

Diffusion processes in *b*-Zr(Al) phase: a thermodynamic approach

A LAIK, K BHANUMURTHY and G B KALE*

Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

MS received 17 September 2004; revised 10 March 2005

Abstract. The diffusion behaviour in the *b*-Zr(Al) solid solution phase was investigated in the temperature range 1203–1323 K using a thermodynamic approach. The Boltzmann–Matano relation used for determining interdiffusion coefficients and the Darken’s equations used for evaluating the intrinsic diffusion coefficients from velocity of movement of markers in diffusion couples were modified suitably. The composition dependent thermodynamic interdiffusion coefficients were evaluated using chemical potential gradient. Composition and temperature dependence of the thermodynamic interdiffusion coefficients were also established. The thermodynamic intrinsic diffusion coefficients of Al and Zr and their temperature dependence were determined using the modified Darken’s equations.

Keywords. Interdiffusion; diffusion coefficient; activation energy; zirconium; aluminium.

1. Introduction

Solid-state diffusion plays a critical role in metallurgical reactions such as precipitation, dissolution and formation of phases during heat treatments. A large number of solid-state phase transformations are diffusion controlled. The rate at which these reactions proceed is determined primarily by the diffusivity values of the components in the individual phases. Therefore, the diffusion coefficient values are very vital in estimation of the time for completion of the solid state reactions. Conventionally, the diffusion coefficients are calculated assuming the concentration gradient as the driving force for diffusion, which sometimes results in unrealistic values. The actual driving force for diffusion is the chemical potential gradient, which is often approximated as the concentration gradient. Garg *et al* (1999) introduced a new form of diffusion coefficient, termed as ‘thermodynamic diffusion coefficient’, which is calculated considering the chemical potential gradient as the driving force for diffusion. They showed that this new approach for evaluation of the diffusion coefficients has distinct advantages over the conventional method. The results produced by the thermodynamic approach provide better interpretation of the relative diffusivity of the components and an appropriate estimation of the activation energy for the diffusion processes.

Zirconium based alloys are used extensively in the nuclear industry. The materials of construction of the in-pile structural components of thermal nuclear reactors are essentially zirconium based alloys. They have distinct advantages of low neutron absorption cross-section coupled with requi-

red mechanical properties and good corrosion resistance, which make them indispensable as structural materials in thermal reactors. Zr–Al based alloys are proposed as candidate structural materials for thermal reactors (Schulson 1975, 1994). In such a case, a proper evaluation of the diffusional behaviour of the Zr–Al system is required, as it governs the phase stability and creep properties of the materials. The literature on diffusion properties of the Zr–Al system is limited to multi-phase diffusion reactions (Kidson and Miller 1964; Gukelberger and Steeb 1978; Laik *et al* 2004). In a recent work, the present authors have investigated the diffusion behaviour in the *b*-Zr(Al) solid solution phase where they used the conventional method to determine the interdiffusion, intrinsic and tracer diffusion coefficients (Laik *et al* 2002). It may be mentioned here that single-phase diffusion couple experiments yield a better estimation of the diffusion coefficients than multi phase diffusion couples. Even the activation energy values determined by the two methods have been seen to vary to a great extent in certain cases (Kim and Chang 2000). This difference is attributed mainly to the presence of phase boundaries in multi phase diffusion couples, which influence the atomic flux of the diffusing species. The phase boundaries act as source and sink for point defects in multi phase couples.

The present paper reports a detailed study of the solid-state diffusion behaviour in the *b*-Zr(Al) phase in the temperature range 1203–1323 K employing single-phase diffusion couples and using the thermodynamic approach for evaluation of the diffusion coefficients. The Boltzmann–Matano relation and the Darken’s equations have been suitably modified to evaluate the thermodynamic interdiffusion and intrinsic diffusion coefficients.

*Author for correspondence (gbkale@apsara.barc.ernet.in)

2. Experimental

A dilute alloy of Al in Zr with nominal composition, Zr–2.8 wt% Al, was prepared in an arc-melting furnace under high-purity argon atmosphere. The button was hot rolled at 1233 K after encapsulating it in a steel jacket under vacuum to prevent oxidation. Samples of the size, $10 \times 8 \times 3 \text{ mm}^3$, were cut from the rolled alloy and were sealed in quartz capsules under helium atmosphere. Rectangular pieces of about the same size of pure Zr were also sealed separately in quartz tubes under helium atmosphere. These sealed pieces of pure Zr and Zr–2.8% Al alloy were then annealed at 1250 K for 72 h to homogenize, promote grain-growth and hence obtain a well-annealed coarse-grained microstructure.

The surfaces of these annealed pieces were metallographically prepared to a 0.25 mm finish. Diffusion couples were prepared by keeping the polished surface of a pure Zr piece in contact with that of a Zr–2.8% Al alloy piece under a compressive stress of 5 MPa and then heating them at 1173 K for 1 h under vacuum better than 10^{-3} Pa. Thin wires of tungsten were placed in between the end members of the couples while preparing them, which act as markers. The bonded couples were subsequently annealed at constant temperatures of 1203, 1233, 1263, 1293 and 1323 K for 72 h each under He atmosphere in sealed quartz capsules. The furnace temperature was controlled to within ± 1 K using a proportional type temperature controller. After annealing, the diffusion couples were quenched in water and sectioned perpendicular to the bond interface using a low-speed diamond saw. The cross-sections were prepared using standard metallographic techniques to a surface finish of 0.25 mm. The details of preparation of diffusion couples and the subsequent heat treatment are discussed elsewhere (Laik *et al* 2002).

These metallographically prepared diffusion annealed couples were analysed using a CAMECA SX100 electron probe microanalyser (EPMA) equipped with wavelength dispersive spectrometers (WDS). The analysis was carried out using a stabilized, focussed electron beam of 20 keV energy and 20 nA current. The X-ray lines of Al-K α and Zr-L α were diffracted by thallium acid phthalate (TAP) and pentaerythritol (PET) crystals, respectively. For quantitative analysis in the diffusion zones of the couples, pure Zr and pure Al were used as standards and PAP correction method was used for the atomic number, absorption and fluorescence corrections (Pouchou and Pichoir 1985). Quantitative analyses were carried out at points at regular intervals of 1–2 mm perpendicular to the bond interface. The concentration profiles established in the diffusion zones of the couples after annealing were determined by plotting the concentrations against distance.

3. Thermodynamic diffusion coefficients

The conventional flux equation for diffusion in a binary system is expressed as

$$\tilde{J}_i = \frac{\tilde{D}_{(N)}}{V_m} \left(\frac{\partial N_i}{\partial x} \right), \quad (1)$$

assuming the concentration gradient as the driving force for diffusion, where \tilde{J}_i is the interdiffusion flux of component, i , $\tilde{D}_{(N)}$ the composition dependent interdiffusion coefficient, V_m the molar volume of the alloy (assumed here as concentration independent) and N_i is the mole fraction of component, i . The chemical potential of a component is expressed as

$$m_i = m_i^0 + RT \ln a_i, \quad (2)$$

where, a_i is the activity of the component, i . The actual driving force for diffusion, the chemical potential gradient, is equal to

$$\frac{\partial m_i}{\partial x} = RT \frac{\partial \ln a_i}{\partial x}. \quad (3)$$

Thermodynamic diffusion coefficient, $\tilde{D}_{(m)}$ can be defined using the chemical potential gradient as the driving force (Garg *et al* 1999). The flux equation then can be expressed as

$$\tilde{J}_i = -\frac{\tilde{D}_{(m)}}{V_m} N_i \left(\frac{\partial \ln a_i}{\partial x} \right), \quad (4)$$

where $\tilde{D}_{(m)}$ is the thermodynamic interdiffusion coefficient. We have used the notations $D_{(N)}$ and $D_{(m)}$ to denote the conventional diffusion coefficient and thermodynamic diffusion coefficient, respectively in order to distinguish between the two.

A concentration dependent interdiffusion coefficient is generally determined by the Boltzmann–Matano method (Boltzmann 1894; Matano 1933). According to this method, the interdiffusion coefficient, $\tilde{D}_{(N)}$, at concentration N^* , of a binary system A–B, is expressed as

$$\tilde{D}_{(N)} = -\frac{1}{2t} \left(\frac{\partial x}{\partial N_B} \right)_{N^*} \int_{N=N^*}^{N^*} (x - x_0) dN_B, \quad (5)$$

where, x_0 is the position of the Matano interface and N^{∞} the concentration at the extreme end. To determine the thermodynamic diffusion coefficient, $\tilde{D}_{(m)}$, (5) needs to be suitably modified. The interdiffusion flux at a plane, in the diffusion zone, with composition N^* , is given by

$$\tilde{J} = -\frac{1}{2tV_m} \int_{N=N^*}^{N^*} (x - x_0) dN_B. \quad (6)$$

Substituting this expression for interdiffusion flux in (4), the thermodynamic interdiffusion coefficient, $\tilde{D}_{(m)}$, at composition, N^* , can be written as

$$\tilde{D}_{(N)} = -\frac{1}{2tN^*} \left(\frac{\partial x}{\partial \ln a_B} \right)_{N^*} \int_{N=N^*}^{N^*} (x - x_0) dN_B. \quad (7)$$

This is the modified Boltzmann–Matano relation, which can be used to determine the composition dependent thermodynamic interdiffusion coefficient.

The intrinsic diffusion coefficients, $D_{A(N)}$ and $D_{B(N)}$, of components A and B, in a binary system A–B, are conventionally determined by diffusion couple experiments using markers. The values of $D_{A(N)}$ and $D_{B(N)}$ are evaluated from the interdiffusion coefficient, $\tilde{D}_{(N)}$ and the velocity of the markers, n , using the Darken's (1948) equations

$$n = [D_{B(N)} - D_{A(N)}] \left(\frac{\partial N_B}{\partial x} \right) \quad (8a)$$

$$\tilde{D}_{(N)} = N_A D_{B(N)} + N_B D_{A(N)}. \quad (8b)$$

Similar relations can be deduced for thermodynamic diffusion coefficient assuming the chemical potential gradient as the driving force. The marker velocity (n) is equal to the net mass flow, which is the vacancy flux (J_v) times the molar volume (V_m). Therefore, the velocity of the markers can be expressed as

$$n = J_v V_m = -(J_A + J_B) V_m. \quad (9)$$

Substituting for the intrinsic diffusion flux and using Gibbs–Duhem relation ($N_A d \ln a_A + N_B d \ln a_B = 0$), we get

$$n = (D_{B(i)} - D_{A(i)}) N_B \left(\frac{\partial \ln a_B}{\partial x} \right) \quad (10)$$

where $D_{A(i)}$ and $D_{B(i)}$ are the thermodynamic intrinsic diffusion coefficient of components A and B, respectively. A relation similar to (8b) can be deduced for the thermodynamic diffusion coefficients and is expressed as

$$\tilde{D}_{(i)} = N_A D_{B(i)} + N_B D_{A(i)}. \quad (11)$$

These modified Darken's equations can be used to determine the thermodynamic intrinsic diffusion coefficients.

4. Results and discussion

4.1 Activity profile across diffusion zone

The excess free energy of mixing, $\Delta G_{\text{mix}}^{\text{xs}}$, in an n component system is expressed by the relation

$$\Delta G_{\text{mix}}^{\text{xs}} = RT \sum_{i=1}^n N_i \ln g_i, \quad (12)$$

where, N_i and g_i are the mole fraction and the activity coefficient of component, i , respectively. For a binary system A–B, therefore, $\Delta G_{\text{mix}}^{\text{xs}}$ can be given as

$$\Delta G_{\text{mix}}^{\text{xs}} = RT [N_A \ln g_A + N_B \ln g_B], \quad (13)$$

which can be modelled and expressed in the form of an algebraic expression

$$\Delta G_{\text{mix}}^{\text{xs}} = N_A N_B \sum_{j=0}^m (a_j - a'_j T) (N_A - N_B)^j. \quad (14)$$

The value of m can be integers 0, 1, 2, 3... depending upon the model, which the solid solution is assumed to follow. For a regular solution, $m = 0$, for a sub-regular solution, $m = 1$ and for a real solution the value of m can have values 2 or more (Saunders and Miodownik 1998). The values of a_j and a'_j for m greater than 2 are not available. Hence the value of $m = 2$ is taken for our calculation. It also gives more realistic values of $\Delta G_{\text{mix}}^{\text{xs}}$ as higher degree terms are considered.

In the present study, we are concerned with a dilute alloy of Al in Zr, and the concentration of Al in the diffusion zone varies from zero to a maximum of 2.8 wt% only. Therefore, we may assume $g_{\text{Zr}} = 1$. Combining (12) and (14) and imposing the above mentioned conditions, the activity coefficient of Al is expressed as

$$\ln g_{\text{Al}} = \frac{N_{\text{Zr}}}{RT} \sum_{j=0}^2 (a_j - a'_j T) (N_{\text{Zr}} - N_{\text{Al}})^j. \quad (15)$$

Therefore, the activity of Al can be calculated using the relation

$$\ln a_{\text{Al}} = \ln N_{\text{Al}} + \frac{N_{\text{Zr}}}{RT} \sum_{j=0}^2 (a_j - a'_j T) (N_{\text{Zr}} - N_{\text{Al}})^j. \quad (16)$$

The parameters, a_j and a'_j , for *bcc* solid solution of Zr and Al, were reported by Saunders and Rivlin (1986) in their work on thermodynamic assessment of the Zr–Al system. These parameters were used for evaluating the activity of Al at various concentrations in the diffusion zone using (16).

The concentration profiles were determined by electron micro-probe analysis across the diffusion zones in the diffusion couples. The activity at each point can be calculated from the concentration of Al using (16). The logarithmic values of activity of Al were plotted against distance to obtain the activity profiles. Figure 1 shows a typical concentration profile for Al along with the corresponding activity profile across the diffusion zone of the couple annealed at 1293 K for 72 h.

The profile shows a monotonic increase in the activity of Al throughout the diffusion zone from pure Zr to Zr–2.8%Al alloy. However, the profile can be divided into two distinct parts based on the rate of increase of activity, or in other words, the slope of the activity profile. In the region towards the pure Zr side of the couple, the activity gradient is steeper, whereas, the activity increases at a slower rate on the alloy side of the couple. This implies that the driving force for diffusion of Al in pure Zr is higher than that in the Zr–Al alloy. It can also be noticed from figure 1 that the nature of the concentration profile across the diffusion zone is contrary to that of the activity profile. The concentration gradient of Al in the alloy side is steeper than in the pure Zr side. Therefore, the present binary system (Zr–Al) shows that the magnitude and the variation of the driving force for diffusion may not be often depicted correctly by concentration profiles.

The asymmetry in both, the concentration and the activity profiles, about the Matano interface is due to unequal rate of mass transfer in the two directions. These unequal rates give rise to the shift in the markers from their original positions during the process of annealing.

4.2 Thermodynamic interdiffusion coefficient

The values of the thermodynamic interdiffusion coefficients ($\tilde{D}_{(m)}$) were calculated at various concentrations of Al across the diffusion zone for all the temperatures of annealing using the modified Boltzmann–Matano relation, i.e. (7). These values are plotted against the concentration of Al in figure 2. It can be seen from the figure that the diffusion coefficient, $\tilde{D}_{(m)}$, increases monotonically with an increase in concentration of Al. The phase diagram of Zr and Al clearly shows that addition of Al decreases the liquidus temperature (Peruzzi and Abraitia 1990). Since the diffusion coefficient at the melting point is moderately constant for all compositions (Brown and Ashby 1980), a decrease in the melting point with increase in Al concentration causes an increase in the interdiffusion coefficient. The rate of increase of $\tilde{D}_{(m)}$ is higher at higher concentration of Al. The values of $\tilde{D}_{(m)}$, calculated at the five temperatures of annealing, are listed in table 1 at an interval of 1 at% in the *b*-Zr(Al) phase. The values of $\tilde{D}_{(m)}$ evaluated in the present study range from 1.43×10^{-15} to 1.14×10^{-14} m²/s. The data points of figure 2 fit well to quadratic relation of the type, $\tilde{D}_{(m)} = X + Y C_{Al} + Z C_{Al}^2$, for all the temperatures. The values of the coefficients *X*, *Y* and *Z* are given in table 2.

In general, the temperature dependence of diffusion coefficients is expressed by an Arrhenius type of relation

$$D = D_0 \exp(-Q/RT), \quad (17)$$

where *Q* is the activation energy for diffusion, *T* the temperature in absolute scale and *R* the universal gas constant.

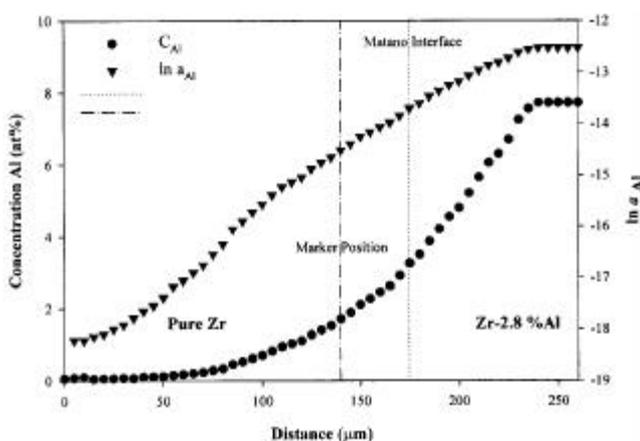


Figure 1. Concentration and activity profile of Al across the diffusion zone of Zr/Zr–2.8 wt%Al couple annealed at 1293 K for 72 h.

The constant, D_0 , is termed as pre-exponential factor or frequency factor. To determine the temperature dependence of the thermodynamic interdiffusion coefficient, the values of $\ln \tilde{D}_{(m)}$ were plotted against the inverse of temperature ($1/T$). Figure 3 shows such a plot where the values of $\ln \tilde{D}_{(m)}$ were plotted for compositions at an interval of 1 at%. The data points for each composition were fitted with straight lines using the least square method (linear regression). The values of the activation energy ($\tilde{Q}_{(m)}$) and the frequency factor ($\tilde{D}_{0(m)}$) were determined from the slope and intercept of the straight lines. Table 3 shows the values of $\tilde{Q}_{(m)}$ and $\tilde{D}_{0(m)}$ at various concentrations of Al evaluated from figure 3. The values of the activation energy for interdiffusion decrease continuously with increase in the Al concentration and range from 162.24 to 220.46 kJ/mol for the composition range $1\text{at}\% \leq C_{Al} \leq 8$ at%.

The values of the frequency factors, $\tilde{D}_{0(m)}$, also decrease continuously with an increase in the concentration of Al. In order to determine the nature of variation of $\tilde{Q}_{(m)}$ and $\tilde{D}_{0(m)}$, these values are plotted against the concentration of Al in figure 4. A linear variation was observed for both $\tilde{Q}_{(m)}$ and $\tilde{D}_{0(m)}$. The data points were fitted with straight lines by using linear regression. The equation of these fitted lines are

$$\tilde{Q}_{(m)} \text{ (kJ/mol)} = 236.4 - 8.814 C_{Al} \text{ (at\%)},$$

and

$$\ln \tilde{D}_{0(m)} \text{ (m}^2\text{/s)} = -10.798 - 0.782 C_{Al} \text{ (at\%)}. \quad (18)$$

Gukelberger and Steeb (1978) had reported the activation energy for interdiffusion for composition, $C_{Al} > 8$ at%. The values of \tilde{Q} at $C_{Al} = 8$ at%, determined by them is comparable with the present results as shown in figure 4.

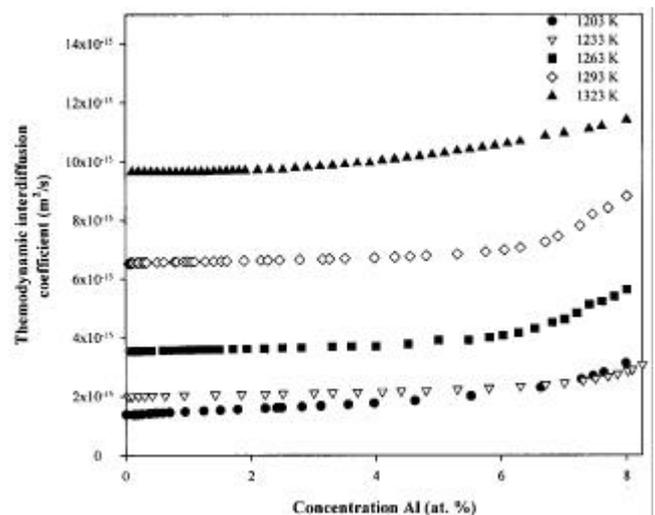


Figure 2. Concentration dependence of thermodynamic interdiffusion coefficient.

Table 1. Thermodynamic interdiffusion coefficient values at various compositions and temperature.

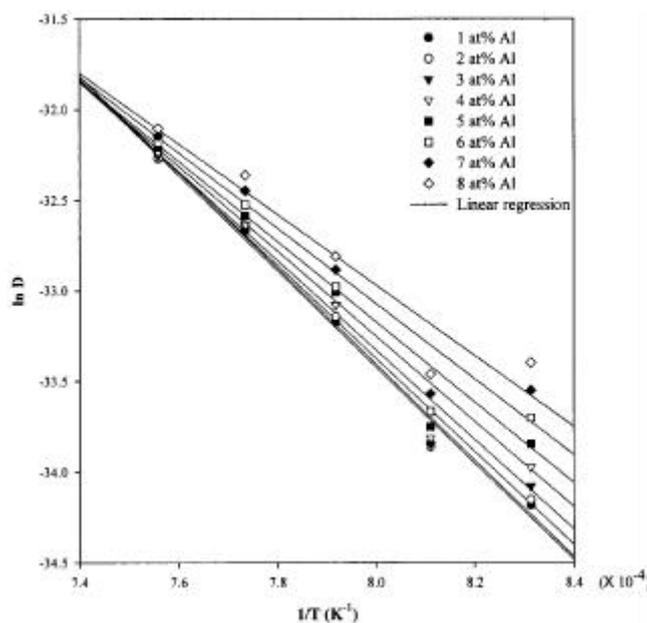
Concentration, Al (at%)	Thermodynamic interdiffusion coefficient, $\tilde{D}_{(m)}$ ($\times 10^{-15} \text{m}^2/\text{s}$)				
	1203 K	1233 K	1263 K	1293 K	1323 K
1	1.43	2.00	3.91	6.49	9.66
2	1.47	1.97	4.04	6.67	9.71
3	1.58	1.99	4.29	6.50	9.83
4	1.76	2.07	4.30	6.71	10.01
5	2.00	2.20	4.61	7.04	10.27
6	2.31	2.39	4.75	7.50	10.58
7	2.69	2.63	5.23	8.10	10.97
8	3.13	2.94	5.63	8.82	11.42

Table 2. The values of the constants X , Y and Z in the quadratic relation, $\tilde{D}_{(m)} = X + Y C_{\text{Al}} + Z C_{\text{Al}}^2$ for the composition dependence of the thermodynamic interdiffusion coefficients in *b*-Zr(Al) phase.

Temperature (K)	$X \times 10^{15}$ (m^2s^{-1})	$Y \times 10^{17}$ ($\text{m}^2\text{s}^{-1} \text{at}\%^{-1}$)	$Z \times 10^{17}$ ($\text{m}^2\text{s}^{-1} \text{at}\%^{-2}$)
1203	1.449 (± 0.045)	-5.559 (± 3.57)	3.317 (± 0.44)
1233	2.094 (± 0.061)	-11.90 (± 3.63)	2.802 (± 0.40)
1263	4.763 (± 0.800)	-256.0 (± 86.8)	49.94 (± 11.8)
1293	6.671 (± 0.010)	-25.07 (± 7.70)	6.493 (± 1.15)
1323	9.671 (± 0.003)	-4.726 (± 0.24)	3.325 (± 0.04)

4.3 Thermodynamic intrinsic diffusion coefficient

The marker plane can be located in the diffusion zone from the chemical composition of regions adjacent to the tungsten markers. Figure 1 shows the location of the markers in the diffusion couple annealed at 1293 K. It is noticed from figure 1 that the markers migrate towards the pure Zr side. The migration of the markers can be attributed to Kirkendall effect and hence the intrinsic diffusivity of Zr is higher than Al. The velocity of the markers was calculated from the displacement of the markers from their original positions and the time of annealing. It was further observed that in all the diffusion couples, the composition of the marker plane is about 2 at% Al. The values of the thermodynamic intrinsic diffusion coefficients of Zr and Al were determined using (10) and (11) for all the diffusion couples. The values are given in table 4. It can be seen from the table that the values of diffusion coefficients of Zr ($D_{\text{Zr}(m)}$) is higher than that of Al ($D_{\text{Al}(m)}$) in the whole temperature range. This difference in the diffusion coefficients leads to Kirkendall effect in the diffusion couples. It is worth noting that the values of $D_{\text{Zr}(m)}$ and $D_{\text{Al}(m)}$ are within one order of magnitude. This implies that the diffusion takes place by vacancy exchange mechanism and both types of atoms, Zr and Al, share the same sites and exchange position with vacancies (Shewmon 1989).


Figure 3. Temperature dependence of thermodynamic interdiffusion coefficients at various concentrations of Al.

Since the composition of the marker locations in all the couples is roughly same, an attempt was made to determine the temperature dependence of the thermodynamic intrinsic diffusion coefficients. Figure 5 shows a plot of

Table 3. The values of activation energy ($Q_{(m)}$) and frequency factor, D_0 , for thermodynamic interdiffusion at various compositions of the b -Zr(Al) solid solution phase.

Concentration, Al (at%)	Activation energy, Q (kJ/mol)	Frequency factor, D_0 ($\times 10^{-6}$) (m^2/s)
1	220.46	4.98
2	220.28	4.97
3	213.32	2.63
4	205.13	1.25
5	195.23	0.52
6	184.25	0.19
7	173.17	0.08
8	162.24	0.03

Table 4. The values of thermodynamic intrinsic diffusion coefficients of Zr and Al in the b -Zr(Al) solid solution phase at various temperatures.

Temperature (K)	$D_{Al(m)} \times 10^{-15}$ (m^2/s)	$D_{Zr(m)} \times 10^{-15}$ (m^2/s)
1203	1.23	2.44
1233	1.95	4.12
1263	3.22	5.48
1293	5.97	8.37
1323	8.50	12.59

$\ln D_{(m)}$ against the reciprocal of temperature. The data points for both $D_{Zr(m)}$ and $D_{Al(m)}$ were fitted with straight lines using least square method. The values of the activation energy, $Q_{(m)}$, and frequency factor, $D_{0(m)}$, for diffusion of Zr and Al were determined from the slope and intercept of these straight lines, the values for Al being $D_{0(m)} = 4.146 \times 10^{-6} m^2/s$, $Q_{(m)} = 219.74$ kJ/mol and for Zr, $D_{0(m)} = 1.128 \times 10^{-7} m^2/s$, $Q_{(m)} = 176.27$ kJ/mol. The activation energy for Zr diffusion is lower than that of Al. This indicates a faster diffusion of Zr than Al, which is in fact observed from the direction of marker movements.

It can be shown that the thermodynamic intrinsic diffusion coefficient is equal to tracer diffusion coefficient (Garg *et al* 1999). Therefore, the tracer diffusion coefficient in a homogeneous alloy of composition equal to that at the marker location can be directly determined without carrying out experiments with radioactive tracers. Hence, the values of thermodynamic intrinsic diffusion coefficient shown in table 4 are also equal to the tracer diffusion coefficients of Al and Zr atoms in a homogeneous alloy of Zr–2 at% Al. The present authors had determined the activation energy for impurity diffusion of Al in b -Zr at infinite dilution (Laik *et al* 2002). It is expected that the activation energy ($Q_{(m)}$) for thermodynamic intrinsic diffusion coefficient (or tracer diffusion coefficient) of Al in Zr–2 at% Al alloy should be nearly equal to that for impurity diffusion coefficient of Al in b -Zr. The value of $Q_{(m)}$ for $D_{(m)Al}$ is 219.74 kJ/mol compared to 220.08 kJ/mol for impurity diffusion of Al in b -Zr. Thus, the values of activation energy for tracer diffusion can be

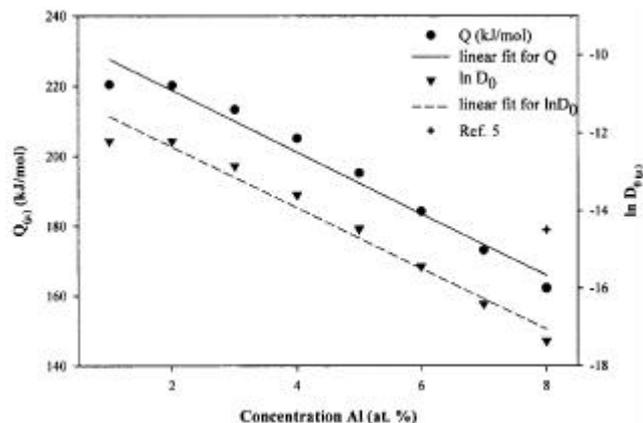


Figure 4. Composition dependence of activation energy (Q) and frequency factor (D_0) for thermodynamic interdiffusion coefficient.

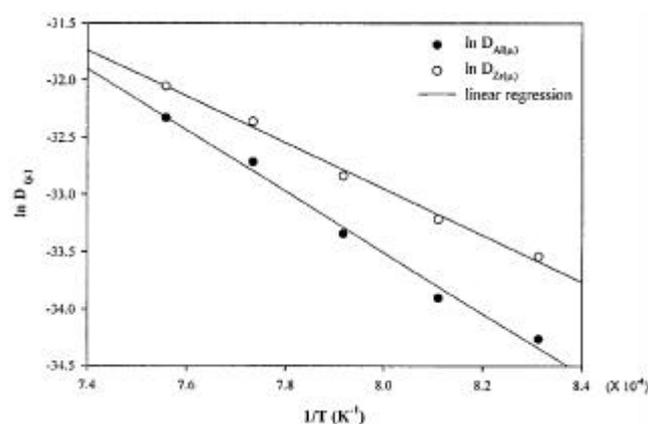


Figure 5. Temperature dependence of the thermodynamic intrinsic diffusion coefficient of Al and Zr.

determined using the present thermodynamic approach, even without carrying out actual radioactive tracer experiments.

5. Conclusions

The diffusion behaviour of Al and Zr in the b -Zr(Al) solid solution was analysed using a thermodynamic approach. In the Zr–Al system it is shown that the driving force for diffusion in a binary system is not always correctly represented by the concentration gradient, as is generally assumed. The thermodynamic interdiffusion coefficients in b -Zr(Al) solid solution phase evaluated from the single phase diffusion couple experiments bear a quadratic relation with Al concentration. The values of the frequency factor ($\tilde{D}_{0(m)}$) and the activation energy ($\tilde{Q}_{(m)}$) for interdiffusion show a linear decrease with an increase in Al concentration. The values of the thermodynamic intrinsic diffusion coefficients of Zr and Al show that Zr diffuses faster than Al. These diffusion coefficients also follow Arrhenius type of temperature dependence. The values of

activation energy for tracer diffusion can be determined using the present thermodynamic approach, even without carrying out actual radioactive tracer experiments.

Acknowledgements

The authors express their gratitude to Dr P K De, Head, Materials Science Division and Dr S Banerjee, Director, Bhabha Atomic Research Centre, Mumbai, for their keen interest in the work. The help extended by Mr P S Gawde in carrying out the experiments is gratefully acknowledged.

References

- Boltzmann L 1894 *Wiedemanns Ann. Physik* **53** 959
Brown A M and Ashby M F 1980 *Acta Met.* **28** 1085
Darken L S 1948 *Trans. AIME* **175** 184
Garg S P, Kale G B, Patil R V and Kundu T 1999 *Intermetallics* **7** 901
Gukelberger A and Steeb S 1978 *Z. Metallkd.* **69** 255
Kidson G V and Miller G D 1964 *J. Nucl. Mater.* **12** 61
Kim S and Chang Y A 2000 *Metall. Mater. Trans.* **A31** 1519
Laik A, Bhanumurthy K and Kale G B 2002 *J. Nucl. Mater.* **305** 124
Laik A, Bhanumurthy K and Kale G B 2004 *Intermetallics* **12** 69
Matano C 1933 *Jpn. J. Phys.* **8** 109
Peruzzi A and Abraita J P 1990 *Alloy binary phase diagrams* (ed) T B Massalski (Ohio: ASM International) 2nd edn. p. 241
Pouchou J L and Pichoir F 1985 *Microbeam analysis* (California: San Francisco Press)
Saunders N and Miodownik A P 1998 *Calphad-calculation of phase diagrams—A comprehensive guide* (New York: Pergamon)
Saunders N and Rivlin V G 1986 *Mater. Sci. & Technol.* **2** 521
Schulson E M 1975 *J. Nucl. Mater.* **57** 98
Schulson E M 1994 *Intermetallic compounds* (eds) J H Westbrook and R L Fleischer (New York: John Wiley) **Vol. 2**, p. 133
Shewmon P G 1989 *Diffusion in solids* (Pennsylvania: The Minerals, Metals and Materials Society) 2nd edn.