloy specimen is described by the 0–15 V–S couple and the couples were annealed at 1013, 1043, 1073 and 1103 K. A combination of the pure copper wires and the 30 at% Zn–Cu alloy specimen (0–30 V–S couple) was annealed at 1103 K only.

The 15 at% Zn–Cu alloy specimens were also annealed in the continuously evacuating furnace at 968, 1013, 1043 and 1058 K. This type of diffusion couple is designated by the 0–15 V couple. After the annealing the solid specimen was weighed. Then, the specimen was cut and the section was polished in the same way as described above. An electron probe microanalyzer (JEOL JXA 733) was used to determine the concentration-penetration profiles and Zn concentration at the specimen surface after annealing. The operating condition of E.P.M.A. were as follows: The accelerating voltage 25 kV; the take-off angle of Zn Kα X-ray 0.222 rad; the specimen current about 5×10^{-6} A; the line scanning speed 0.833 or 1.667 μm/s. The intensity of Zn Kα X-ray was converted to the concentration of zinc by use of a calibration curve.

III. Results

In the α solid solution of the Cu–Zn system the partial molar volumes of copper and zinc, \( \bar{V}_{\text{Cu}} \) and \( \bar{V}_{\text{Zn}} \) are constant and given by 7.1×10^{-6} m³/mol and 8.4×10^{-6} m³/mol, respectively. Therefore, the molar volume \( (V: \text{m}^3/\text{mol}) \) of alloy is represented by the equation\(^{(6)}\):

\[
V = (1.3 \times N_{\text{Zn}} + 7.1) \times 10^{-6}
\]

This situation enable us to analyze the diffusion phenomena in the vapor-solid diffusion couples by employing the volume fraction, \( C_{\text{Zn}} \bar{V}_{\text{Zn}} \), of zinc for the concentration denotation\(^{(4)}\).

After annealing the alloy specimens \( C_{\text{Zn}} \bar{V}_{\text{Zn}} - \chi \) curves are plotted and then the position of the initial surface at the annealing time \( t=0 \) is estimated according to the procedure stated in previously\(^{(4)}\). Here, the origin of the \( X \) coordinate system is the position of the specimen surface at the annealing time, \( t=0 \). By defining that the origin of the \( X' \) coordinate system is the position of the initial surface at the annealing time, \( t=0 \), and \( X' / \sqrt{t} \) is \( \lambda' \) the \( C_{\text{Zn}} \bar{V}_{\text{Zn}} - \lambda' \) curves for the 0–15 V–S couples annealed at 1073 K for 57.6, 90.0, 176.4 and 360 ks are shown in Fig. 1. The \( C_{\text{Zn}} \bar{V}_{\text{Zn}} - \lambda' \) curves for four distinct annealing times may be approximately represented by a master curve.

![Fig. 1 Concentration \( (C_{\text{Zn}} \bar{V}_{\text{Zn}}) \) - penetration \( (\lambda') \) profiles for the 0–15 V–S diffusion couples annealed at 1073 K.](image)
The zinc concentration of the specimen surface determined by E.P.M.A. was zero for the 0-15 V-S and 0-15 V couples and 0.7 at% Zn for 0-30 V-S couples irrespective of the annealing time and temperature. The master $C_{Zn}\bar{V}_{Zn}-\lambda'$ curves for 0-15 V-S, 0-15 V and 0-30 V-S couples at other temperatures can also be plotted with approximately the same accuracy as those in Fig. 1. Because $\partial C_{Zn}/\partial X'$ is equivalent to $\partial C_{Zn}/\partial X$ and the respective partial molar volumes for zinc and copper are kept constant, the diffusion fluxes referred to the $X'$ coordinate system are given by $-D\partial C_{Zn}/\partial X$, i.e., the fluxes with respect to the so-called volume fixed frame of reference.

The interdiffusion coefficients, $D$, at 1103 K obtained by use of the 0-15 and 0-30 V-S couples are shown in Fig. 2 in comparison with $D$ determined by use of the usual solid-solid diffusion couples$^5$, where the diffusion coefficient at a given concentration is the average of ten coefficients calculated from ten $C_{Zn}\bar{V}_{Zn}-X'$ curves without the employment of the master curves. The coefficients in the 0-15 and 0-30 V-S couples are distributed within ±30% and 40% around the average value, respectively. These percentages are larger than ±17% which is estimated for the solid-solid diffusion couples$^5$. Here, the interdiffusion coefficients obtained in this experiment and the coefficients in the usual solid-solid couples are designated by $D_{ss}$ and $D_{vs}$, respectively. In Fig. 2 $D_{ss}$ at zero at% Zn for the 0-15 V-S couple is about two times and $D_{vs}$ at zero at% Zn for the 0-30 V-S couple is about five times larger than $D_{ss}$ at the same concentration of zinc. With increase of zinc concentration, the difference between $D_{ss}$ and $D_{vs}$ decreases and $D_{ss}$ is very close to $D_{ss}$ in the highly concentrated region. A similar relationship between $D_{ss}$ and $D_{vs}$ has also been obtained at other temperatures as shown in Fig. 3.

Figure 4 shows temperature dependence of $D_{ss}$ at various concentration of zinc in the 0-15 V-S and 0-15 V couples. Irrespective of the different types of the couples, logarithms of $D_{ss}$ at a given concentration are represented by a linear function of the reciprocal of the absolute temperature. This cause may be related to that the zinc concentration of the alloy specimen surface is kept to be zero during the annealing period. The activation energy, $Q_{ss}$, and the frequency factor, $D_{0ss}$, have been deter-
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mined by applying the least squares method to Fig. 4. The concentration dependence of $\bar{Q}$ and $D_{\text{ss}}$ is shown in Fig. 5, in which the activation energy, $Q_{\text{vs}}$ and the frequency factor $D_{\text{vs}}$ estimated by use of the solid-solid couples are also shown together with $Q_{\text{zn}}^*$ and $D_{\text{zo}}^*$ for impurity diffusion of zinc in copper. With increasing zinc concentration, $Q_{\text{vs}}$ remains constant or slightly increases, in contrast with the decrease in $Q_{\text{ss}}$. Therefore, the difference between $Q_{\text{vs}}$ and $Q_{\text{ss}}$ becomes maximum at zero at% Zn.

In this experiment the alloy specimen surface moves relative to the coordinate system fixed with respect to the semi-infinite region of the specimen, as a result of the shrinkage due to dezincification. If the fluxes referred to the coordinate system fixed with respect to the specimen surface and the semi-infinite region are designated by $-\beta_{\text{zn}}(\partial C_{\text{zn}}/\partial X)$ and $-D(\partial C_{\text{zn}}/\partial X)$, respectively, and the moving velocity of the surface is given by $v$, the relation between the two types of fluxes is represented by the equation:

$$-\beta_{\text{zn}}(\partial C_{\text{zn}}/\partial X) = -D(\partial C_{\text{zn}}/\partial X) + C_{\text{zn}} v \quad (2)$$

where $C_{\text{zn}}$ is mole concentration of zinc. The zinc flux at the surface, $-\beta_{\text{zn}}(\partial C_{\text{zn}}/\partial X)$, means the numbers of the zinc atoms which diffuse from an alloy specimen to a vapor phase through the unit area of the specimen surface during the unit time of annealing. Because $C_{\text{zn}}$ at the surface in this experiment is zero, two types of the fluxes at the surface become identical with each other. The surface area decreases with increasing annealing time, due to dezincification. In Fig. 1 the position of the specimen surface at the annealing time $t = t_0$ is given by $0.05 \times 10^{-6} \text{m/s}^{1/2}$ on the $\lambda'$ coordinate system. If $t^{1/2}$ is 600, the specimen surface shifts toward the semi-infinite region at a distance of 30 $\mu$m. After annealing for 360 ks, therefore, the shrinkage rate of the rectangular specimen is 0.9% and 1.7% of the initial surface area of the specimen decreases. The change in the surface area is so small that the change can be neglected and one can use $S_0$ as the area $S_t$ at an arbitrary annealing time $t = t_0$. Under this condition, the absolute value of the flux is related to the mass loss, $W_t$, of the specimen as
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\[ W_t = 2M_{Zn}S_0 |J_s| \tau , \]  
(3)

where \( M_{Zn} \) and \( J_s \) are the relative atomic mass of zinc (6.54 × 10^{-2} kg/mol) and the zinc flux at surface of the specimen, respectively. \( J_s \) is given by

\[ J_s = - \left( \frac{\partial C_{Zn}}{\partial X} \right)_s = - \left( \frac{\partial C_{Zn}}{\partial \lambda'} \right)_s \tau^{-1/2} \]  
(4)

and

\[ \left( \frac{\partial C_{Zn}}{\partial \lambda'} \right)_s = \frac{1}{2V_{Zn}} \int_0^{C_{Zn}V_{Zn}} \lambda' d(C_{Zn}V_{Zn}) . \]  
(5)

The right hand side in eq. (5) is the constant which is easily obtained from Fig. 1. The constant is represented by \( K \) and then

\[ J_s = K \tau^{-1/2} . \]  
(6)

Substitution of eq. (6) for eq. (3) yields

\[ W_t/S_0 = 2M_{Zn}K \tau^{1/2} . \]  
(7)

At various temperatures the relation between \( W_t/S_0 \) and the square root of annealing time for the 0–15 V diffusion couples are shown in Fig. 6 in which a good linear relationship holds at all temperatures, as expected from eq. (7). Putting \( K \) obtained from the gradient of each line in Fig. 6 into eq. (6) one can easily obtain \( J_s \). \( J_s \) thus obtained is designated by \( J_{ws} \). Moreover, \( J_s \) was obtained by the ordinary graphical integration with the aid of eq. (5) and is designated by \( J_{cs} \), \( J_{cs} \) and the ratio \( J_{cs}/J_{ws} \) are given in Table 2. \( J_{cs} \) is about 10 to 40% larger than \( J_{ws} \) at all temperatures. Figure 7 shows a scanning electron micrograph of the specimen surface of the 0–15 V–S couple annealed at 1103 K for 28.8 ks, in which many voids due to dezincification are recognized.

Table 2 Values of the slope, \( W_{Zn}/S_0 \), of the lines in Fig. 6, \( J_{ws}, J_{cs} \) and their ratio \( J_{cs}/J_{ws} \). The ratios \( \vec{D}_{cs}/\vec{D}_{ws} \) at surface composition are also shown.

| Temp. (K) | \( W_{Zn}/S_0 \)\(^{1/2} \) (\( = 2M_{Zn}K \)) | \( J_{ws}^{+} \) (\( = K/\tau^{1/2} \)) | \( J_{cs}^{+} \) | \( J_{cs}/J_{ws} \) | \( \vec{D}_{cs}/\vec{D}_{ws} \)
|---------|-----------------|-----------------|-----------|-------------|-------------|
| 1058    | 2.65 × 10^{-4}  | 2.03 × 10^{-3}/\tau^{1/2} | 2.52 × 10^{-3}/\tau^{1/2} | 1.24 | 2.02 |
| 1043    | 2.06            | 1.57            | 2.26      | 1.43 | 2.29 |
| 1013    | 1.64            | 1.26            | 1.58      | 1.26 | 2.27 |
| 968     | 1.26            | 0.96            | 1.10      | 1.14 | 3.14 |

\( \dagger \) The values of \( J_{ws} \) at 1058 K for annealing time \( t = 360 \) ks can be obtained by \( 2.03 \times 10^{-3}/600 = 3.38 \times 10^{-6} \) (mol/m\(^2\)/s) for an example.
After polishing the section of the specimen annealed at 1013 K for 47.6 ks on a buff, however, the voids in a diffusion zone cannot be detected by an optical microscope. Electroplishing by the use of the solution (H₃PO₄: 0.375 kg/l and H₂O: 0.625 kg/l) under an experimental condition of 1.9×10⁻³ kV, 0.14×10⁻⁷ kA/m² at room temperature enables us to recognize the voids as shown in Fig. 8. It can be seen that many voids appear in the vicinity of the surface, although the size of the void may be enlarged by electropolishing. The reason for the difference between \( J_{vs} \) and \( J_{ss} \) is not clear, but it is supposed that voids formed on the specimen surface and in the vicinity of the surface, may act as a cause of the difference.

Molybdenum powder as markers was placed at the specimen surface at the annealing time, \( t=0 \). After annealing the markers remained on the surface as predicted in a previous report.⁴

### IV. Discussion

In the solid-solid diffusion couple consisting of pure copper and Cu–Zn α alloy specimens vacancies are produced in a diffusion zone with a lower zinc concentration and move to a higher zinc concentration side. After the vacancy flux passes through the Kirkendall interface the flux decreases in absolute magnitude because the vacancies are captured by voids and dislocations and then become zero in a semi-infinite region on the higher zinc concentration side. On the contrary, the vacancies in this experiment are formed near the specimen surface and move across the surface from the specimen to the vapor phase at the same time. Because the diffusion flux of zinc atoms becomes maximum at the surface, the vacancy flux toward a reverse direction of the zinc flux is maximum and increases the vacancy concentration in the vicinity of the surface. The absolute magnitude of the vacancy flux decreases with increase in the distance from the surface and becomes zero in the semi-infinite region.

The variation of the vacancy concentration and of the magnitude of the vacancy flux at a given concentration of zinc changes the magnitude of the interdiffusion coefficient.⁴ Therefore, the effect of the vacancies on the coefficient becomes most remarkable on the surface and the difference between \( \bar{D}_v \) and \( \bar{D}_s \) also becomes maximum, as shown in Figs. 2 and 3. The difference between \( \bar{D}_v \) and \( \bar{D}_s \) becomes much greater in the 0–30 V–S couples as more vacancies flow from the surface to the inside. With increase of the zinc concentration the vacancy effect on the interdiffusion coefficient as well as the difference between \( \bar{D}_v \) and \( \bar{D}_s \) decrease, and then \( \bar{D}_v \) and \( \bar{D}_s \) coincide with each other in the semi-infinite region on the higher zinc concentration side. If the activation energy for interdiffusion is in the same situation as in the case of self-diffusion, the activation energy is separated into the energy for vacancy formation and that for the vacancy movement. Though the activation energy for the vacancy movement does not depend on the type of the couples, i.e., the vapor-solid and solid-solid couples, the activation energy for vacancy formation at the specimen surface may differ from that within the specimen. It may be concluded, therefore, that \( \bar{Q}_v \) is smaller than \( \bar{Q}_s \) as shown in Fig. 5.

### V. Conclusion

By use of volatilization phenomenon of zinc atoms, interdiffusion coefficients, \( \bar{D} \), in the Cu–Zn α alloys have been determined using the vapor-solid couples consisting of fine pure copper wires as the vapor absorbent and the
alloy having 15 or 30 at% zinc and by annealing the 15 at% Zn-Cu alloy in an evacuating furnace. The results are summarized as follows,

(1) The values of $D$ obtained by the above two methods coincide with each other. However, they are larger than those obtained previously by the usual solid-solid diffusion couples in the dilute concentration range while they are almost equivalent to $D$ in the solid-solid couple in the semi-infinite region on the higher zinc concentration side.

(2) The activation energy obtained in this experiment is smaller than that in the solid-solid couples. This appears to relate that the vacancies which controls the diffusion in the substitutional alloys are formed in the vicinity of the specimen surface in this experiment and the vacancy formation energy near surface may be lower in comparison with the vacancy formation energy in the solid-solid couples.

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