Chemical Diffusion in Titanium-Molybdenum System

G. B. Kale and R. V. Patil

Metallurgy Division, Bhabha Atomic Research Centre, Bombay 400 085, India

The chemical diffusion in titanium-molybdenum system has been studied in the temperature range of 1200 to 1500 K using pure metal diffusion couples. The concentration penetration profiles have been established by employing an electron probe microanalyser. The chemical diffusion coefficients have been evaluated following the Boltzmann-Matano method. The concentration and temperature dependence of chemical diffusion coefficients have been established. The expression for the chemical diffusion coefficient for a given composition (C_{Ti}) and temperature (T) can be written as

$$\tilde{D}_{(C_{Ti})} = 2.75 \times 10^{-5} \exp(-4.14C_{Ti}) \exp[-(212.647 + 68.16C_{Ti}) \text{ kJ} \cdot \text{mol}^{-1} / RT], \quad \text{m}^2 \cdot \text{s}^{-1}.$$

The data have been rationalised on the basis of the Vignes-Birchenall relationship.

(Received February 17, 1994)

Keywords: chemical diffusion, Boltzmann-Matano method, Vignes-Birchenall relation

I. Introduction

Diffusion in titanium and titanium alloys in bcc phase has been reported to be anomalous⁽¹⁾. Several authors have reported impurity diffusion of transition metals like copper⁽²⁾⁽³⁾, palladium⁽²⁾, silver⁽³⁾, gold⁽⁴⁾ in titanium recently. The impurity diffusion data do not yield any direct evidence for rate controlling mechanism. Inter-diffusion studies on the other hand do exhibit features like the Kirkendall effect which is considered to be the manifestation of vacancy mechanism in substitutional alloys. As such, chemical diffusion studies involving anomalous metals could be quite relevant. The chemical diffusion in various titanium based systems like Ti-V⁽⁵⁾⁻⁽⁸⁾, Ti-Fe⁽⁹⁾, Ti-Nb⁽¹⁾, Ti-Zr⁽⁵⁾⁽¹⁰⁾, Ti-U⁽¹¹⁾, Ti-Mo⁽¹⁾⁽¹²⁾ has been studied. As far as titanium-molybdenum system is concerned only data available are the work by Gurney⁽¹²⁾ who has studied chemical diffusion in titanium molybdenum system and has reported activation energy of diffusion and pre-exponential factor D_0 in the temperature range of 1483 to 1873 K. Moreover, these parameters have been evaluated from only three temperature data points. In view of the limited data available and as the diffusion anomaly is observed in the lower temperature region of the beta phase, the chemical diffusion in titanium-molybdenum system has been carried out in the temperature range between 1200 and 1500 K.

II. Experimental Procedure

The studies involved several steps like preparation of sandwich type diffusion couples, diffusion annealing and determination of concentration penetration profiles. The diffusion couples were made from pure molybdenum (>99.9%) and electron beam melted iodide grade titanium as reported elsewhere⁽¹³⁾. The diffusion couples were then sealed in vacuum (better than 10^{-3} Pa) in silica capsule and diffusion annealed in pre-heated platinum resistance

furnace controlled to ± 1 K with the help of proportional controller in the temperature range of 1200 to 1500 K for durations of 5 to 150 ks. The couples were then polished to a metallographic grade and analysed with the help of Camebax electron-probe microanalyser operating at 15 keV to establish the concentration penetration profiles of titanium and molybdenum across the diffusion zone. The intensities of titanium and molybdenum were measured by diffracting MoL_α on PET and TiK_α on LiF crystals. The raw intensities were corrected for ZAF correction by employing computer software⁽¹⁴⁾ and finally converted to atomic fractions to establish the concentration penetration profiles. As titanium-molybdenum system forms complete solid solution over entire range of compositions in the β phase, the concentration profiles were analysed in accordance with the Boltzmann-Matano relation

$$\tilde{D}(C') = (-1/2t)(dx/dC)_C \int_0^{C'} x dC \quad (1)$$

to yield chemical diffusion coefficients $\tilde{D}(C')$ at concentration C' . For this purpose, the Matano interface was established and designated as the origin of x axis. The values of slope $(dC/dx)_C$ and integral $\int x dC$ were evaluated from mathematically represented concentration profiles by numerical differentiation and integration respectively for accuracies better than in earlier paper⁽¹³⁾. The flux of both the components at any plane in the diffusion zone was found to satisfy conditions that $\Sigma J=0$ and $\Sigma dC/dX=0$ indicating that there is no molar volume change involved and hence the Boltzmann-Matano method can be applied for this system.

III. Results and Discussions

1. Concentration penetration profiles

The typical concentration penetration profile for the couple annealed at 1199 K for 149.4 ks is shown in Fig. 1. The nature of the profile is typical of the solid solution

Fig. 1 Concentration profile for Ti in Ti-Mo diffusion couple.

type. The profile is asymmetric about the Matano interface and shows a long tail on the titanium side. This indicates that diffusion is faster in titanium as compared to that in molybdenum.

2. Chemical diffusion coefficients

The chemical diffusion coefficients at various concentrations and temperatures are given in Table 1. The chemical diffusion coefficients are in the range of 10^{-14} to $10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$. The diffusion coefficients vary by 2 orders of magnitude from pure molybdenum to pure titanium.

3. Temperature dependence of $\tilde{D}$

The $\ln \tilde{D}$ values have been plotted against the reciprocal of the temperature of the diffusion anneal to establish the temperature dependence of $\tilde{D}$. The typical $\ln \tilde{D}$ vs. T^{-1} plots are shown in Fig 2. Temperature dependence of diffusion coefficients can be described by the Arrhenius expression of the type

$$\tilde{D} = \tilde{D}_0 \exp(-\tilde{Q}/RT). \quad (2)$$

Table 1 Chemical diffusion coefficients at various compositions and temperatures.

Temp. K C_{Ti} (at%)	1199	1217	1330	1364	1479	1518
	$\tilde{D} \times 10^{14} / \text{m}^2 \cdot \text{s}^{-1}$					
10	2.3	3.2	13.0	22.0	80.0	170.0
20	2.5	4.2	19.0	22.0	110.0	200.0
30	3.7	4.3	20.0	23.0	120.0	205.0
40	4.0	4.7	23.0	30.0	130.0	210.0
50	5.0	6.0	29.0	43.0	150.0	220.0
60	6.4	7.5	36.0	50.0	180.0	280.0
70	8.9	10.3	45.0	62.0	210.0	330.0
80	17.0	18.2	70.0	96.0	270.0	390.0
90	21.0	24.2	92.0	122.0	370.0	550.0

Fig. 2 $\ln \tilde{D}$ vs $1/T$ plot for Ti-Mo system.

The values of the activation energy $\tilde{Q}$ and frequency factor $\tilde{D}_0$ for interdiffusion have been evaluated from the slopes and intercepts by linearly fitting $\ln \tilde{D}$ vs reciprocal of the temperature of the diffusion anneal ($1/T$) using least mean square method. The values of $\tilde{Q}$ and $\tilde{D}_0$ along with their standard deviations are listed in Table 2. The activation energies and frequency factors for interdiffusion coefficients in titanium-molybdenum system for higher temperature range⁽¹²⁾ of 1573 to 1873 K are also tabulated in Table 2 for comparison. It is seen from the table that activation energy values in two different temperature ranges are comparable only for alloys containing up to 40% titanium. As the concentration of titanium increases beyond 40%, the difference in the two activation energies also increases.

The activation energy for chemical diffusion $\tilde{Q}_{AB}$ can be expressed as a function of the activation energies of diffusion coefficients of A in B, $\tilde{Q}_{A(B)}$ and that of B in A, $\tilde{Q}_{B(A)}$ at infinite dilutions by equation

$$\tilde{Q}_{AB} = N_B \tilde{Q}_{A(B)} + N_A \tilde{Q}_{B(A)} + k\Delta T_s^{AB} \quad (3)$$

Table 2 Activation energy ($\tilde{Q}$) and frequency factor, ($\tilde{D}_0$) values at various compositions.

C_{Ti} (at%)	$\tilde{D}_0 / \text{m}^2 \cdot \text{s}^{-1}$	$\tilde{Q} / \text{kJ} \cdot \text{mol}^{-1}$ Present work	Ref. (12)
10	227.0^{+360}_{-140}	207.2 ± 7.5	196.6
20	81.3^{+120}_{-48}	194.5 ± 7.2	196.6
30	100^{+150}_{-60}	192.5 ± 7.4	209.2
40	44.0^{+60}_{-25}	185.2 ± 6.8	217.6
50	31.0^{+40}_{-17}	179.1 ± 6.5	234.3
60	33.0^{+42}_{-18}	177.5 ± 6.5	255.2
70	19.0^{+22}_{-10}	168.9 ± 6.2	263.6
80	4.9^{+5}_{-2}	148.7 ± 5.4	217.6
90	9.2^{+10}_{-5}	152.8 ± 5.6	219.2

where N_A and N_B are atomic fractions of A and B and ΔT_s^{AB} is the difference between the solidus temperature and the temperature which would be computed if the solidus temperature varied linearly with the composition and k is the structure dependent constant⁽¹⁵⁾.

The activation energy for impurity diffusion can be related to the melting point of the solvent by expressions $Q_{A(B)} = k_B T_B$ and $Q_{B(A)} = k_A T_A$ where k_A , k_B and T_A , T_B are proportionality constants and melting points of elements A and B, respectively. The proportionality constants k_A and k_B have values of 34 for normal metals and approximately 17 for anomalous metals. The eq. (3) can be re-written as

$$\bar{Q}_{AB} = N_A(k_A T_A - k_B T_B) + k_B T_B + k \Delta T_s^{AB}. \quad (4)$$

If element A is anomalous and element B is normal then k_A (≈ 17) is less than k_B (≈ 34) and hence first term in eq. (4) will decrease with increase in N_A . In the present case of titanium-molybdenum system, titanium is known to behave anomalously in the lower β temperature range. There is not much variation in the activation energies for interdiffusion (196 to 263 kJ·mol⁻¹) in the high temperature range⁽¹²⁾. However, in the lower temperature range $\bar{Q}_{AB}$ decreases with increase in titanium content (Table 2). The difference in the activation energies in the two temperature ranges is plotted against the titanium content in Fig. 3. It is seen that the difference increases with increase in titanium content as per eq. (4). The increasing difference in the activation energies in the two temperature ranges indicates that the chemical diffusion is also anomalous for the alloys containing higher content of anomalous element.

4. Concentration dependence of $\bar{D}$

The log values of interdiffusion coefficients for titanium-molybdenum system are plotted against concentration of titanium in Fig. 4 to establish the concentration dependence of $\bar{D}$. It shows that $\ln \bar{D}$ increases more or less linearly with increase in titanium content.

Fig. 3 Concentration dependence of $\bar{Q}$.

Fig. 4 Concentration dependence of $\bar{D}$.

Melting point of the alloy in a binary system and hence reduced temperature T/T_s (where T is the temperature of the diffusion anneal and T_s is the solidus temperature of the alloy at certain composition) changes with the composition, as such the interdiffusion coefficient $\bar{D}$ should change with composition at a given diffusion annealing temperature. LeClaire⁽¹⁶⁾ has pointed out that an increase in the concentration of the solute increases $\bar{D}$ if it is accompanied by a decrease in the melting point of the solvent and vice versa. In the titanium-molybdenum system, solidus temperature decreases continuously with increase in titanium content and hence $\bar{D}$ increases with increase in titanium content following the solidus line monotonically.

The activation energy $\bar{Q}$ and frequency factor $\bar{D}_0$ are plotted against the concentration of titanium to establish their concentration dependence in Figs. 5 and 6. The activation energy $\bar{Q}$ and frequency factor $\bar{D}_0$ decrease linearly with increase in concentration of titanium. The concentration dependence of $\bar{D}_0$ and $\bar{Q}$ can be expressed by the equation of the type

$$\ln \bar{D}_0 = \ln A + BC_{Ti} \quad (5)$$

$$\bar{Q} = M + NC_{Ti} \quad (6)$$

where A , B , M , N are constants and C_{Ti} is the concentration of titanium. The values of A and M have been evaluated from the intercepts and those of B and N from the slopes of the plots in Figs. 5 and 6 by using least mean square method. The frequency factor $\bar{D}_0$ and activation energy $\bar{Q}$ can be written as

$$\bar{D}_0 = 2.75 \times 10^{-5} \exp(-4.14C_{Ti}) \quad (7)$$

Fig. 5 Concentration dependence of $\tilde{D}_0$. Fig. 6 Concentration dependence of $\bar{Q}$.

$$\bar{Q} = (212.647 - 68.16C_{Ti})10^3. \quad (8)$$

The concentration dependence of the interdiffusion coefficient $\tilde{D}$ at concentration C_{Ti} of titanium is obtained by combining eqs. (7) and (8) as

$$\begin{aligned} \tilde{D}_{(C)} = & 2.75 \times 10^{-5} \exp(-4.14C_{Ti}) \\ & \times \exp[-(212.647 + 68.16C_{Ti}) \\ & \text{kJ} \cdot \text{mol}^{-1}/RT], \text{ m}^2 \cdot \text{s}^{-1} \end{aligned} \quad (9)$$

5. Vignes-Birchenall relationship

Vignes and Birchenall⁽¹⁵⁾ have shown that for a binary system forming continuous solid solution over the entire range of composition, chemical diffusion coefficient $\tilde{D}$ can be related to limiting values of chemical diffusion coefficients and deviation of solidus temperature from linearity with the following relation

$$\tilde{D} = (D_{AB}^0)^{N_A} \times (D_{BA}^0)^{N_B} \times (\alpha_{AB}) \exp(-k\Delta T_s^{AB}/RT) \quad (10)$$

where α_{AB} is the thermodynamic factor. D_{AB}^0 and D_{BA}^0 are limiting values of interdiffusion coefficients and ΔT_s^{AB} is the difference between the actual solidus temperature and the solidus temperature if it would have varied linearly with the composition in a binary system of elements A and B. k is the structure dependent constant and is equal to 16 for fcc⁽¹⁵⁾ and 22 for bcc⁽¹⁷⁾ system, respectively. According to these authors if the above relation is valid then $\ln D_{AB}$ which is given as

$$\ln D_{AB} = \ln(\tilde{D}/\alpha_{AB}) + k\Delta T_s^{AB}/RT \quad (11)$$

should vary linearly with the composition.

Hoch and Viswanathan⁽¹⁸⁾ have measured the activities of the titanium-molybdenum system using a triple Knudsen effusion cell, and have given the relation between the activity coefficient, the concentration of titanium and the temperature. Values of the thermodynamic factor α_{AB} ($=1 + d \ln \gamma_A / d \ln N_A$) were evaluated from the above relationship for the whole range of composition at 1199 K. The values of $\ln D_{AB}$ as evaluated from eq. (11) have been plotted against the composition of titanium in Fig. 7. The figure shows linear variation of $\ln D_{AB}$ with concentration and indicates that Vignes-Birchenall relationship is valid for the titanium-molybdenum system.

Vignes-Birchenall relationship is based on the fact that the activation energy for interdiffusion is a function of activation energies of diffusing components into each other and deviation of solidus temperature from the linearity. Diffusion of molybdenum in titanium and self-diffusion

Fig. 7 Concentration dependence of $\tilde{D}$ and D_{AB} in Ti-Mo system.

of titanium is anomalous with respect to the activation energies which are lower than the normal vacancy diffusion values, i.e. lower than $34 T_m$. Validity of Vignes-Birchenall relationship in this system shows that the anomaly in diffusion behaviour in titanium systems may not be due to extrinsic factors like dislocations or grain boundaries. As data could be analysed on the basis of relationship with bulk properties like solidus temperature which are not influenced by these extrinsic factors but it seems to be the intrinsic property of bcc transition metals like titanium, zirconium, hafnium etc.⁽⁶⁾

6. Interrelation between $\tilde{D}_0$ and $\tilde{Q}$

Frequency factor $\tilde{D}_0$ and activation energy $\tilde{Q}$ are the two parameters which govern the mechanism as well as the rate of diffusion. The linear relationship between $\tilde{D}_0$ and $\tilde{Q}$ depicting the internal consistency of diffusion parameters have been developed for self-diffusion⁽¹⁹⁾⁽²⁰⁾ as well as for impurity diffusion⁽²¹⁾. In analogy with the self and impurity diffusion data a linear relation is found to exist even for interdiffusion⁽²²⁾.

The values of $\ln \tilde{D}_0$ have been plotted against $\tilde{Q}$ in Fig. 8. The plot is linear as described by the relation

$$\ln \tilde{D}_0 = a\tilde{Q} + b. \quad (12)$$

The values of slope 'a' and intercept 'b' are found to be equal to 0.060 and -23.55 respectively. These values are comparable to those for other systems like titanium-vanadium⁽²²⁾, iron-vanadium⁽²³⁾, iron-cobalt⁽²⁴⁾, and gold-nickel⁽²⁵⁾ (Table 3). It may be concluded that diffusion mechanism in this system may be identical with those for other bcc or fcc systems where it is established that diffusion takes place by vacancy mechanism.

Fig. 8 $\ln \tilde{D}_0$ vs $\tilde{Q}$ plot for Ti-Mo system.

Table 3 Linear relationship between $\ln \tilde{D}_0$, $\text{m}^2 \cdot \text{s}^{-1}$ and $\tilde{Q}$, $\text{kJ} \cdot \text{mol}^{-1}$, for interdiffusion in various systems.

System	Structure	<i>a</i>	$-b$	Reference
Ti-V	bcc	0.071	26.29	(22)
Fe-V	bcc	0.093	30.21	(23)
Ti-Mo	bcc	0.060	23.55	Present work
Fe-Co	fcc	0.074	30.21	(24)
Au-Ni	fcc	0.093	30.21	(25)

V. Conclusions

(1) The concentration dependence of interdiffusion coefficients is more or less exponential.

(2) The interdiffusion coefficient at a given temperature and concentration (C_{Ti}) can be written as

$$\begin{aligned} \tilde{D}_{(C_{Ti})} = & 2.75 \times 10^{-5} \exp(-4.14C_{Ti}) \\ & \times \exp[-(212.647 - 68.16C_{Ti}) \\ & \text{kJ} \cdot \text{mol}^{-1} / RT], \text{m}^2 \cdot \text{s}^{-1}. \end{aligned}$$

(3) The activation energy in low temperature range is less than that in high temperature range for compositions beyond 40 at% of titanium indicating that there is an anomaly in the temperature dependence of interdiffusion coefficient for higher content of anomalous element.

(4) Vignes-Birchenall relationship is valid for titanium-molybdenum system. The diffusion anomaly observed may be attributed to intrinsic properties of the system.

Acknowledgements

The authors wish to thank Dr. S. Banerjee, Head, Metallurgy Division and Dr. P. Mukhopadhyaya, Head, Physical Metallurgy Section, for their keen interest and permission to publish this paper.

REFERENCES

- (1) A. D. LeClairs: *Diffusion in BCC Metals*, Metals Park Ohio, American Institute for Metals, (1965), p. 3.
- (2) S. Y. Lee, Y. Iijima, O. Taguchi and K. Hirano: *J. Japan Inst. Metals*, **54** (1990), 502.
- (3) S. Y. Lee, Y. Iijima, O. Taguchi and K. Hirano: *Trans. JIM*, **32** (1991), 451.
- (4) S. Y. Lee, Y. Iijima and K. Hirano: *Defect and Diffusion Forum*, **95-98** (1993), 623.
- (5) R. P. Elliot: US Report AD 290336, (1962).
- (6) G. B. Kale, S. K. Khera and G. P. Tiwari: *Trans. Indian Inst. of Metals*, **29** (1976), 422.
- (7) D. Goold: *J. Inst. Metals*, **88** (1960), 444.
- (8) A. Brunch and S. Steeb: *High Temp. High Pressure*, **6** (1974), 155.
- (9) G. B. Kale, S. K. Khera and G. P. Tiwari: *Proc. Int. Conf. of Ti-80*, Sendai, Japan (1980), p. 549.
- (10) A. Brunch and S. Steeb: *Z. Naturforsch.*, **A 29** (1974), 1319.
- (11) Y. Adda and J. Philibert: *Acta Met.*, **8** (1960), 700.
- (12) F. J. Gurney: Master Thesis, Air Force Inst. of Technology, USA, (1964).
- (13) G. B. Kale, K. Bhanumurthy, S. K. Khera and M. K. Asundi: *Mater. Trans., JIM*, **32** (1991), 1034.
- (14) G. B. Kale: Ph. D. Thesis, University of Bombay, Bombay, India (1987).

- (15) A. Vignes and G. E. Birchenall: *Acta Met.*, **16** (1968), 1117.
- (16) A. D. LeClaire: *Progress in Metal Physics*, Pergamon Press Inc., N. Y. Butterworth, (1949), p. 306.
- (17) Y. E. Ugaste and Y. A. Zaykin: *Fiz. Metall. Metalloved*, **40** (1975), 567.
- (18) M. Hoch and R. Viswanathan: *Met. Trans.*, **2** (1971), 2765.
- (19) C. Zener: *J. Appl. Phys.*, **22** (1951), 372.
- (20) R. A. Swalin: *J. Appl. Phys.*, **27** (1956), 554.
- (21) J. Pelleg: *Acta Met.*, **14** (1966), 229.
- (22) G. B. Kale: M. Sc. Tech. Thesis, University of Bombay, Bombay, India, (1979).
- (23) R. E. Hanneman, R. E. Ogilvie and H. C. Gatton: *Trans. Met. Soc. AIME*, **233** (1965), 691.
- (24) K. Hirano, Y. Iijima, K. Araki and H. Homma: *Trans. ISIJ, Japan*, **17** (1977), 194.
- (25) J. E. Reynolds, B. L. Averbash and M. Cohen with an Appendix by J. E. Hilliard: *Acta Met.*, **5** (1957), 29.