Quaternary Diffusion in the α Solid Solutions of Al-Zn-Mg-Cu Alloys[†]

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Quaternary interdiffusion experiments of Al-rich α Al-Zn-Mg-Cu alloys have been performed in the temperature range from 755 to 833 K. The concentration profiles indicate that the diffusion distance of Cu is shorter than those of Zn and Mg in the solid solutions. The direct interdiffusion coefficients $\bar{D}_{ZnZn}^4$, $\bar{D}_{MgMg}^4$ and $\bar{D}_{CuCu}^4$ are positive, and indirect coefficients are negative. The impurity diffusion coefficients of Zn (or Cu) in Al-Cu (or Zn)-Mg alloys can be expressed by the following equations.

$$D_{Zn(Al-1.15Cu-2.01Mg)}^* = 3.9 \times 10^{-5} \exp(-124 \text{ kJ mol}^{-1}/RT^{-1}) \text{ m}^2/\text{s},$$

$$D_{Cu(Al-3.37Zn-2.75Mg)}^* = 5.7 \times 10^{-5} \exp(-132 \text{ kJ mol}^{-1}/RT^{-1}) \text{ m}^2/\text{s}.$$

The ratio values of indirect to direct diffusion coefficients suggest that attractive interactions of Zn-Mg, Zn-Cu and Cu-Mg atoms exist in the Al-Zn-Mg-Cu alloys.

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I. Introduction

Extensive studies about the metallography and materials structure have been carried out in Al-Zn-Mg-Cu alloys, because these alloys originated from Extra super duralmin are the promising structural materials⁽¹⁾. In order to obtain superior mechanical properties in such aluminum alloys, the alloys are heat-treated for recovering, recrystallization, the homogenization, aging, precipitation, etc. Diffusion is a basic and important factor for understanding and discussing such phenomena and heat treatments. Therefore, it is necessary to obtain the information for diffusion in such Al-base quaternary alloys⁽²⁾.

Interdiffusion in n-component alloys is represented by the extended Fick's law;

$$\tilde{J}_i = - \sum_{k=1}^{n-1} \tilde{D}_{ik} \partial C_k / \partial x \quad (i=1, 2, \dots, n-1), \quad (1)$$

where $\tilde{J}_i$ is the interdiffusion flux, $\tilde{D}_{ij}^n$ the interdiffusion coefficient ($\tilde{D}_{ij}^n$ ($i=j$) is called the direct coefficient and $\tilde{D}_{ij}^n$ ($i \neq j$) is the indirect coefficient), C_i the concentration

of element i and x the distance. Many experimental studies of diffusion in Al-base binary alloys have been performed⁽²⁾⁻⁽⁴⁾ in order to determine only one interdiffusion coefficient. On the other hand, a few investigations of diffusion have been made in Al-base ternary alloys⁽⁵⁾⁻⁽⁷⁾ in which four coefficients were required to represent interdiffusion. Especially, the number of studies on diffusion in practical ternary Al-Zn-Mg alloys is very small in spite of its importance; only one report on the interdiffusion⁽⁸⁾ and two reports on the impurity diffusion coefficients of Zn or Mg in this Al-Zn-Mg alloy system⁽⁹⁾⁽¹⁰⁾ have been published. In the case of quaternary alloys of Al-Zn-Mg-Cu system, the diffusion in the quaternary Al-Zn-Mg-Cu alloys has not been investigated⁽¹¹⁾ because the nine interdiffusion coefficients should be evaluated by more complicate experiments.

The purposes of the present work are (a) to determine the ternary interdiffusion coefficients in the α -phase region of the ternary Al-Zn-Mg system at 755 K, (b) to determine the quaternary interdiffusion coefficients and impurity diffusion coefficients in the quaternary Al-Zn-Mg-Cu system in a temperature range from 755 to 833 K, and (c) to discuss the thermodynamic interactions between solute atoms in α Al-Zn-Mg-Cu solid solutions.

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Table 1 Terminal compositions of diffusion couples in (a) quaternary Al–Zn–Mg–Cu system and (b) ternary Al–Zn–Mg system.

Couple name	Composition (at%)	Characteristics of terminal alloys
A1	Al–1.43Zn–2.57Mg–1.30Cu / Al–4.88Zn–2.41Mg–1.27Cu	Similar Mg, Cu at%
A2	Al–3.49Zn–1.42Mg–1.33Cu / Al–3.29Zn–3.50Mg–1.28Cu	Similar Zn, Cu at%
A3	Al–3.38Zn–2.70Mg–0.51Cu / Al–3.44Zn–2.30Mg–2.01Cu	Similar Zn, Mg at%
B1	Al–3.37Zn–2.75Mg / Al–3.17Zn–2.45Mg–1.20Cu	Similar Zn, Mg at%
B2	Al–1.15Cu–2.01Mg / Al–3.17Zn–2.45Mg–1.20Cu	Similar Mg, Cu at%

(b)

Couple name	Composition (at%)
C1	Al / Al–2.12Zn–4.21Mg
C2	Al / Al–3.24Zn–3.10Mg
C3	Al / Al–4.56Zn–1.89Mg
C4	Al / Al–5.56Zn–1.64Mg
D1	Al–3.24Zn / Al–3.24Mg
D2	Al–3.24Zn / Al–4.32Mg
D3	Al–3.94Zn / Al–4.32Mg

II. Experimental Procedures

The Al–Zn, Al–Mg, α Al–Zn–Mg and α Al–Zn–Mg–Cu alloys for diffusion couples were prepared from 99.99 mass%Al, 99.998 mass%Zn, 99.99 mass%Mg and a Al–39.61 mass%Cu mother alloy by high frequency induction melting in an argon atmosphere. These alloy ingots were annealed at 773 K for 432 ks for homogenization and grain coarsening. These alloys have a single phase of α -phase solid solution and the grain diameter more than about 1 mm.

The alloy ingots were cut into 10 mm $\times$ 10 mm diffusion plates of about 2 mm in thickness. The surfaces of the alloy plates were metallographically polished by SiC paper, 0.3 μ m alumina powder and diamond paste. The polished plates for diffusion couples were held together by means of stainless steel clamps. The terminal compositions of diffusion couples are listed in **Tables 1(a)** and **(b)**. The diffusion couples are designated A1–A3, B1–B2, C1–C4 and D1–D3 according to the combination of metals. In the quaternary system, the A1–A3 and B1–B2 couples are Darken type couples⁽¹²⁾ in which the terminal compositions of two elements are nearly constant. The A1–A3 couples enable us to determine the interdiffusion coefficients in the quaternary Al–Zn–Mg–Cu alloys, while the B1–B2 couples do to evaluate the impurity diffusion coefficients of Cu or Zn in the ternary aluminum alloys. On the other hand, the C1–C4 and D1–D3 couples are for the determination of the interdiffusion coefficients in the ternary Al–Zn–Mg alloys.

The assembled diffusion couples and Ti powder enclosed an aluminum foil were vacuum-sealed into a Pyrex tube. These diffusion couples were annealed in a temperature range from 755 to 833 K for 17.45 to 86.03 ks, and then quenched in ice water. The annealed diffusion couples were cut at their center parallel to the diffusion

direction in order to expose sections which had no oxidation and evaporation of elements, and then they were mounted in synthetic resin. The exposed section of each couple was metallographically polished. In order to obtain diffusion profiles in the diffusion couples, the characteristic X-ray intensities of Zn, Mg and Cu in these diffusion couples were measured by a JEOL JXA-8900 electron microanalyzer (EPMA), and then their characteristic X-ray intensities were converted into concentration values of Zn, Mg and Cu by the ZAF method using the bulk alloy compositions at the ends of the couples as standards⁽¹³⁾⁽¹⁴⁾.

Interdiffusion coefficients in n-components alloy system can be obtained from the diffusion profiles by using the extended Matano-Kirkaldy method to the n-component alloy system⁽¹⁵⁾⁽¹⁶⁾.

$$\int_{C_i^{(-\infty)}}^{C_i^{(+\infty)}} x dC_i = -2t \sum_{k=1}^{n-1} \tilde{D}_{ik} \partial C_k / \partial x \quad (i=1, 2, \dots, n-1), \quad (2)$$

where C_i ($i=1, 2, \dots, n-1$) is the concentration of solute i , $C_i^{(-\infty)}$ and $C_i^{(+\infty)}$: the terminal compositions at the ends of the diffusion couples, t : the diffusion time, and x : the distance from the Matano interface located at $x=0$, which can be determined for diffusion profile from the relation:

$$\int_{C_i^{(-\infty)}}^{C_i^{(+\infty)}} x dC_i = 0 \quad (i=1, 2, \dots, n-1). \quad (3)$$

For an n-component system, $(n-1)$ independent diffusion couples are needed, in general, for determination of $(n-1)^2$ interdiffusion coefficients at one common compositions of intersection of the diffusion paths. In other words, the extended Matano-Kirkaldy method for quaternary system requires us to prepare three diffusion couples whose diffusion paths intersect at one common composition. This experimental condition is quite difficult. Therefore, we prepared the Darken type couples which have nearly constant concentration of the elements except element i . In the Darken type diffusion couples, $\partial C_j / \partial x \approx 0$, eq. (1) becomes quite simple as follows;

$$\int_{C_i^{(-\infty)}}^{C_i^{(+\infty)}} x dC_i = -2t \tilde{D}_{ii}^n \partial C_i / \partial x \quad (i=1, 2, \dots, n-1). \quad (4)$$

From this equation, the direct $\tilde{D}_{ii}^n$ can be easily evaluated

by the same way in the case of binary interdiffusion. Also, the impurity diffusion coefficients of Zn (or Cu) in Al-Cu (or Zn)-Mg alloys have been evaluated by Hall's method⁽¹⁷⁾⁽¹⁸⁾.

On the other hand, Thompson and Morral⁽¹⁹⁾ have presented an elegant method for the determination of the diffusion coefficients in a multicomponent alloy in the case that interdiffusion coefficients is independent of concentration. According to them, the diffusivity matrix $[D]$ is related to a square root diffusivity matrix $[r]$.

$$[\tilde{D}] = [r][r] \quad (5)$$

The relation between $\tilde{D}_{ij}^4$ and r_{ij} ($i, j = 1, 2, 3$) in quaternary alloys of this experiment is;

$$\begin{bmatrix} \tilde{D}_{11}^4 & \tilde{D}_{12}^4 & \tilde{D}_{13}^4 \\ \tilde{D}_{21}^4 & \tilde{D}_{22}^4 & \tilde{D}_{23}^4 \\ \tilde{D}_{31}^4 & \tilde{D}_{32}^4 & \tilde{D}_{33}^4 \end{bmatrix} = \begin{bmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33} \end{bmatrix} \begin{bmatrix} r_{11} & r_{12} & r_{13} \\ r_{21} & r_{22} & r_{23} \\ r_{31} & r_{32} & r_{33} \end{bmatrix} \quad (6)$$

The values of r_{11} to r_{33} can be obtained experimentally from the following eqs. (7) and (8).

$$S_i = -(t/\pi)^{0.5} (r_{i1}\Delta C_1 + r_{i2}\Delta C_2 + r_{i3}\Delta C_3) \quad (7)$$

$$\Delta C_i = C_i^{(+\infty)} - C_i^{(-\infty)} \quad (i = 1, 2, 3) \quad (8)$$

The terms S_1 , S_2 and S_3 represent the amounts of solute which have crossed the initial interface, and ΔC_i is the concentration difference obtained by subtracting the initial concentrations on the right and left sides of the couples.

III. Results and Discussion

1. Concentration profiles and diffusion paths

Figures 1(a), (b) and (c) show the concentration profiles of the A1, A2 and A3 couples annealed at 755 K for 86.03 ks, respectively. The origin of each abscissa in Figs. 1(a) to (c) is the Matano interface. The diffusion distance of Cu is shorter than those of Zn and Mg. This indicates that the diffusion rate of Cu is smaller than those of Zn and Mg in the Al-Zn-Mg-Cu alloys. Since the A1, A2 and A3 couples have the similar concentrations of the two solute elements in the terminal alloys as listed in Table 1(a), the concentration distribution of such elements are almost constant over the entire diffusion zone. However, it is noticed that the slight redistribution of elements are observed; for instance, the concentration profiles of Cu in the A1 couple and Mg in the A3 couple. These redistributions of the elements suggest that there exist some interactions between solute elements in such alloys.

Figures 2(a) and (b) show the projections of the diffusion paths for the quaternary A1, A2 and A3 couples at 755 K onto the at%Mg-at%Zn plane and the at%Cu-at%Zn plane, respectively. The open squares, closed squares and triangles indicate the terminal alloy compositions of the couples, and open circles and closed circles do the average compositions of each diffusion couple. The average compositions are nearly equal to those at the

Fig. 1 Typical concentration profiles in diffusion couples (a) A1, (b) A2 and (c) A3 annealed at 755 K for 86.03 ks.

Fig. 2 Projections of the diffusion paths for quaternary diffusion couples A1, A2 and A3 at 755 K for 86.03 ks: (a) projections onto the at%Mg-at%Zn plane and (b) projections onto the at%Cu-at%Zn plane.

Matano interface, and are located in the quite vicinity of the compositions of intersection of the diffusion paths. **Figure 3** shows the diffusion paths of the ternary Al-Zn-Mg alloys couples at 755 K. The diffusion path of the Al-Zn/Al-Mg couple (D2) shows the S-shaped curve. The S-shaped diffusion paths have been also observed in the Al-Cu-Mg⁽⁵⁾⁽⁶⁾ and Al-Cu-Zn⁽⁷⁾ systems.

2. Concentration and temperature dependence of diffusion couples

Four interdiffusion coefficients of $\tilde{D}_{\text{ZnZn}}^{\text{Al}}$, $\tilde{D}_{\text{ZnMg}}^{\text{Al}}$, $\tilde{D}_{\text{MgMg}}^{\text{Al}}$ and $\tilde{D}_{\text{MgZn}}^{\text{Al}}$ in the ternary Al-Zn-Mg alloys at 755 K were evaluated at the intersection compositions of the diffusion paths by using the extended Matano method, and they are shown in **Figs. 4(a) to (d)**. The direct coefficients $\tilde{D}_{\text{ZnZn}}^{\text{Al}}$ and $\tilde{D}_{\text{MgMg}}^{\text{Al}}$ are positive. On the other hand, the values of indirect coefficients $\tilde{D}_{\text{ZnMg}}^{\text{Al}}$ and $\tilde{D}_{\text{MgZn}}^{\text{Al}}$ are judged to be negative, although the $\tilde{D}_{\text{MgZn}}^{\text{Al}}$ coefficients have the positive values and negative values in the vicinity of the terminal compositions where the error are induced into the coefficients, because the $[\partial C_k / \partial x]$ and $[\int_{C_i(-\infty)}^{C_i} x dC_i]$ factors in eq. (2) become smaller when approaching to the terminal compositions⁽²⁰⁾⁽²¹⁾. As shown in Fig. 4, the interdiffusion coefficients are not sensitive to the solute concentrations in the α Al-Zn-Mg solid

Fig. 3 Diffusion paths for ternary diffusion couples annealed at 755 K for 56.92 ks.

solutions. Their average interdiffusion coefficient s are as follows:

$$\begin{aligned}\tilde{D}_{\text{ZnZn}}^{\text{Al}} &= 14.9 \times 10^{-14} \text{ m}^2/\text{s}, \\ \tilde{D}_{\text{ZnMg}}^{\text{Al}} &= -1.8 \times 10^{-14} \text{ m}^2/\text{s}, \\ \tilde{D}_{\text{MgMg}}^{\text{Al}} &= 12.9 \times 10^{-14} \text{ m}^2/\text{s}, \\ \tilde{D}_{\text{MgZn}}^{\text{Al}} &= -0.68 \times 10^{-14} \text{ m}^2/\text{s},\end{aligned}\quad (9)$$

where the positive values of $\tilde{D}_{\text{MgZn}}^{\text{Al}}$ were excepted from the calculation of the average values of $\tilde{D}_{\text{MgZn}}^{\text{Al}}$. The value of $\tilde{D}_{\text{ZnZn}}^{\text{Al}}$ is slightly larger than that of $\tilde{D}_{\text{MgMg}}^{\text{Al}}$. The absolute value of the indirect coefficients $\tilde{D}_{\text{ZnMg}}^{\text{Al}}$ is larger than that of $\tilde{D}_{\text{MgZn}}^{\text{Al}}$.

In the quaternary diffusion couples as shown in Figs. 1(a) to (c), the concentration gradients of the components $\partial C_i / \partial x$ are approximately equal to zero at the Matano interface, because the concentration profiles have nearly constant concentration of the two components in the three solute components. For instance, the values of $\partial C_{\text{Mg}} / \partial x$ and $\partial C_{\text{Cu}} / \partial x$ are equal to zero in the concentration profiles of the diffusion couple A1 as shown in Fig. 1(a). In this case, eq. (4) is written as follows,

$$\int_{C_{\text{Zn}}(-\infty)}^{C_{\text{Zn}}} x dC_{\text{Zn}} = -2t(\tilde{D}_{\text{ZnZn}}^{\text{Al}} \partial C_{\text{Zn}} / \partial x). \quad (10)$$

By using eq. (4) the three direct interdiffusion coefficients can be easily evaluated from the diffusion profiles of Darken-type couples at 755 K in the Al-Zn-Mg-Cu system in Fig. 1, although the indirect coefficients cannot be obtained. The obtained three direct diffusion coefficients are;

$$\begin{aligned}\tilde{D}_{\text{ZnZn}}^{\text{Al}} &= 13.9 \times 10^{-14} \text{ m}^2/\text{s}, \\ \tilde{D}_{\text{MgMg}}^{\text{Al}} &= 9.0 \times 10^{-14} \text{ m}^2/\text{s}, \\ \tilde{D}_{\text{CuCu}}^{\text{Al}} &= 2.9 \times 10^{-14} \text{ m}^2/\text{s}.\end{aligned}\quad (11)$$

Fig. 4 Direct and indirect interdiffusion coefficients (a) $\tilde{D}_{ZnZn}^{Al}$, (b) $\tilde{D}_{ZnMg}^{Al}$, (c) $\tilde{D}_{MgMg}^{Al}$ and (d) $\tilde{D}_{MgZn}^{Al}$ of ternary Al-Zn-Mg system at 755 K.

The interdiffusion coefficients in the ternary Al-Zn-Mg alloys were obtained by the Thompson and Morral method⁽¹⁹⁾ and Matano-Kirkaldy method using the concentration profiles of Al/Al-5.37 at%Zn-1.88 at%Mg and Al-3.40 at%Zn/Al-2.28 at%Mg diffusion couples at 778 K for 42.6 ks in order to compare the results by the two methods. The interdiffusion coefficients are as follows:

$$\begin{aligned}\tilde{D}_{ZnZn}^{Al} &= 23[24] \times 10^{-14} \text{ m}^2/\text{s}, \\ \tilde{D}_{ZnMg}^{Al} &= -17[-18] \times 10^{-14} \text{ m}^2/\text{s}, \\ \tilde{D}_{MgMg}^{Al} &= 17[18] \times 10^{-14} \text{ m}^2/\text{s}, \\ \tilde{D}_{MgZn}^{Al} &= -0.49[-0.82] \times 10^{-14} \text{ m}^2/\text{s}.\end{aligned}\quad (12)$$

The values by the Thompson-Morral method are in good agreement with the values in brackets which are the data

evaluated by the Matano-Kirkaldy method. This agreement experimentally supports that Thompson-Morrall method is applicable to the ternary Al-Zn-Mg alloys.

In the quaternary Al-Zn-Mg-Cu alloys, the nine interdiffusion coefficients were evaluated from the concentration profiles of the diffusion couples (A1, A2, A3) at 755 and 803 K by the Thompson-Morrall method, as listed in **Tables 2(a)** and **(b)**. The direct interdiffusion coefficients $\tilde{D}_{\text{ZnZn}}^4$, $\tilde{D}_{\text{MgMg}}^4$ and $\tilde{D}_{\text{CuCu}}^4$ at 755 and 803 K are positive, and almost all the indirect coefficients are negative. The magnitude of the direct coefficients are in the order of $\tilde{D}_{\text{ZnZn}}^4 > \tilde{D}_{\text{MgMg}}^4 > \tilde{D}_{\text{CuCu}}^4$, and they are similar to those in eq. (11) evaluated by Matano method. This indicates that the Thompson-Morrall method is also applicable to the quaternary system. In addition, the value of $\tilde{D}_{\text{MgMg}}^4$ in the quaternary alloys is slightly smaller than that of the average $\tilde{D}_{\text{MgMg}}^{\text{Al}}$ as shown in eq. (9). It is thought that the diffusion of magnesium is somewhat retarded by the addition of copper.

Sisson and Dayananda⁽²³⁾ have correlated the direct and cross interdiffusion coefficients with the intrinsic and self-diffusion coefficients as follows:

$$\tilde{D}_{ij}^3 = D_{ij}^3 - N_i \sum_{k=1}^3 D_{kj}^3 \quad (i, j = 1, 2) \quad (13)$$

Table 2 Interdiffusion coefficients of quaternary Al-Zn-Mg-Cu system at (a) 755 K and (b) 803 K.

(a) 755 K A1, A2, A3

Units $10^{-8} \text{ m} / \sqrt{\text{s}}$				
[r_{ij}]	i \ j	Zn	Mg	Cu
	Zn	35.3	-1.7	-1.9
	Mg	-1.7	29.6	-5.1
	Cu	0.3	0.4	16.9

Units $10^{-14} \text{ m}^2 / \text{s}$				
[D_{ij}]	i \ j	Zn	Mg	Cu
	Zn	12.5	-1.1	-0.9
	Mg	-1.1	8.8	-2.3
	Cu	0.1	0.2	2.8

(b) 803 K A1, A2, A3

Units $10^{-8} \text{ m} / \sqrt{\text{s}}$				
[r_{ij}]	i \ j	Zn	Mg	Cu
	Zn	58.5	-1.5	-2.8
	Mg	-6.4	51.2	-9.7
	Cu	-3.3	0.6	40.4

Units $10^{-14} \text{ m}^2 / \text{s}$				
[D_{ij}]	i \ j	Zn	Mg	Cu
	Zn	34.5	-1.7	-2.6
	Mg	-6.7	26.2	-8.7
	Cu	-3.3	0.6	16.3

$$D_{ij}^3 = D_i^* C_i \partial \ln a_i / \partial C_j \quad (i, j = 1, 2) \quad (14)$$

where D_{ij}^3 and D_{kj}^3 are the intrinsic diffusion coefficients; D_i^* , the tracer-diffusion coefficient of element i ; a_i , the thermodynamic activity of i and N_i , the atom fraction of i . These relationships of eqs. (13) and (14) can be extended to the quaternary diffusion for $\tilde{D}_{11}^4$, $\tilde{D}_{12}^4$ and D_{11}^4 , D_{12}^4 as follows:

$$\tilde{D}_{11}^4 = D_{11}^4 - N_1 (D_{11}^4 + D_{21}^4 + D_{31}^4 + D_{41}^4) \quad (15)$$

$$\tilde{D}_{12}^4 = D_{12}^4 - N_1 (D_{12}^4 + D_{22}^4 + D_{32}^4 + D_{42}^4) \quad (16)$$

$$D_{11}^4 = D_1^* C_1 \partial \ln a_1 / \partial C_1 \quad (17)$$

$$D_{12}^4 = D_1^* C_1 \partial \ln a_1 / \partial C_2. \quad (18)$$

The values of $(C_1 \partial \ln a_1 / \partial C_1)$ and $(C_1 \partial \ln a_1 / \partial C_2)$, respectively, go to 1 and zero when N_1 approaches zero. Therefore, the following relations can be obtained from eqs. (15) through (18) when N_1 approaches zero⁽²⁴⁾:

$$\lim_{N_1 \rightarrow 0} \tilde{D}_{11}^4 = D_{1(2-3-4)}^* \quad (19)$$

$$\lim_{N_1 \rightarrow 0} \tilde{D}_{12}^4 = 0 \quad (20)$$

where $D_{1(2-3-4)}^*$ is the tracer diffusion coefficient of element 1 in a ternary 2-3-4 alloy.

According to eqs. (19) and (20), the direct coefficient becomes equal to the tracer diffusion coefficient of element 1 in the ternary 2-3-4 alloy, and the cross coefficient goes to zero at infinite dilution of element 1. In the present work, $D_{1(2-3-4)}^*$ corresponds to the impurity diffusion coefficient of Zn in the Al-Cu-Mg alloy. The impurity diffusion coefficients of Zn (or Cu) in Al-Cu (or Zn)-Mg can be determined by Hall's method⁽¹⁷⁾⁽¹⁸⁾ at the terminal compositions of the diffusion profiles obtained from the ternary alloy sides of the diffusion couples B1 and B2.

Figure 5 shows the temperature dependence of the impurity diffusion coefficients of Zn in Al-Cu-Mg alloys $D_{\text{Zn(Al-1.15Cu-2.01Mg)}}^*$ (squares) and that of the diffusion coefficients of Cu in Al-Zn-Mg alloys $D_{\text{Cu(Al-3.37Zn-2.75Mg)}}^*$ (closed circles) with the tracer diffusion coefficients of Zn in Al-2.12Zn-2.28Mg alloys drawn by the broken line⁽⁹⁾. Although the impurity diffusion coefficients of Zn in the alloying constituents have been reported elsewhere in the Al-Zn-Mg system⁽²⁵⁾, those of a foreign atom (e.g., the impurity diffusion coefficients of Zn in the Al-Cu-Mg alloys) have been not reported yet. As shown in Fig. 5, the impurity diffusion coefficients of Cu in the Al-Zn-Mg alloys are smaller than those of Zn in the alloys. A plot of the logarithms of $D_{\text{Zn(Al-Cu-Mg)}}^*$ and $D_{\text{Cu(Al-Zn-Mg)}}^*$ for the reciprocal of the absolute temperature follows an Arrhenius-type equation and exhibits a linear relationship. The impurity diffusion coefficients are expressed by

$$D_{\text{Zn(Al-1.15Cu-2.01Mg)}}^* = 3.9 \times 10^{-5} \exp(-124 \text{ kJ mol}^{-1} / RT^{-1}) \text{ m}^2 / \text{s} \quad (21)$$

and

$$D_{\text{Cu(Al-3.37Zn-2.75Mg)}}^* = 5.7 \times 10^{-5} \exp(-132 \text{ kJ mol}^{-1} / RT^{-1}) \text{ m}^2 / \text{s}. \quad (22)$$

Fig. 5 Temperature dependence of impurity diffusion coefficients of Zn in Al-Cu-Mg alloys and Cu in Al-Zn-Mg alloys.

The magnitude of the activation energy for the impurity diffusion of Cu (132 kJ/mol) in Al-Zn-Mg alloys is slightly larger than that of Zn (125 kJ/mol) in the alloys.

3. Thermodynamic interactions among the solute components

The relation between $\tilde{D}_{ij}^3/\tilde{D}_{ii}^3$ and Wagner's interaction parameter, $\varepsilon_i^{(j)}$ has been presented in very dilute solutions of the ternary alloy by Kirkaldy *et al.*⁽²⁶⁾, as follows.

$$\tilde{D}_{ij}^3/\tilde{D}_{ii}^3 = \{1 + \varepsilon_i^{(j)}\} N_i. \quad (23)$$

According to eq. (23), the relations of the $\tilde{D}_{MgZn}^4/\tilde{D}_{MgMg}^4$ to Mg concentration and the $\tilde{D}_{ZnMg}^4/\tilde{D}_{ZnZn}^4$ to Zn concentration in the Al-Zn-Mg system at 796 K are respectively plotted by the closed circles in Figs. 6(a) and (b). These figures also include the ratios of $\tilde{D}_{MgZn}^4/\tilde{D}_{MgMg}^4$, $\tilde{D}_{MgCu}^4/\tilde{D}_{MgMg}^4$, $\tilde{D}_{ZnMg}^4/\tilde{D}_{ZnZn}^4$ and $\tilde{D}_{ZnCu}^4/\tilde{D}_{ZnZn}^4$ in the quaternary Al-Zn-Mg-Cu alloy, the previous data of $\tilde{D}_{MgCu}^4/\tilde{D}_{MgMg}^4$ in the Al-Mg-Cu alloy at 813 K⁽⁵⁾, and $\tilde{D}_{ZnCu}^4/\tilde{D}_{ZnZn}^4$ in the Al-Zn-Cu alloy at 817 K⁽⁷⁾. The broken lines are drawn by eq. (23) with the values of $\varepsilon_{Zn}^{(Mg)} = -7$ in Al-Zn-Mg alloy. The experimental values of $\tilde{D}_{MgZn}^4/\tilde{D}_{MgMg}^4$ and $\tilde{D}_{ZnMg}^4/\tilde{D}_{ZnZn}^4$ respectively decrease with increasing the Mg concentration and Zn concentration in the Al-Zn-Mg alloys, although they scatter around the line of $\varepsilon_{Zn}^{(Mg)} = -7$. The (ratio) values of $\tilde{D}_{MgZn}^4/\tilde{D}_{MgMg}^4$, $\tilde{D}_{MgCu}^4/\tilde{D}_{MgMg}^4$, $\tilde{D}_{ZnMg}^4/\tilde{D}_{ZnZn}^4$ and $\tilde{D}_{ZnCu}^4/\tilde{D}_{ZnZn}^4$ in the quaternary Al-Zn-Mg-Cu alloy exhibit the negative values. These negative ratios and $\varepsilon_{Zn}^{(Mg)}$ indicate that attractive interactions of Zn-Mg and Zn-Cu atoms exist in the Al-Zn-Mg, Al-Zn-Cu and Al-Zn-Mg-Cu systems.

On the other hand, since all of $\tilde{D}_{MgCu}^4/\tilde{D}_{MgMg}^4$ have the positive values in the Al-Mg-Cu system as shown in Fig. 6(a), it is evident that the repulsive interactions of Mg and Cu atoms exist in the ternary system⁽⁵⁾. In the

Fig. 6 (a) Relation between $\tilde{D}_{ij}^4/\tilde{D}_{ii}^4$ ($i=Mg, j=Cu$ or Zn) and Mg concentration in Al-Zn-Mg, Al-Mg-Cu and Al-Zn-Mg-Cu systems.

Fig. 6 (b) Relation between $\tilde{D}_{ij}^4/\tilde{D}_{ii}^4$ ($i=Zn, j=Cu$ or Mg) and Zn concentration in Al-Zn-Mg, Al-Zn-Cu and Al-Zn-Mg-Cu systems.

quaternary system, the values of $\tilde{D}_{CuMg}^4/\tilde{D}_{MgMg}^4$ have positive small values (0.02) at both 755 and 803 K, and those of $\tilde{D}_{MgCu}^4/\tilde{D}_{MgMg}^4$ have comparatively large negative values of (−0.26 at 755 K) and (−0.33 at 803 K) as listed in Tables 2(a) and (b). From these results, the attractive interaction between Mg and Cu atoms exist in the quaternary alloy. The diffusion mechanism in the quaternary Al-Zn-Mg-Cu system differs from that in the ternary Al-Cu-Mg system, that is, the diffusion of Mg is affected by the copper atoms. This interaction of Mg and Cu atoms is consistent with the results that the diffusion of Mg is controlled by the addition of Cu in the Al-Zn-Mg-Cu alloys as mentioned in the results of interdiffusion coefficients in Table 2(a).

IV. Summary

Quaternary and ternary interdiffusion experiments of Al-rich α Al-Zn-Mg-Cu alloys have been performed in the temperature range from 755 to 833 K. The results are summarized as follows.

(1) The concentration profiles indicate that the diffusion distance of Cu is shorter than those of Zn and Mg in

the solid solutions. The average compositions in the diffusion couples A1, A2 and A3 are nearly equal to those of the Matano interface, and are located in the vicinity of the compositions of intersection of the diffusion paths.

(2) It is confirmed that Thompson-Morrall method is applicable to the determination of interdiffusion coefficients in the quaternary Al-Zn-Mg-Cu system as well as the ternary Al-Zn-Mg system.

(3) The direct interdiffusion coefficients $\tilde{D}_{\text{ZnZn}}^4$, $\tilde{D}_{\text{MgMg}}^4$ and $\tilde{D}_{\text{CuCu}}^4$ are positive, and indirect coefficients are negative in the quaternary alloys. The impurity diffusion coefficients of Zn (or Cu) in Al-Cu(or Zn)-Mg alloys can be expressed by the following equations.

$$D_{\text{Zn(Al-1.15Cu-2.01Mg)}}^* = 3.9 \times 10^{-5} \exp(-124 \text{ kJ mol}^{-1} / RT^{-1}) \text{ m}^2/\text{s},$$

$$D_{\text{Cu(Al-3.37Zn-2.75Mg)}}^* = 5.7 \times 10^{-5} \exp(-132 \text{ kJ mol}^{-1} / RT^{-1}) \text{ m}^2/\text{s}.$$

From the ratio values of indirect coefficient to direct one, it suggests that attractive interactions of Zn-Mg, Zn-Cu and Cu-Mg atoms exist in the Al-Zn-Mg-Cu alloys.

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