INTERDIFFUSION IN Ti-V ALLOYS

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Introduction

Many problems on the anomalous diffusion behaviour in bcc metals have been discussed at the ASM seminor held in 1964[1], however, the diffusion mechanism of these metals remained to be resolved at that time. In the subsequent fifteen years, new experimental techniques, such as heat treatment in ultra high vacuum, chemical- and sputter-microsectioning and semiconductor radioactivity detector, have been developed. Recently, using these new powerful techniques and very high purity specimens, the diffusion studies on the bcc metals have been carried out actively[2]. In 1971, Neumann[3] has compiled the diffusion data on the bcc metals and proposed that only the monovacancy-divacancy mechanism operates in all these bcc metals. Recent studies have revealed that the diffusion occurs by the particular mechanism for each metal[2]. The diffusion in the anomalous bcc metals is characterized by smaller values of the frequency factor and activation energy than the normal metals. The curved Arrhenius plot of self-diffusion data in vanadium has been explained by a superposition of the vacancy mechanism and the Kidson mechanism [4,5] in which the extrinsic vacancies introduced by impurities enhance the diffusion in the lower temperature. There is now dispute on the self-diffusion mechanism in β-titanium[6]. The increased diffusivity in the lower temperature range has been attributed to dislocations induced by phase transformation[7], single highly relaxed vacancy like defect[8], ω embryo[9] and etc. To examine the diffusion mechanism in the anomalous bcc metals, diffusion studies have been extended to binary alloys, such as Ti-V[10] and Ti-Nb[11] alloys. V and Nb are β phase stabilizers. Both the Ti-V and Ti-Nb systems form complete solid solutions. Further, both the systems are interesting because of the ability to form a metastable ω phase. Temperature dependence of self-diffusion coefficients of both components in Ti-V alloys has been found to show curved Arrhenius plots over the whole composition range[10]. Another interesting result on the self-diffusion in Ti-V alloys[10] is that the order of magnitude in the self-diffusion coefficients of the components is reversed between Ti-rich alloy and V-rich alloy. The Ti-V system is the only binary alloy which has been reported to show this reversal phenomenon in the magnitude of diffusion coefficients in a single phase. Interdiffusion in Ti-V alloys has been studied by Goold[12] and Carlson[13,14]. Goold has shown that the intrinsic diffusion coefficient of vanadium is much larger than that of titanium in Ti-3.5 at% V alloy at 1523 K. Carlson has studied the vacancy flow effect by using many incremental couples and shown that the experimental results reflect a greater influence of the vacancy flow phenomenon on the intrinsic flux of each component than that predicted on the basis of the random alloy model[15].

In the present work, an attempt is made to examine the Arrhenius relationship of the interdiffusion coefficient in the whole concentration range in Ti-V alloys. The interdiffusion coefficient for Ti-V alloys over the wide temperature range between 1223 and 1787 K has been determined using pure metal couples. The concentration and temperature dependence of the interdiffusion coefficient has been discussed based on Manning's theory[15] and Vignes and Birchenall's empirical relation[16].

Experimental Procedure

Pure titanium discs, 9 mm in diameter and 5 mm in thickness, were machined from a rod supplied by Kobe Steel Ltd. Pure vanadium discs of the same dimension were machined from a rod supplied by Showa Denko Co. Chemical analysis of the metals is shown in Table 1. To cause grain growth, the Ti and V discs were annealed at 1573 K and 1173 K, respectively, for 1 h in vacuum.

Table 1 Chemical analysis of the specimens

Specimen	Ti	V
Element	wt%	wt%
C	0.009	0.012
O	0.045	0.15
N	0.0031	0.027
H	0.001	0.0016
Cu		0.016
Fe	0.009	0.25
Si	0.019	
Ti	balance	
V		balance

The resultant grain sizes of both metals were large enough to neglect the effect of grain boundary diffusion. One flat face of each specimen was polished by abrasive papers and buff. Fine alumina powder of about 10 μm diameter was used as the Kirkendall marker. It was dispersed in ethyl alcohol and a few drops of it were put on the polished surface of the vanadium disc. After evaporation of ethyl alcohol, the titanium disc was put on the vanadium disc to make a couple and then the couple was set between copper blocks in the clamp made of heat resistant steel and pressed tightly by screws. The couple was diffusion-welded by heating at 1023 K for 1 h in vacuum. The diffusion width produced by this treatment was negligible compared with that obtained by the diffusion anneal.

The diffusion couple was annealed in the temperature range between 1223 and 1787 K. For the diffusion below 1516 K, the couple was wrapped with pure titanium foil and sealed in a quartz tube evacuated to 1.3 mPa. The titanium foil prevented the couple from oxidizing and reacting with the quartz tube. The couple was annealed in electric furnaces controlled within ±1 K. For the diffusion above 1573 K, the couple was put into a pure titanium capsule, 12 mm in diameter and 35 mm in depth, and annealed in the furnace with molybdenum heating element in a vacuum of 0.27∿1.3 mPa. The temperature of the furnace was controlled within ±2 K at 1573 K and ±5 K at 1787 K, respectively. After the diffusion anneal, the couple was moved away from the heating element and cooled rapidly by the blow of helium gas passed through liquid nitrogen cold trap. The diffusion which took during heating up and cooling down was negligible and the correction for diffusion time was not necessary.

To determine the concentration-penetration curve of the diffused couple by an electron probe microanalyzer(JXA-3A type), the couple was cut parallel to the diffusion direction, and the cut surface was ground on abrasive papers and buff. The operating conditions of the microanalyzer were as follows: electron accelerating voltage, 20 kV;take-off angle of radiation, 20 deg; specimen current for pure V, 0.15 μA; X-ray analyzed, V-Kα. To determine the penetration profile the concentration of about 100 locations in a diffused zone was measured by point counting method. The scanning was repeated three times for each couple. The relative intensity of the X-ray radiation V-Kα to pure vanadium was converted into concentration using the calibration curve shown in Fig. 1 obtained by using the standard specimens. The curve was consistent very well with the curve calculated by Philibert's method[17] of the obsorption effect modified by Duncumb and Shielas[18].

The interdiffusion coefficient was determined as a function of concentration at intervals of 2.5 at% V by Matano's method[19]. It is noted that the molar volume of Ti-V alloys is nearly proportional to the mole fraction of vanadium[20] and hence the partial molar volume of each component in the alloy is constant and independent of concentration. As a result, the molar concentration of vanadium per cubic meter can be used as the concentration without any correction for the variation of volume with composition[21]. Numerical calculations for Matano's analysis were carried out using Electronic Computer(IBM 1620).

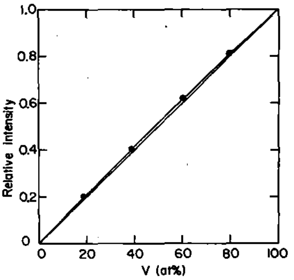

Fig.1 Standard calibration curve for electron probe microanalysis of Ti-V alloys.

Results and Discussion

1. Concentration dependence of interdiffusion coefficient

A typical concentration-penetration profile in the diffused couple is shown in Fig. 2. The concentration gradient is significantly steeper in the vanadium rich zone and much slower in the titanium rich zone. As shown in Fig. 3, the interdiffusion coefficient($\tilde{D}$) decreases gradually with vanadium

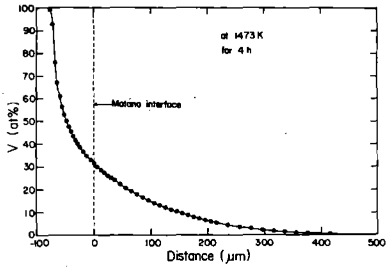

Fig.2 Concentration-penetration curve in the specimen diffused at 1473 K for 4 h.

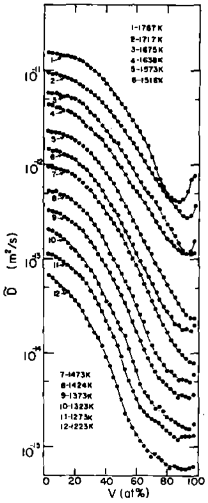

Fig.3 Concentration dependence of interdiffusion coefficient($\widehat{D}$) in Ti-V alloys.

concentration up to 30 at% V and then decreases more rapidly with further increase of vanadium concentration. Generally, it is recognized that the self-diffusion coefficient in alloy increases with the decrease of the melting temperature[22]. The liquidus temperature in the Ti-V system decreases with vanadium content from 1993 K at pure Ti up to 1893 K at 30 at% V and then increases with further increase of vanadium to 2173 K at pure V[23]. Then, $\widetilde{D}$ may be expected to take a maximum value at 30 at% V, however, such a maximum peak in $\widetilde{D}$ is not observed in agreement with the results obtained by pure metal couples by Carlson[13] and also with the concentration dependence of the self-diffusion coefficients of ^{44}Ti and ^{48}V determined by Murdock and McHargue [10].

According to Darken[24], the interdiffusion coefficient in an binary alloy of composition N_1 (atomic fraction of component 1) is expressed by

$$\widetilde{D}(N_1) = N_2\ D_1(N_1) + N_1\ D_2(N_1) \tag{1}$$

and

$$D_i(N_1) = D_i^*(N_1)\ m(N_1) \tag{2}$$

where D_i and D_i^* are the intrinsic diffusion and tracer self-diffusion coefficients ($i=1,2$), respectively, and N_2 (the atomic fraction of component 2)$=1-N_1$. m is the thermodynamic factor defined by

$$m(N_1) = 1 + \frac{\ln \gamma_1(N_1)}{\ln N_1} \tag{3}$$

where $\gamma_1(N_1)$ is the activity coefficient of the component 1 in the alloy of concentration N_1. According to Manning[15], eq.(2) is modified as

$$D_1(N_1) = D_1^*(N_1)\ m(N_1)\ [\ 1 + V_1(N_1)\ ] \tag{4}$$

$$D_2(N_1) = D_2^*(N_1)\ m(N_1)\ [\ 1 - V_2(N_1)\ ] \tag{5}$$

where

$$V_i(N_1) = \frac{2\ N_i\ [\ D_1^*(N_1) - D_2^*(N_1)\ ]}{M_0\ [\ N_1\ D_1^*(N_1) + N_2\ D_2^*(N_1)\ ]} \tag{6}$$

is the term which arises from the vacancy flow effect. M_0 is a constant and has the value of 5.33 for bcc systems. From eqs.(4),(5) and (6), it can be seen that V_i raises the intrinsic diffusion coefficient of the faster diffusing component and reduces the intrinsic diffusion coefficient of the slower diffusing component with respect to the values predicted from Darken's original analysis[24]. Substituting eqs.(4), (5) and (6) into eq.(1), the interdiffusion coefficient is rewritten by

$$\widetilde{D}(N_1) = [\ N_2\ D_1^*(N_1) + N_1\ D_2^*(N_1)\ ]\ m(N_1)\ S(N_1) \tag{7}$$

where

$$S(N_1) = 1 + \frac{2\ N_1\ N_2\ [\ D_1^*(N_1) - D_2^*(N_1)\ ]^2}{5.33\ [\ N_2 D_1^*(N_1) + N_1 D_2^*(N_1)\ ][\ N_1 D_1^*(N_1) + N_2 D_2^*(N_1)\ ]} \tag{8}$$

Using the experimental data on the tracer diffusion of both components[10] and the thermodynamic factor calculated by Carlson[13] based on the thermodynamical data by Rolinski et al.[25], the interdiffusion coefficient at 1573 K is calculated and shown in Fig. 4. Because of the small difference in the values of tracer diffusion coefficients, the value of S is less than 1.01 in the wide concentration range from 10 to 70 at% V and at most 1.07 at 90 at% V. Then, the value of the interdiffusion coefficient calculated by eq.(7) is in good

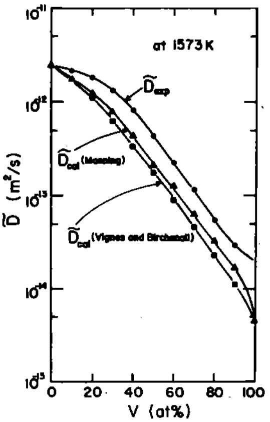

Fig.4 Concentration dependence of experimental and calculated values of $\tilde{D}$ in Ti-V alloys at 1573 K.

agreement with the value calculated by eqs. (1) and (2), suggesting that the vacancy flow effect in the Ti-V system is small. As shown in Fig. 4, the calculated value is about one half of the experimental value in the whole concentration range, although the concentration dependence of both the experimental and calculated values is consistent with each other.

According to Vignes and Birchenall[16], the concentration dependence of the interdiffusion coefficient in a binary complete solid solution is expressed by the following empirical equation:

$$\tilde{D}(N_1) = (D^*_{1/2})^{N_2}\ (D^*_{2/1})^{N_1}\ m(N_1)\ \exp[-67\ \Delta T_s(N_1)/RT] \qquad (9)$$

where $D^*_{1/2}$ and $D^*_{2/1}$ are the self-diffusion coefficients of component 1 in pure component 2 and of component 2 in pure component 1, respectively. $\Delta T_s(N_1)$ is the difference between the solidus temperature $T_s(N_1)$ of the alloy in the phase diagram and the hypothetical temperature under an assumption that the solidus varies linearly with composition; that is

$$\Delta T_s(N_1) = T_s(N_1) - [\ T_s(1) - T_s(0)\ ]\ N_1 - T_s(0) \qquad (10)$$

Putting the impurity diffusion data[10,26] and the value of m[13] into eq.(9), the value of $\tilde{D}$ at 1573 K is calculated and also shown in Fig. 4. The interdiffusion coefficient calculated by eq.(9) is slightly smaller than that calculated by eq.(7), however, the difference is much smaller than the difference between the calculated values and the experimental value. This discrepancy exists in the same extent at all the temperatures of the present experiments. One of the reasons for this disagreement may be the different content of impurities in the specimens which have been used by the different authors. It has been pointed out that the diffusivity in bcc refractory metals is easily influenced by impurities in the specimens and the extent of the influence depends on species and amount of the impurities[2].

2. Temperature dependence of interdiffusion coefficient

The interdiffusion coefficient at 0.01 at% V is determined by Hall's method[27]. As shown in Fig. 5, $\tilde{D}$ at 0.01 at% V is in good agreement with the value of the tracer diffusion coefficient of ^{48}V in pure Ti[26] and the temperature dependence of them shows the curved Arrhenius plots, like as the cases of anomalous bcc metals[1,10]. Temperature dependence of $\widetilde{D}$ at 0.01 at% V can be expressed by the following Arrhenius equation:

$$\widetilde{D} = 1.24\times10^{-4}\exp(-239\ \mathrm{kJ\ mol^{-1}}/RT) + 4.46\times10^{-8}\exp(-140\ \mathrm{kJ\ mol^{-1}}/RT) \tag{11}$$

According to Darken's analysis[24], this value can be regarded as the impurity diffusion coefficient of V in pure Ti.

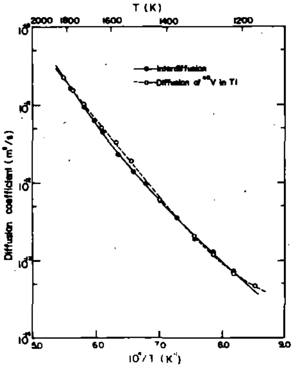

Fig.5 Temperature dependence of interdiffusion coefficient at 0.01 at% V and diffusion coefficient of ^{48}V in Ti.

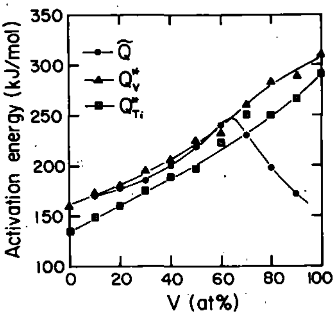

Fig.6 Concentration dependence of activation energies for interdiffusion and self-diffusion.

The temperature dependence of $\widetilde{D}$ in other compositions also shows similarly curved Arrhenius plots as in the cases of the diffusion of ^{44}Ti and ^{48}V in Ti-V alloys[10]. The apparent activation energy, $\widetilde{Q}$, for interdiffusion below 1573 K is calculated and the concentration dependence of it is shown in Fig. 6. $\widetilde{Q}$ increases with the vanadium content up to 65 at% V and then decreases rapidly with further increase of vanadium concentration. In Fig. 6, the apparent activation energies for self-diffusion of both components in Ti-V alloys are also shown. These values[10] have been obtained for the same temperature range as $\widetilde{Q}$. The activation energies for both components increase monotonously with the vanadium concentration.

According to eq.(7), the activation energy for interdiffusion is composed of three parts, Q^*, Q_m and Q_S, corresponding to the temperature dependence of $(N_2D_1^* + N_1D_2^*)$, m and S, respectively. Thus,

$$\widetilde{Q} = Q^* + Q_m + Q_S \tag{12}$$

According to Hilliard[28],

$$Q^* = p\,Q_1^* + (1 - p)\,Q_2^* \tag{13}$$

where

$$p = 1/[1 + (N_1D_{02}^*/N_2D_{01}^*)\exp(Q_1^* - Q_2^*)/RT] \tag{14}$$

D_{01}^*, D_{02}^*, Q_1^* and Q_2^* are the frequency factors and the activation energies for the self-diffusion of components 1 and 2 in the alloy, respectively. Q_m and Q_S can be calculated as follows:

$$Q_m = - R\, d(\ln m)/d(1/T) \tag{15}$$

$$Q_S = (Q_1^* - Q_2^*)(1 - \frac{1}{S})\left[\frac{2}{1 - (D_2^*/D_1^*)} - \frac{1}{1 + (N_1 D_2^*/N_2 D_1^*)} - \frac{1}{1 + (N_2 D_2^*/N_1 D_1^*)}\right] \tag{16}$$

Thus, using the experimental data on the self-diffusion[10] and the activity of each component in the alloy[13], the activation energy $\widetilde{Q}$ can be estimated. The value obtained is in good agreement with the experimental value in the concentration range from 0 to 65 at% V, however, the estimated $\widetilde{Q}$ increases monotonously with further increase of vanadium concentration. The small experimental value of $\widetilde{Q}$ in the V-rich alloy is due to some enhanced diffusions at lower temperatures, as shown in Fig. 3.

3. Kirkendall effect

The Kirkendall effect has been observed in pure metal couples diffused at 1473 K. The concentration of vanadium at the marker position has been confirmed to be 31.9 at% V. In the present work, the distance between the marker and the Matano interface has been measured to determine the marker shift. The marker movement occurs toward Ti-rich side. The marker shift versus the square root of diffusion time plots have shown a linear relationship through the origin. Putting the data on the interdiffusion coefficient and the marker velocity in Darken's relation[24], the intrinsic diffusion coefficients in Ti-31.9 at% V alloy at 1473 K have been calculated to be $D_{Ti} = 4.87\times10^{-13}$, $D_V = 4.17\times10^{-13}$ m^2/s and $D_{Ti}/D_V = 1.17$. The marker movement toward Ti-rich side is consistent with the general tendency that the marker movement occurs toward the compositions corresponding to lower liquidus temperatures. However, according to Carlson[13,14], the marker in pure metal couples diffused above 1373 K moves toward V-rich side and in the couples diffused below 1273 K, it moves toward Ti-rich side. The composition at the marker varies with temperature from 24.1 at% V at 1173 K to 40.1 at% V at 1773 K. Based on his results, Carlson has shown that $D_{Ti} < D_V$ above 1373 K and $D_{Ti} > D_V$ below 1273 K in contrast to the present results. Goold[12] has reported that in Ti-3.5 at% V alloy $D_{Ti} < D_V$ at 1523 K in accordance with the results by Carlson. The contradictory results on the Kirkendall effect obtained by the present experiments and the others[12,13,14] may be related to some particular characters of the Ti-V system. According to Murdock and McHargue[10], the self-diffusion coefficient of ^{48}V is larger than that of ^{44}Ti in the Ti-rich side less than 50 at% V and vice versa in the V-rich side more than 50 at% V. Then, from eqs.(4), (5) and (6), both the intrinsic diffusion coefficients of D_{Ti} and D_V in Ti-50 at% V alloy take the same value with each other and the vacancy flow effect in the alloy is equal to zero. However, the difference in the self-diffusion coefficients of the components is small over the whole concentration range and the vacancy flow effect is very small, as discussed in section 1. Then, the order of the magnitude in the intrinsic diffusion coefficients may be changed by some enhanced diffusions which arise from the impurities and defects induced in these anomalous bcc alloys.

Conclusions

Experimental results on the interdiffusion in Ti-V alloys are summarized as follows:

(1) The interdiffusion coefficient in Ti-V alloys decreases gradually up to 30 at% V and then decreases rapidly with further increase of vanadium.

(2) Temperature dependence of $\tilde{D}$ at 0.01 at% V shows the curved Arrhenius plot which can be expressed by the following equation:

$$\tilde{D} = 1.24\times10^{-4}\ \exp(-239\ \text{kJ mol}^{-1}/RT) + 4.46\times10^{-8}\ \exp(-140\ \text{kJ mol}^{-1}/RT)\ \text{m}^2/\text{s}.$$

(3) The activation energy for interdiffusion below 1573 K increases with the vanadium content up to 65 at% V and then decreases rapidly with further increase of vanadium content due to some enhanced diffusions at lower temperatures.

(4) Kirkendall marker in pure metal couples at 1473 K moves toward Ti-rich side, showing that titanium atom diffuses faster than vanadium atom in this system.

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