JOURNAL OF MATERIALS SCIENCE **34** (1999) 2449–2454

Diffusion of zinc in commercial Al-Zn alloys under high pressure

KOJI HISAYUKI, TOSHIMI YAMANE
Department of Mechanical Engineering, Hiroshima Institute of Technology, 2-1-1 Miyake, Saeki-ku, Hiroshima 731-5193, Japan

TOMOSHI TAKAHASHI
Department of Material, Science and Engineering, Niihama National College of Technology, 7-1 Yagumo-cho, Niihama 792-8580, Japan

YORITOSHI MINAMINO*, KEIICHI HIRAO‡, HIDEKI ARAKI‡
*Department of *Adaptive Machine Systems and ‡Materials Science and Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan*

The effective interdiffusion coefficients of zinc in commercial Al-Zn alloys are obtained within the temperature range 773 to 883 K under pressures from 0 to 0.41 GPa. From the temperature dependence of the effective interdiffusion coefficients, the activation energies for the 701, 703 and 705 alloys are evaluated to be 125, 124 and 127 kJ/mol respectively, and their pre-exponential factors are 3.0×10^{-5}, 4.0×10^{-5} and 3.9×10^{-5} m^2/s respectively. The activation volumes, ΔV, for diffusion of zinc in the commercial Al-Zn alloy are 8.30×10^{-6} and 8.60×10^{-6} m^3/mol at 823 and 883 K, respectively. The ratios of the activation volume to the molar volume of aluminum, $\Delta V/V_0$, are 0.83 at 823 K and 0.86 at 883 K. This means that the diffusion of zinc in the commercial Al-Zn alloys occurs predominantly by the monovacancy mechanism at 823 and 883 K. © *1999 Kluwer Academic Publishers*

1. Introduction

Many studies of diffusion have been performed in aluminum and aluminum alloys [1, 2]. For unidirectional diffusion in n-component system, the interdiffusion flux $\tilde{J}_i$ of a component i referred to a laboratory fixed frame of reference is defined by Fick's first law as follows:

$$\tilde{J}_i = -\sum_{j=1}^{n-1} \tilde{D}_{ij}^n \frac{\partial C_j}{\partial x} \quad (i = 1, 2, \ldots, n-1) \tag{1}$$

where the $\tilde{D}_{ij}^n$'s are the interdiffusion coefficients, $\partial C_j/\partial x$ is the concentration gradient of j, and $n-1$ the refers to the number of independent concentrations [3]. For example, an only one interdiffusion coefficient in a binary system can be easily obtained from one experimental diffusion profile of one component. However, four interdiffusion coefficients are required to express the interdiffusion in a ternary system. As for the commercial alloys of n-components, it is experimentally quite difficult to obtain all $(n-1)^2$ interdiffusion coefficients if n is more than 5. However, Dayananda have presented a convenient method to evaluate the diffusion coefficients in the n-component system [4]. This method enables us to obtain the effective interdiffusion coefficient of element i from only the experimental diffusion profile of element i in the single diffusion couple, even in the n-component system.

In fact, most commercial alloys contain more than 5 components (see Table I). Therefore, as the first step, it is worthwhile to investigate the effect of many constituent elements on diffusion of important elements such as zinc in the commercial aluminum alloys.

It is also interesting to know diffusion mechanisms in such commercial alloys. One of the powerful methods to give us the information of the diffusion mechanism is to measure activation volumes. The activation volumes for diffusion can be obtained from the pressure dependence of the diffusion coefficients [5]. In the self-diffusion of aluminum, it is considered that the diffusion occurs by the contribution of divacancies at high temperatures [6]. On the other hand, little contribution of divacancies to impurity diffusion is concluded [7, 8]. In this paper, the activation volumes and activation energies for effective interdiffusion coefficients of zinc in commercial Al-Zn alloys are evaluated, and the diffusion mechanism in the commercial aluminum-zinc alloys is discussed.

2. Experimental

Chemical compositions of three kinds of commercial Al-Zn alloys listed in Table I. In order to prepare diffusion couples for the atmospheric pressure experiments, alloy bars (5 mm × 5 mm × 60 mm) were cut from the alloy plates. A hole (6 mm ϕ diameter × 60 mm length) was drilled in the center of a 99.99 mass% purity aluminum block. The surface of alloy bars and the holes of the aluminum blocks were metallographically polished.

TABLE I Chemical compositions of commercial Al-Zn alloys (mass%)

Al	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Zr	Pb	Bi	Sn
701 Bal	0.05	0.16	0.48	<0.01	0.85	<0.01	5.69	0.03	0.13	<0.01	<0.01	<0.01
703 Bal	0.05	0.12	0.47	<0.01	0.92	<0.01	9.56	0.03	0.12	<0.01	<0.01	<0.01
705 Bal	0.05	0.11	0.46	<0.01	0.5	<0.01	7.5	0.03	0.12	<0.01	<0.01	<0.01

The bar of the alloy was inserted into the hole in the pure aluminum block, and then this composite metal was strongly rolled at room temperature. The alloy bar and the pure aluminum block were bonded with a clean interface for the diffusion couples, because the oxide films on the surface of the alloy bar and hole in the aluminum block were broken into fine pieces and distributed over much wider area at the bonding interface of the alloy and pure aluminum by the hard rolling [9]. These rolled metals were cut into 5 mm lengths as diffusion couples. A diffusion couple for the high pressure experiments was a composite metal which consists of the alloy (3 mm diameter × 5 mm height) and 99.99 mass% aluminum (3 mm diameter × 5 mm height). Above diffusion couples are reffered to as the Al/701, Al/703 and Al/705 diffusion couples according to the combination of pure Al and the commercial alloys listed in Table I.

Zinc solute concentration profiles in these diffusion couples were measured by an EPMA (Electron probe micro analyser). The intensities of ZnK_α radiation were converted to the zinc concentration with the ZnK_α intensities of some standard alloys. It was found that diffusion did not occur during the above bonding treatments.

The diffusion couples for the atmospheric pressure experiments were annealed at the temperature range from 773 to 883 K for 10.8 to 21.6 ks. The diffusion temperatures were controlled within ±1 K. On the other hand, the high pressure was produced in an Instron type testing machine with a compression piston device. The diffusion couples were heated by an external heater. The temperature of the diffusion couple was measured by an alumel-chromel thermocouple located near the diffusion couple. The diffusion couple under high pressures were annealed within the temperature range from 773 to 883 K for 4.5 to 14.4 ks.

After diffusion annealing, the diffusion couples were ground to expose the diffusion zone where oxidation, evaporation and surface diffusion did not occur. They were metallographically polished parallel to the diffusion direction with 1 μm alumina powder with water, and then they were measured for the intensity of ZnK_α radiation along the diffusion direction by the EPMA.

According to Equation 1, the interdiffusion flux of element i is caused by the concentration gradients of elements included in the n-component system. Since the amount of the elements except for Zn included in the commercial alloys are quite small when compared with that of Zn as shown in Table I, the concentration gradients of the elements except for Zn is reasonably considered to be so small. This means that we will be able to evaluate the direct interdiffusion coefficients of Zn from the diffusion profile of Zn by the application of Boltzmann-Matano's analysis [10], which is usually used to evaluate the interdiffusion coefficients in a binary alloy. This diffusion coefficient will give us rough information about the magnitude of Zn diffusion coefficients in commercial alloys and their concentration dependence.

The effective interdiffusion coefficients in a multicomponent alloy system can be evaluated by the following Equation 2,

$$\tilde{D}_{i,\mathrm{R}}^{\mathrm{eff}} = 1/2t\left[\int_{C_i^0}^{C_i^{(+\infty)}} (X - X_0)^2\,\mathrm{d}C_i\right]\Big/\left(C_i^{(+\infty)} - C_i^0\right) \tag{2}$$

where X_0 is the position of the Matano interface, C_i^0 the concentration at X_0, and $\tilde{D}_{i,\mathrm{R}}^{\mathrm{eff}}$ the effective interdiffusion coefficients for the component i over the concentration range $C_i^{(+\infty)}$ to C_i^0 on the right hand side of the Matano interface. The effective interdiffusion coefficients on the left hand side of the Matano interface $\tilde{D}_{i,\mathrm{L}}^{\mathrm{eff}}$ are also expressed by a similar equation. The average effective interdiffusion coefficients $\tilde{D}_i^{\mathrm{eff}}$ are given by:

$$\tilde{D}_i^{\mathrm{eff}} = \tilde{D}_{i,\mathrm{R}}^{\mathrm{eff}} Y_i + \tilde{D}_{i,\mathrm{L}}^{\mathrm{eff}}(1 - Y_i) \tag{3}$$

where $Y_i = (C_i^0 - C_i^{(+\infty)})/(C_i^{(+\infty)} - C_i^{(-\infty)})$. These effective interdiffusion coefficients are closely related to the interdiffusion coefficients and the concentration gradients of the elements in the n-component alloy.

3. Experimental results and discussions

Fig. 1 shows, as an example, the concentration profiles of zinc in the Al/701 diffusion couple annealed at 883 K for 10.8 ks under 0.1 MPa and one at 883 K for 9 ks under 0.41 GPa. The origin of the abscissa in Fig. 1 is the Matano interface. Both diffusion profiles exhibit the typical S-shaped diffusion profiles, but it is clear that high pressure suppresses the diffusion of zinc in the Al-Zn alloy. Fig. 2a and b show the concentration dependences of the diffusion coefficients of zinc in Al/701 diffusion couple under 0.1 MPa and 0.41 GPa evaluated by the application of Boltzmann-Matano's analysis [10]. It is observed that those diffusion coefficients of zinc in the Al/701 diffusion couple have quite a small concentration dependence. As for the 703, 705 alloys, the diffusion coefficients also have very small concentration dependence. However, the interdiffusion coefficients in the binary Al-Zn alloys are reported to have the large concentration dependence that the interdiffusion coefficients increase with increasing

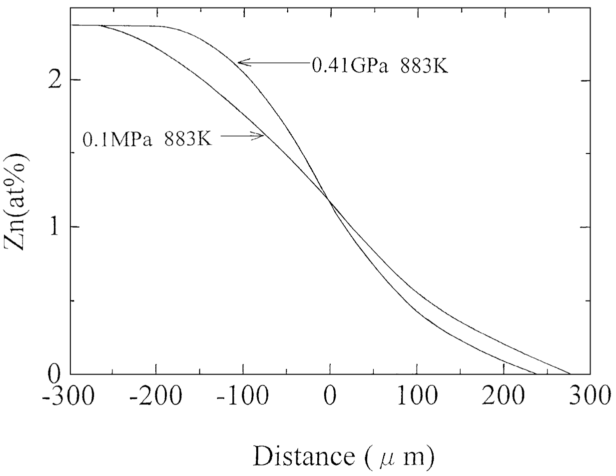
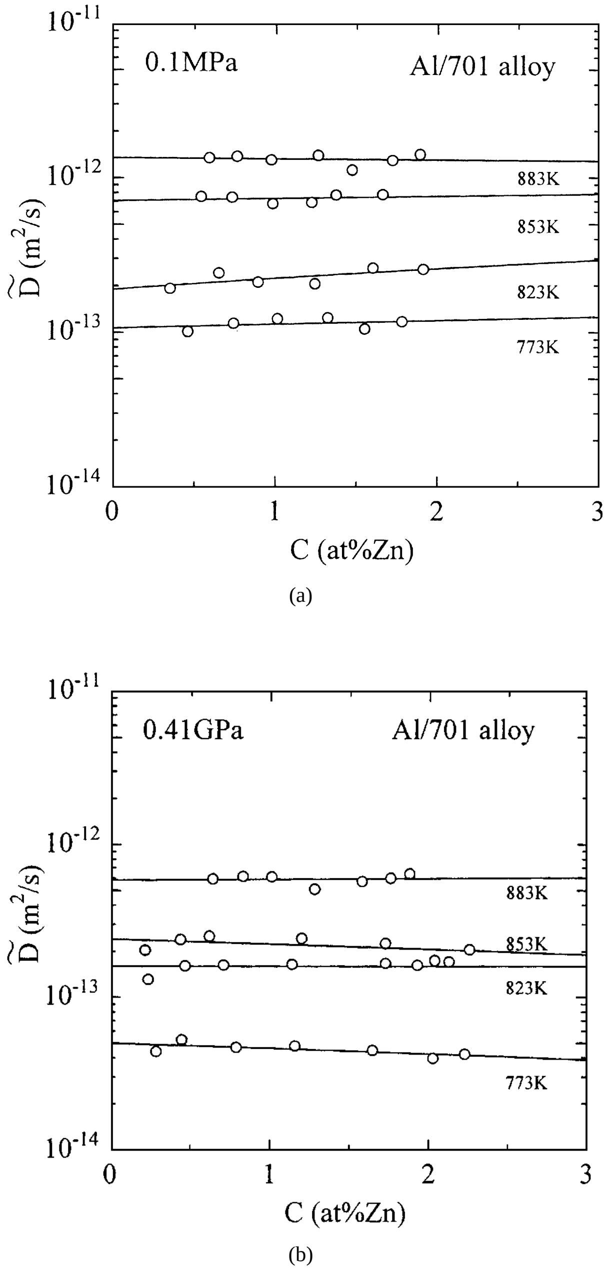


Figure 1 Diffusion profiles of zinc concentrations in diffusion couple Al/701 alloy annealed at 883 K for 10.8 ks under 0.1 MPa, and at 883 K for 9 ks under 0.41 GPa.



(a)

(b)

Figure 2 Diffusion coefficients as a function of zinc concentration in Al/701 alloy under (a) 0.1 MPa, and (b) 0.41 GPa.

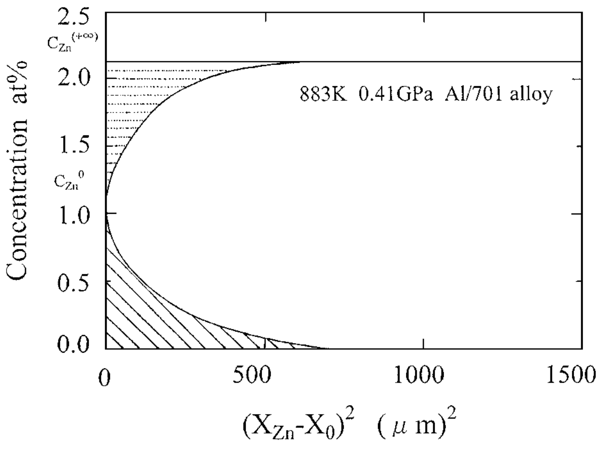


Figure 3 A schematic plot of concentration C_{Zn} of component *i* vs. $(X_{Zn} - X_0)^2$.

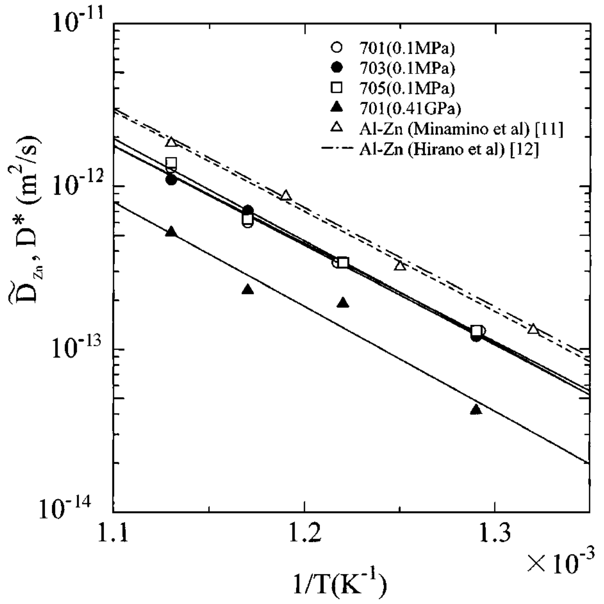


Figure 4 Temperature dependences of average effective interdiffusion coefficients of zinc in Al-Zn alloys.

concentration of Zn [11, 12]. In Fig. 3, the diffusion profile in the Al/701 diffusion couple annealed at 883 K 0.41 GPa is replotted vs. $(X - X_0)^2$. The dotted areas were graphically determined according to Equation 2, and then the effective interdiffusion coefficients were evaluated. Table II lists the effective interdiffusion coefficients on the left and right hand side of the Matano interface. These effective interdiffusion coefficients on the left and right side are almost equal to each other, and they are also equivalent to the diffusion coefficients obtained from the Boltzmann-Matano's analysis. The equality between the effective interdiffusion coefficients on the left and right side is consistent with the no concentration dependence of the diffusion coefficients in Fig. 2.

Fig. 4 shows the temperature dependences of the average effective interdiffusion coefficients in Al/701, Al/703 and Al/705 Al-Zn diffusion couples under 0.1 MPa and 0.41 GPa. These average effective interdiffusion coefficients of zinc fall on straight lines, and the diffusion coefficients satisfy the Arrhenius type equation;

$$\tilde{D}_i^{\mathrm{eff}} = D_0 \exp(-Q/RT) \quad (4)$$

TABLE II Effective interdiffusion coefficients (m^2/s) in the Al/Al-Zn couples

T (K)	$\tilde{D}^{\mathrm{eff}}_{\mathrm{Zn,R}}$	$\tilde{D}^{\mathrm{eff}}_{\mathrm{Zn,L}}$	$\tilde{D}^{\mathrm{eff}}_{\mathrm{Zn}}$
(a) Al/701 couple			
0.1 MPa			
773	1.5×10^{-13}	1.2×10^{-13}	1.3×10^{-13}
823	3.0×10^{-13}	3.8×10^{-13}	3.4×10^{-13}
853	5.6×10^{-13}	6.4×10^{-13}	6.0×10^{-13}
883	1.3×10^{-12}	1.0×10^{-12}	1.1×10^{-12}
0.21 GPa			
823	2.0×10^{-13}	2.3×10^{-13}	2.2×10^{-13}
883	6.7×10^{-13}	7.3×10^{-13}	7.0×10^{-13}
0.31 GPa			
883	6.9×10^{-13}	6.2×10^{-13}	6.5×10^{-13}
0.41 GPa			
773	4.0×10^{-14}	4.3×10^{-14}	4.2×10^{-14}
823	2.2×10^{-13}	1.8×10^{-13}	1.9×10^{-13}
853	2.2×10^{-13}	2.5×10^{-13}	2.3×10^{-13}
883	5.6×10^{-13}	5.9×10^{-13}	5.7×10^{-13}
(b) Al/703 couple			
0.1 MPa			
773	1.3×10^{-13}	1.1×10^{-13}	1.2×10^{-13}
853	7.2×10^{-13}	7.0×10^{-13}	7.1×10^{-13}
883	1.0×10^{-12}	1.1×10^{-12}	1.1×10^{-12}
(c) Al/705 couple			
0.1 MPa			
773	1.4×10^{-13}	1.1×10^{-13}	1.3×10^{-13}
823	3.0×10^{-13}	3.8×10^{-13}	3.4×10^{-13}
853	5.6×10^{-13}	7.1×10^{-13}	6.3×10^{-13}
883	1.5×10^{-12}	1.3×10^{-12}	1.4×10^{-12}

where D_0 is the pre-exponential factor, Q the activation energy, R the gas constant, T the diffusion temperature. The values of Q and D_0 evaluated from Fig. 4 are listed with other authors' data in Table III. The previous data by the other researchers are tracer diffusion coefficients in pure Al. Though the activation energies have similar values to other authors' ones and the pre-exponential factors also have similar ones, the values of the average effective interdiffusion coefficients of zinc in the commercial alloys in this work are somewhat smaller than those of previous data of the interdiffusion coefficient of Zn in Al [11].

Thus, the commercial alloys exhibit diffusion characteristics different from those in the pure Al. These small diffusivities and their lack of concentration dependence are attributed to the change in the situation of vacancies and the metallurgical structure of alloys as follows. Fujikawa *et al.* reviewed the effect of the additional element on the aging in aluminum alloys [19]. According to their review, the formation of G.P.zones in Al-Zn and Al-Cu alloys are suppressed by the addition of Si, Sn, In, Cd, and so on. The low temperature aging in ternary Al-Zn-Mg alloys are also retarded by addition of the elements V, Ti, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Y, Si, Ge, Sn, Cd, In, Hg, Ia, Li and Be. These suppressions of formation of G.P.zone by the additional elements are attributed to the strong binding between the additional elements and vacancies. In general, the elements which have the lower solid solubilities in aluminum have the larger binding energies between the element and vacancies. Especially, since the transition elements have quite low solid solubilities, then they are considered to have large binding energies. In addition, they also have quite low diffusivity in aluminum. Once such transition elements capture the large amount of vacancies due to their large binding energies, they suppress the free migration of vacancies because they diffuse fairly slowly, that is, the transition elements decrease the number of vacancies which contribute to diffusion in the matrix phase and suppress the diffusion rates in the matrix phase. As shown in Table I, the commercial alloys contain transition elements such as Fe (maximum solid solubility of Fe in Al; 0.052 mass% Fe), Mn (1.82 mass% Mn), Ti (1.323 mass% Ti), Zr (0.28 mass% Zr), Cr (0.77 mass% Cr) and so on. Among them, the Fe element content in the commercial alloys is up to 0.16%, which is over the maximum solid solubility of Fe in Al. Therefore, the effect of Fe element should play an important role for the suppression of diffusion rates in the commercial alloys. As for the structure of alloys, the commercial alloys are added with various elements to have a lot of fine precipitates in order to obtain fine grains, high strength and so on. In the Al side of Al/commercial alloy diffusion couple, the Zn element can diffuse in the aluminum matrix without such precipitates. On the other hand, in the commercial alloy side, the fine precipitates limit the diffusion area and partially obstruct the diffusion flux of Zn inside of the commercial alloy, and cancel the concentration dependence of diffusion coefficients.

TABLE III Activation energies and pre-exponential factors of effective interdiffusion of zinc in commercial Al-Zn alloys

Pressure		D_0 (m^2/s)	Q (kJ/mol)
0.1 MPa	701	3.0×10^{-5}	125
	703	4.0×10^{-5}	124
	705	3.9×10^{-5}	127
0.41 GPa	701	2.5×10^{-5}	130
Minamino *et al.* [11]		4.06×10^{-5}	124
Hilliard *et al.* [13]		1.1×10^{-4}	129
Ceresara *et al.* [14]		9.0×10^{-5}	127
Hirano *et al.* [12]		1.77×10^{-5}	118
Peterson *et al.* [2]		2.59×10^{-5}	121
Godeny *et al.* [15, 16]		3.0×10^{-5}	121
[17]		2.0×10^{-5}	121
[18]		2.7×10^{-5}	120

The activation volume of effective interdiffusion can be also evaluated from the pressure dependence of the effective interdiffusion coefficients.

$$\Delta\tilde{V} = -RT\left[\frac{\partial \ln D_i^{\mathrm{eff}}}{\partial P}\right]_T \qquad (5)$$

where $\Delta\tilde{V}$ is the activation volume for average effective interdiffusion and P the pressure. Fig. 5 shows the pressure dependence of average effective interdiffusion coefficients of zinc. The average effective interdiffusion coefficients of zinc decrease with pressure. The activation volumes for average effective interdiffusion of zinc in the commercial alloys are evaluated to be $8.60 \times 10^{-6}\ m^3/mol$ at 883 K and $8.30 \times 10^{-6}\ m^3/mol$ at 823 K from Equation 5. When the diffusion occurs

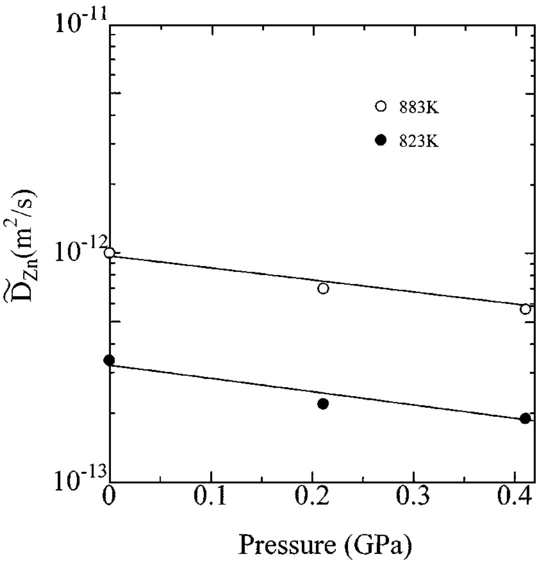


Figure 5 Pressure dependences of average effective interdiffusion coefficients of zinc in 701 Al-Zn alloys.

by the vacancy mechanism, the activation volume of diffusion is the sum of the migration volume ΔV_m and formation volume ΔV_f, of a lattice defect [20],

$$\Delta V = \Delta V_m + \Delta V_f \tag{6}$$

The ratio of $\Delta V / V_0$ is evaluated to be 0.86 and 0.83 where V_0 is the molar volume of aluminum at atmospheric pressure and its value is 10×10^{-6} m^3/mol. Fig. 6 [21] shows the activation volumes of diffusion as the ratio of $\Delta V / V_0$ with other author's results. The activation volumes of self-diffusion are also shown in the same figure [22–27].

Although these activation volumes are very scattered and not consistent with each another, it is found that the activation volumes separate into two groups which are in the regions of the monovacancy diffusion and divacancy mechanisms respectively. The activation volumes of this work are in the range of the monovacancy diffusion mechanism. The activation energies $Q(P)$ for diffusion at high pressure P are larger by the amount of $P \cdot \Delta V$ than those at zero pressure,

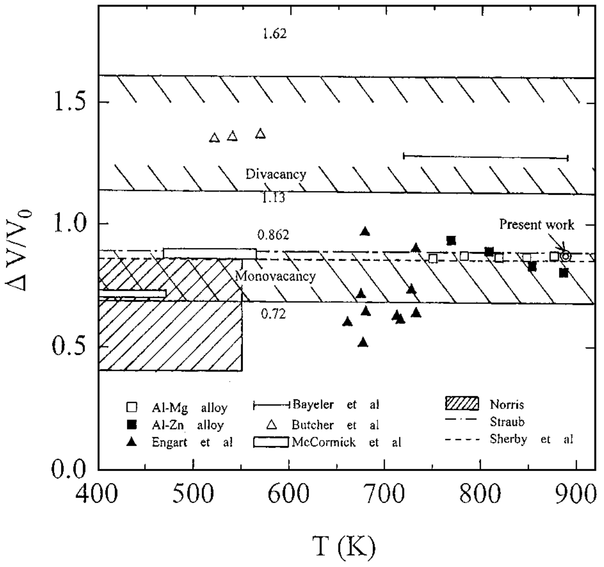


Figure 6 Ratio of activation volume of effective interdiffusion of zinc in Al-Zn alloys ΔV to molar volume of aluminum V_0 as a function of absolute diffusion temperature.

$$Q(P) = Q(0) + P \cdot \Delta V \tag{7}$$

where $Q(0)$ and $Q(P)$ are the activation energies of diffusion at pressure 0 and P, and ΔV is the activation volume for diffusion. The values of $P \cdot \Delta V$ calculated from $\Delta V = 8.30 \times 10^{-6}$ m^3/mol and $P = 0.41 \times 10^9$ N/m^2 is 3.5 kJ/mol. The experimental difference 5 kJ/mol of the activation energies at high pressure of 0.41 GPa and atmospheric pressure of 0.1 MPa agrees well with that of the calculation result.

4. Summary

The effective interdiffusion coefficients of zinc in commercial Al-Zn alloys are obtained. The activation energy for average effective interdiffusion coefficients of Zn in the commercial Al-Zn alloy are 125 kJ/mol (Al/701 alloy 0.1 MPa). Activation volumes ΔV for average effective interdiffusion of zinc in the commercial Al-Zn alloy are 8.30×10^{-6} m^3/mol at 823 K and 8.60×10^{-6} m^3/mol at 883 K. The activation volume measurements show that the diffusion of zinc in commercial alloys is an intermediate region in the range of monovacancies. The activation energy for effective interdiffusion of zinc under high pressure is similar to $Q(0) + P \cdot \Delta V$ where $Q(0)$ is the activation energy, P the pressure and ΔV the activation volume.

Acknowledgements

This research work was financially supported by the Light Metals Educational Foundation Inc.

References

1. Y. MINAMINO, Y. YAMANE, K. TSUKAMOTO, J. TAKAHASHI and H. KIMURA, *Z. Metallkde* **75** (1984) 943.
2. T. TAKAHASHI, Y. MINAMINO and T. YAMANE, *J. Mater. Sci. Soc. Japan* **34** (1997) 96.
3. R. D. SISSSON, JR. and M. A. DAYANANDA, *Met. Trans. A* **8A** (1977) 1849.
4. M. A. DAYANANDA, *Defect and Diffusion Forum* **95–98** (1993) 521–536.
5. L. A. GRIFARCO, in "Metallugy at High Pressures and High Temperatures," edited by K. A. Gschneidner, Jr., M. T. Hepworth and N. A. D. Parlee (Gordon and Breach Science Publishers, New York, 1964).
6. A. SEEGER, D. WOLF and H. MEHRER, *Phys. Stat. Sol.* (*b*) **48** (1971) 481.
7. N. L. PETERSON and S. J. ROTHMAN, *Phys. Rev.* **B1** (1970) 3264.
8. K. HIRANO and S. FUJIKAWA, *Trans. Jpn. Inst. Met.* **27** (1976) 809.
9. J. B. MURPHY, *Acta Metall.* **9** (1961) 563.
10. C. MATANO, *Japan J. Phys.* **8** (1933) 109.
11. Y. MINAMINO *et al.*, *Z. Metallkde. Bd.* **73** (1982) 124.
12. K. HIRANO and S. FUJIKAWA, *J. Nucl. Mater.* **69+70** (1978) 564.

13. J. E. HILLIARD, B. L. AVERBACH and M. COHEN, *Acta Met.* **7** (1959) 86.
14. S. CERESSA, T. FEDERIGHI and F. PIERAGOSTINI, *Phys. Stat. Sol.* **16** (1966) 439.
15. I. GÖDĖNY, D. BEKE, F. J. KEDVES and G. GROMA, *Phys. Stat. Sol. (a)* **32** (1975) 195.
16. *Idem., ibid.* **13** (1972) K155.
17. D. BEKE, I. GÖDĖNY and F. J. KEDVES, *Acta Met.* **25** (1977) 539.
18. G. ERDELYI, D. L. BEKE, F. J. KEDVES and I. GÖDĖNY, *Phil. Mag. B* **38** (1978) 445.
19. S. FUJIKAWA, K. HIRANO and Y. BABA, *Bulletin of Japan Inst. Met.* **7** (1968) 495.
20. Y. ADDA and J. PHILLIBERT, "La Diffusion dans les Solides" (Presses Universitaires de France, Paris, 1977).
21. TOMOSHI TAKAHASHI, TOSHIMI YAMANE, TOMOHIKO YAMAMOTO, HIDEKI ARAKI, YORITOSHI MINAMINO and YOSHINARI MIYAMOTO, *Z. Metallkd.* **85** (1994) 492.
22. R. D. ENGARDT and R. G. BARNES, *Phys. Rev.* **B3** (1971) 2391.
23. M. BEYELER and Y. ADDA, *J. Phys.* **29** (1968) 345.
24. B. M. BUTCHER, H. HUTTO and A. L. RUOFF, *Appl. Phys. Lett.* **7** (1965) 34.
25. P. G. McCORMICK and A. L. RUOFF, *J. Appl. Phys.* **40** (1969) 4812.
26. O. D. SHERBY, J. L. ROBBINS and A. GOLDBERG, *ibid.* **41** (1970) 3961.
27. K. STRAUB, *J. Nucl. Mater.* **69+70** (1978) 529.

Received 10 October 1997
and accepted 16 November 1998